

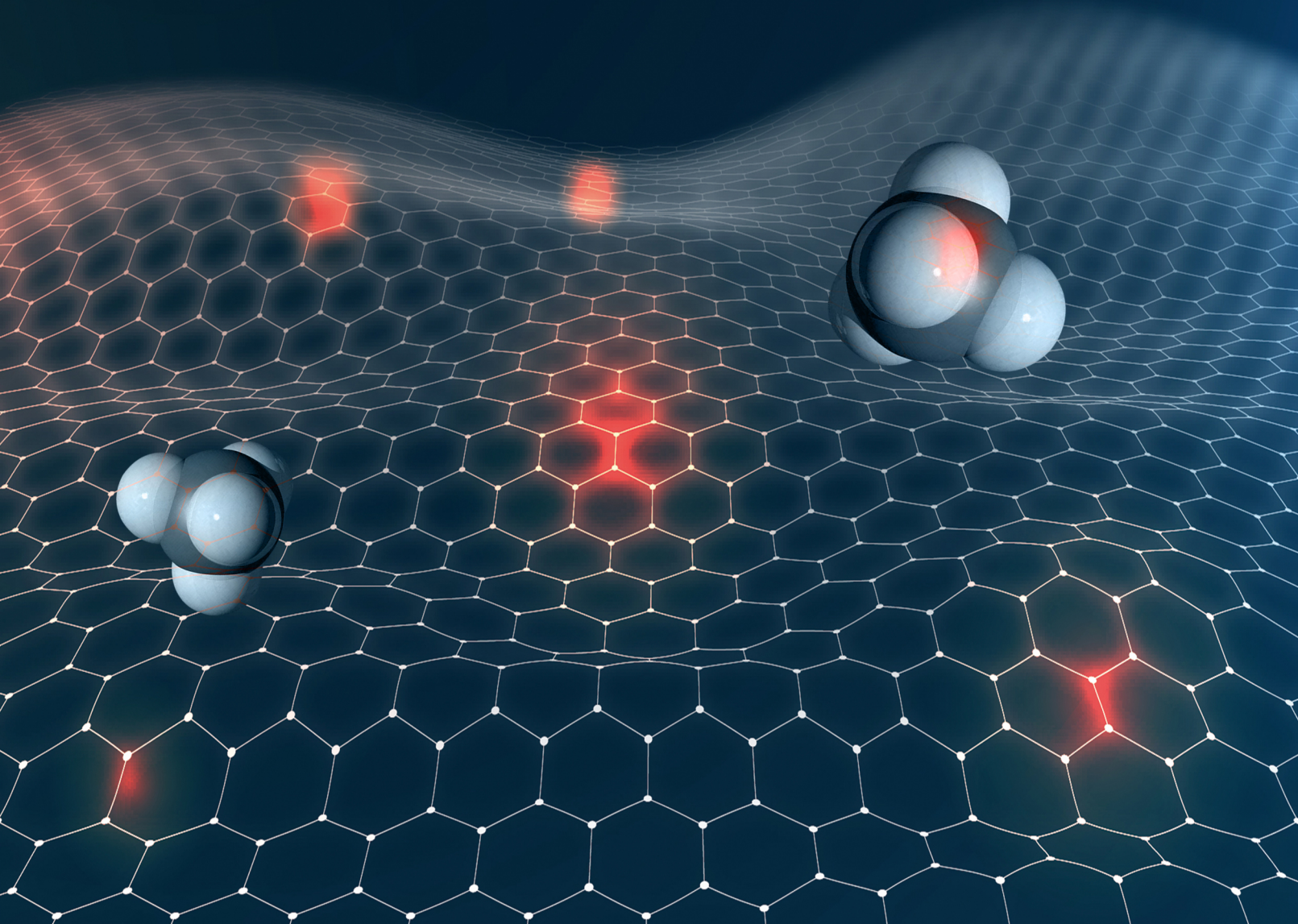


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Research Advances of Typical Two Dimensional Layered Thermoelectric Materials

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Abstract:

Thermoelectric technologies have caught our intense attention due to their ability of heat conversion into electricity. The considerable efforts have been taken to develop and enhance thermoelectric properties of materials over the past several decades. Recently, two-dimensional layered materials are making the promise for potential applications of thermoelectric devices because of the excellent physical and structural properties. Here, a comprehensive coverage about recent progresses in thermoelectric properties of typical two dimensional (2D) layered materials, including the theoretical and experimental results, is provided. Moreover, the potential applications of 2D thermoelectric materials are also involved. These results indicate that the development of 2D thermoelectric materials take a key role in the flexible electronic devices with thermoelectric technologies.

Keywords: thermoelectric properties; transport properties; 2D layered materials; figure of merit, first-principle calculations

1 Introduction

Thermoelectric (TE) conversion technology, which is a kind of green energy technology and can convert waste heat into electricity, has been considered to be an alternative for relieving energy shortage. TE devices have been used in different directions, including solid state cooling and deep space exploration^[1-2], and also shown the high potential in other areas, such as sensors and power generators^[3-5]. These make TE materials a kind of important compounds which support the development of sustainable energies and technologies with high efficiency. The performance of TE materials usually is characterized by the figure of merit ZT which is a dimensionless parameter and expressed as^[6], $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient and σ is the electrical conductivity. κ presents the thermal conductivity and T is the abbreviation of absolute temperature. There are two parts for the thermal conductivity κ which are including the electronic (κ_e) and lattice contributions (κ_l). These parameters are coupled to each other and strongly depend on the electronic structure and carrier concentration of the materials. There are usually two approaches to improve the TE performance. One way is to decrease the thermal conductivities κ_e and κ_l , and the other is to increase the power factor $S^2 \sigma$. In the past few decades, the TE field has made great progress, including various strategies to increase

the power factor and reduce the thermal conductivity. In the TE materials family there are a lot of candidates which have been reported to achieve an obvious enhancement for the value of ZT ^[7-12]. Among these kinds of strategies, low-dimensional material system has become a focus with the development of the nanotechnologies and has been applied to the thermoelectrics. Moreover, TE devices on the basis of flexible materials with large size have shown the great potential with the rapid emergence of the concept of the "Internet of Things (IoT)"^[13], especially in flexible wearable devices. It has many advantages, such as long lifetime and maintenance-free. In addition, the devices of TE energy conversion don't give rise to the vibrations or noises, while they are suitable at moderate temperatures^[14]. Thus, TE properties of low-dimensional materials have attracted much attention^[15-16].

To date, the research of TE materials has shown the prominent progress with the enhancement of ZT value, due to the inspirations by the design of low-dimensional structures, mainly two-dimensional (2D) structures for TE proposed in 1990s^[17]. The core idea behind with low-dimensional structures to enhance the TE performance is to introduce the dramatic differences in the electronic density of states (DOS) near the Fermi level. In this way, the electrical conductivity, thermal conductivity and Seebeck coefficient can be modulated quasi-independently by

quantum-confinement effects from three-dimensional to two-dimensional^[18]. With the development of preparation technologies, A series of 2D materials have been fabricated successfully^[19-28]. It is possible to develop new low-dimensional TE materials from the perspective of two-dimensional materials.

Initially, the research on 2D TE materials was mainly focused on quantum well and super-lattice thin film materials^[29-31], such as GaAs/AlAs, Bi₂Te₃/Sb₂Te₃ and SrTiO₃/SrTi_{0.8}Nb_{0.3}O₃. To date, although there have been some summaries on the related researches about 2D TE materials and the progress of the TE devices based on 2D materials^[14-15, 32], an interesting review about new layered 2D materials with different structure types for the potential applications in TE field is still missing. In this short review, we are focused on the progress in the new 2D thermoelectric materials theoretically and experimentally, such as group IV-VI layered materials, III-VI layered materials, group IV-V compounds and transition metal dichalcogenides (TMDs). We review the new TE properties in these types of 2D structures and also provide some insight for designing the new layered TE materials in the future.

2 TE Properties of typical 2D TE Materials

2.1 Group IV-VI two-dimensional layered materials

As a typical one of layered group IV-VI materials, SnSe with the special atomic structure has the excellent electronic transport and thus has attracted wide attention. It possesses a orthorhombic structure with layered atomic arrangement under space group of *Pnma*^[21]. In figure1a, its structure is along the *b*-axis in the perspective view. Due

to this special layered structure, the carriers' mobilities are highly anisotropic along different transport directions. As depicted in figure 1b, the carrier's mobility at room temperature is 250 cm² V⁻¹s⁻¹ along the *b*-axis. This value is 10 times as high as that of *a*-axis which is outside the plane. Due to the folded plane, the mobility of carrier along *c*-axis is also obvious different, compared with that along the *a*-axis. On account of the lone electron pairs of the Sn²⁺ atoms, SnSe also exhibits ultralow thermal conductivity of 0.34 W m⁻¹ K⁻¹ at 773 K along the *b*-axis. Combined superior mobility and ultralow thermal conductivity, the SnSe shows a high *ZT* value along *b*-axis at 773K for *p*-type which is 2.3, as shown in figure1c. This value is a higher value among the recent experimental reports in the published literatures. Moreover, because of the layers' weak van der Waals interaction, the single-layer with in-layer strong covalent bonds can be fabricated from the bulk SnSe. The cleavage energy for splitting layers is about 200 meV/atom theoretically^[33]. The calculation results show that the single-layer SnSe is with an energy gap of 1.28 eV and possesses the thermodynamic stability^[34-35]. It has been reported that the *ZT* value of single-layer SnSe at 773 K could reach to 3.27. Furthermore, it has been demonstrated that SnSe with orthorhombic *Pnma* symmetry (denoted as α -SnSe) has a phase transition at 796 K and becomes to be the β -SnSe with orthorhombic structure under space group *Cmcm*^[36]. These suggested that the new phases may be realized by changing growth temperature. Since then, the electronic and TE properties of many potential new phases (the polymorph structures of SnSe are shown in figure1d) have been researched^[37]. The theoretical results show that the β -SnSe phase has a *ZT* value of 2.06 at room temperature^[37].

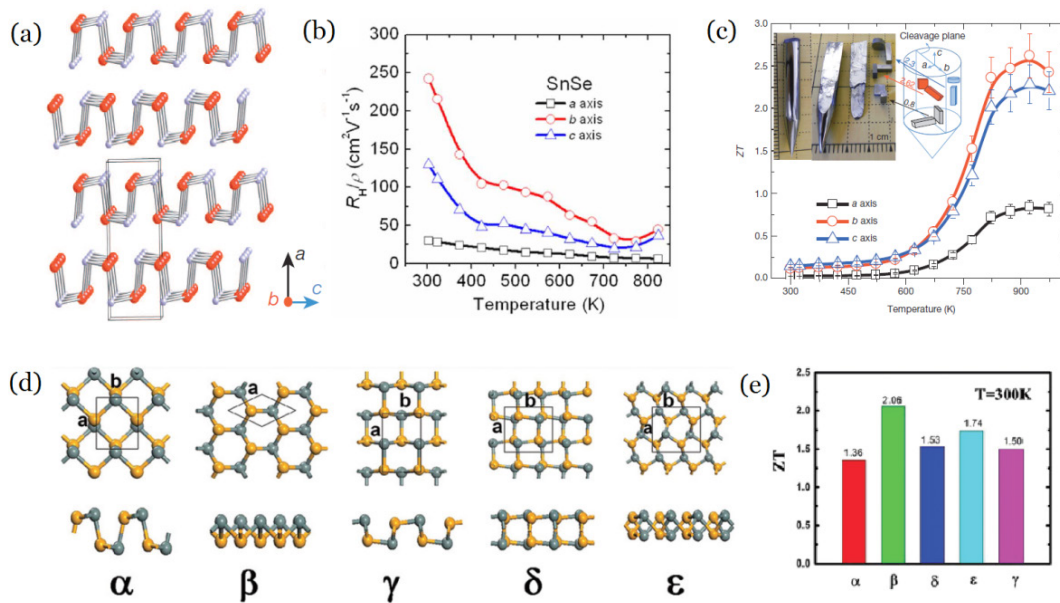


Figure 1 (a) Crystal structure of SnSe. (b) R_H/ρ (ρ , electrical resistivity) of SnSe along different axial directions. (c) *ZT* values of SnSe along different directions. Reproduced with permission from ref. 21. Copyright 2014, NPG. (d) Geometric structures of α -, β -, γ -, δ - and ϵ -SnSe monolayers. Gray atoms denote Sn atoms and yellow atoms denote Se atoms. (e) *ZT* values of different monolayer SnSe phases at 300 K. Reproduced with permission from ref.37. Copyright 2017, RSC.

These results above have sparked interest in exploring other group IV-VI two-dimensional materials^[38-42], such as GeSe, SnS, GeS, SnS₂, SnSe₂, SiS and SiSe. Theoretical calculations have revealed that group IV-VI compounds with folded structure could exhibit high Seebeck coefficient, relative low thermal conductivity and had the potential toward TE applications^[43]. The thermal transport property of group IV-VI single-layer materials (GeS, GeSe, SnS and SnSe) has been investigated by first-principles calculations^[42]. The average thermal conductivity calculated is 6.38 Wm⁻¹K⁻¹, 5.23 Wm⁻¹K⁻¹, 3.08 Wm⁻¹K⁻¹ and 2.77 Wm⁻¹K⁻¹, respectively. Among these IV-VI materials studied, GeS has the largest Seebeck coefficient (2810 VK⁻¹) at room temperature^[41]. Compared with their bulk materials, the optimal *ZT* values of single-layer GeSe, GeS and SnS are high and 1.99, 1.85 and 1.88, respectively. Therefore, these materials are expected to have the potential applications in TE devices. In addition, as typical group IV-VI materials, SiSe and SiS possess high Seebeck coefficient arising from the sharp DOS near Fermi level^[44]. The calculation results about the power factor indicate that the peak values of the *p*-type and *n*-type are 16 mWm⁻²K⁻² and 11 mWm⁻²K⁻², respectively. these values are similar to the experimental report on the state-of-the-art material SnSe with the layered structure^[35].

2.2 Group III-VI two-dimensional layered materials

As the potential TE materials, the compounds which belong to III-VI group have aroused much attention during the past few years. These materials, including InSe, GaSe, GaS and Tl₂O, have been extensively studied in the TE field^[45-47]. Taking InSe as an example, with the stoichiometric ratio of 1:1, it has the typical structure of group III-VI layered materials shown in figure 2a. It has been also noticed that In-Se system is complex and there are other different stoichiometric ratios^[48], such as In₄Se₃^[49], In₂Se₃^[50], InSe^[51], In₆Se₇^[52] and In₃Se₄^[53]. In addition, with the same stoichiometric ratio, different phases and crystal structures may coexist. Geim *et al.*^[54] reported that the carrier's mobility of the thin InSe was very high. It exceeds 10³ cm²V⁻¹s⁻¹ at RT and is about 10⁴ cm²V⁻¹s⁻¹ at liquid-helium temperature. Moreover, experimental studies show that the thermal conductivity of bulk In₄Se_{2.35} is very low along the *b*-*c* plane (1.2 Wm⁻¹K⁻¹ at 300 K), and it decreases with increasing temperature (0.74 Wm⁻¹K⁻¹ at 705 K)^[55].

Based on the analysis of the electronic structure of III-VI compounds with single-layer and multi-layer, it is found that the valence band of these materials have a “Mexican hat” dispersion^[56-59], which can increase the density of states near the band edge (as seen in figure 2b), and further increases the Seebeck coefficient. Single- and multi-layer materials of InSe, GaSe and GaS have been successfully fabricated experimentally^[60-63]. Subsequently, the electronic and TE properties of these materials from single-layer to multi-layer have been researched extensively. The results show that the power factor increases, following the material's thickness decreases^[64-65]. As an example, the maximum power factor of single-layer InSe reaches to

16 mWm⁻²K⁻². The TE performance of single-layer InSe has been also investigated theoretically through using mechanical strain. Under the strain, the energy bands will converge and thus lead to an increase of power factor, while the thermal conductivity is also found to decrease^[66].

Some works have revealed that the sharp conduction band edge with high DOS due to the quantum confinement could lead to the enhancement of the Seebeck coefficient^[67]. The DOS and the information of electronic wave functions at conduction band maximum CBM for 9-layers and 36-layers InSe films are shown in figure 2c. With the combination of theoretical simulations and experimental tests, it is found that the power factor is increased obviously, by following the thickness of InSe sample decreases, especially less than the thermal wavelength (seen in figure 2d). This may provide a guideline for further optimizing the TE properties of 2D layered structures.

2.3 Group IV-V two-dimensional layered materials

With the emergence of group IV and group V 2D layered materials, including graphene, silicene, germanene, phosphorene and antimonene, group IV-V 2D compound materials have been also explored^[68-70]. Group IV-V compounds are known to form the layered structures. A few structures have been synthesized at high pressure^[71], such as SiP, SiAs, GeAs and GeP. The layered crystal structure with space group *C2/m* is shown in figure 3a.

As a typical one, GeAs with anisotropic atomic structure has demonstrated highly anisotropic properties of transport^[72]. As shown in figure 3b, the resistivity perpendicular to the layers is very high due to large distance of layers with weak coupling. It is 2 orders of magnitude higher than that along the layers at 300 K. The TE properties of Sn-doped GeAs have been studied. The results revealed that at high temperature, Sn-doped GeAs exhibited superior transport properties, compared to the pristine GeAs. It has shown that Sn-doped GeAs possesses a remarkable *ZT* with a maximum of 0.35 at 660 K (as shown in figure 3c)^[72]. On the Ge-As phase diagram, there are another compound GeAs₂ with an orthorhombic crystal structure (in figure 3d)^[73]. It exhibits the strong interlayer coupling due to its special stacking of layers with small layers' spacing along vertical direction (about 1 Å). The power factor of the *n*-type GeAs₂ along the *b*-axis can reach to 4.2 mW/mK². This are comparable to the value (4 mW/mK²) of SnSe^[74]. Monolayer GeAs₂ has complex bonding characteristic, and this is similar to the structural characteristic of SnSe. The calculated in-plane lattice thermal conductivities is 0.68 Wm⁻¹K⁻¹ along the *a*-axis and 6.03 Wm⁻¹K⁻¹ along *c*-axis at RT, respectively^[75]. These research achievements suggest that the group IV-V compound materials are the promising candidates for environmentally friendly TE applications.

2.4 TMD materials

It has been well known, TMDs are with typical layered stacking and the coupling of layers is by van der Waals interaction. For the single layer, there are usually two different structural types. One is the hexagonal structure (H-phase). The typical materials include Mo and W based

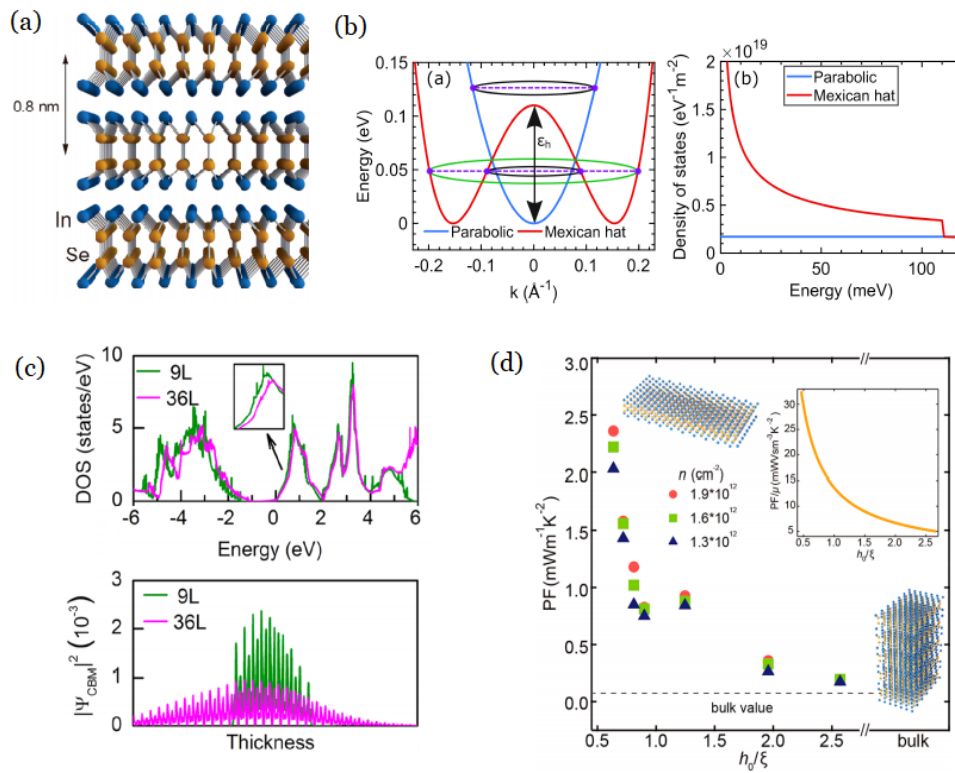


Figure 2 (a) Crystal structure of InSe. Reproduced with permission from ref. 67. Copyright 2018, ACS. (b) Comparison of a parabolic and Mexican hat dispersion and density of states of both. Reproduced with permission from ref. 59. Copyright 2019, APS. (c) Total density of states and planar-averaged squared magnitude of wave functions (which are from the states of conduction band maximum and plotted along the direction perpendicular to layers) of 9-layers and 36-layers InSe films (upper panel), (lower panel). (d) Power factor as functions of films' thickness with quantum confinement effect (h_0/ξ) for the different carrier concentrations. (h_0 is for quantum confinement of length, and ξ is for heat wavelength). Reproduced with permission from ref. 67. Copyright 2018, ACS.

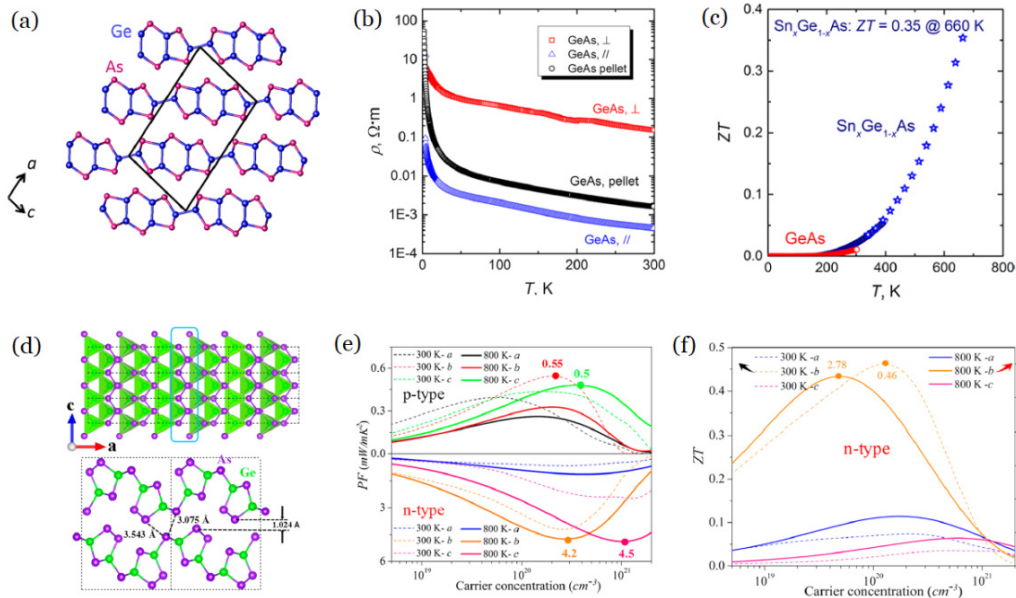


Figure 3 (a) Crystal structure of GeAs. (b) Resistivity of GeAs pellet and the GeAs crystal as functions of temperature. (c) ZT value as functions of temperature for $\text{Sn}_x\text{Ge}_{1-x}\text{As}$ pellet and GeAs. Reproduced with permission from ref. 72. Copyright 2016, ACS. (d) Top view and side view of GeAs_2 atomic structure. (e) Power factors as functions of carrier concentration with different temperature for the p-type and n-type along different axes. (f) Calculated ZT value for the n-type GeAs_2 . Reproduced with permission from ref. 73. Copyright 2017, ACS.

dichalcogenides, such as MX_2 ($\text{M}=\text{Mo}, \text{W}$, and $\text{X}=\text{S}, \text{Se}, \text{Te}$). The other one is the $1\text{T}-\text{CdI}_2$ type with trigonal structure^[76]. In both structures, single layer of metal atoms is sandwiched between two chalcogen layers. Hexagonal structure is shown in figure 4a. They have been widely explored in various fields, such as electronics and optoelectronics, due to their diverse physical and chemical properties^[77]. TMDs have been also researched as candidate materials for TE devices because of their high Seebeck coefficients and low thermal conductivities^[78-82].

The TE properties of 2D TMDs, such as MoS_2 , have been studied by both theoretical calculations and experimental works. The electronic structure has a significant layered effect for TMDs. For an example, their indirect band gap in multi-layers and bulk changes into direct band gap in their monolayer limit^[83]. The band structure exhibits obvious changes by following the increase of atomic layer's number from monolayer to multilayer^[84-86]. The TE transport properties of few-layer MoS_2 have been reported^[87]. As shown in figure 4b and 4c, the electrical conductivities, Seebeck coefficient and power factor have been measured^[87]. The power factor increases correspondingly, by following the increase of applied gate voltage V_g on account of increasing electrical conductivity. Apparently, the device with double layer MoS_2 has a large effective mobility of $64 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with a maximum power factor of $8.5 \text{ mWm}^{-1}\text{K}^{-2}$ at RT. The value of power factor is the highest one among that measured in semiconducting TMDs as the TE materials. The enhancement of transport performance is not only due to the quantum-confinement effect but also due to their valley degeneracies and large effective masses. Similar behavior was also found in other TMDs, such as MoSe_2 , WS_2 , and WSe_2 ^[88-89].

The 2D materials, such as TiX_2 , Zr X_2 , and HfX_2 , are typically with CdI_2 type. They have attracted much attention because of their lower lattice thermal conductivity than those of W and Mo based TMDs. The lower thermal conductivity is originated mainly from the strong hybridization between low lying optical phonon modes and acoustic phonon modes^[90-91]. For instance, the theoretical calculation results indicate that the lattice thermal conductivity at RT are $1.2 \text{ Wm}^{-1}\text{K}^{-1}$ for ZrSe_2 and $1.8 \text{ Wm}^{-1}\text{K}^{-1}$ for HfSe_2 , which is lower than those values of MoS_2 -type monolayers^[79, 92-93] and comparable to those of some popular bulk TE materials, such as Bi_2Te_3 ^[94] and PbTe ^[95].

Recently, another class highly desirable 2D material has been theoretically predicated and explored experimentally^[96-100]. They are formed by the combination of chalcogens and noble metals, such as Pt and Pd. They have usually bulked or puckered pentagonal structure with low symmetry. Oyedele *et al.* has been exfoliated monolayer PdSe_2 from its bulk crystals^[98]. This typical 2D noble transition metal dichalcogenide monolayer with a puckered morphology is air-stable. The theoretical results demonstrate that the mobility of holes can reach $1929 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for monolayer PdSe_2 . It possesses the lower lattice thermal conductivity of $3.7 \text{ Wm}^{-1}\text{K}^{-1}$ ^[100], which is much

lower than that of MoS_2 . It indicates that PdSe_2 monolayer could have a quite potential for TE applications. Recently, a novel Pd_2Se_3 monolayer phase, which is reconstructed from a few layers of PdSe_2 by the interlayer fusion, has been reported experimentally^[101]. Figure 4d shows the experimental TEM image with atomic resolution (grey) of the monolayer and correspondingly theoretical TEM image by the simulation. The ultralow lattice thermal conductivity has been found in Pd_2Se_3 monolayer. Theoretical analysis reveals that in the region of low frequency a strong hybridization is between $[\text{Se}_2]^{2-}$ ion and Pd^{2+} , as verified by the phonon DOS in figure 4e^[102]. Thus, it is proposed that the low thermal conductivity is due to the softening of phonon modes and the anharmonicity between covalently bonded $[\text{Se}_2]^{2-}$. The lattice thermal conductivity of Pd_2Se_3 is calculated and is about $2 \text{ Wm}^{-1}\text{K}^{-1}$. This small value is 90, 27, and 6 times lower than that of MoS_2 ^[103], WSe_2 ^[79], and TiS_3 ^[104], respectively.

3 Potential applications of two-dimensional thermoelectric materials

Traditionally, TE materials are mainly used as TE power generation and TE refrigeration. The TE generator can be applied in the TE power station with the long distance and unmanned maintenance, such as in man-made satellite. They can be applied in the low-grade TE generation, such as industrial waste heat, waste heat in our daily life and heats from vehicle exhaust. TE materials with the characteristics of both cooling and heating can control easily the temperature timing and are used to provide the constant temperature environment for different systems, such as electronic computers, cameras with CCD and communication devices. They are also used as the sensors and temperature controllers with extensive applications in microelectronic systems and devices. Here, we won't discuss these traditional applications in details. Following the device miniaturization, TE materials will expand their applications in other potential areas further. Especially, two-dimensional TE materials have wide application prospect in wearable/flexible systems.

With the recent appearing of the IoT era, and the wide range use of microelectronic devices by that people can communicate with each other at anytime and anywhere, the research of wearable electronic systems is growing. However, it still remains a problem for the power supplies of wearables. At present, batteries can power these wearable devices. But the frequent recharging and replacement are unavoidable problems. To solve this issue, one of most effective strategy is to integrate self-powered system with wearable electronic devices. Here, the energy conversion by TE effect on basis of large-area flexible materials is expected to serve as the energy harvester with self-powered way. This has received large attention because of its advantages^[105-109]. For examples, the heat energy from body may be enough and the long lifetime prevents them from frequent replacement. In addition, the TE conversion process don't create any noise¹⁴.

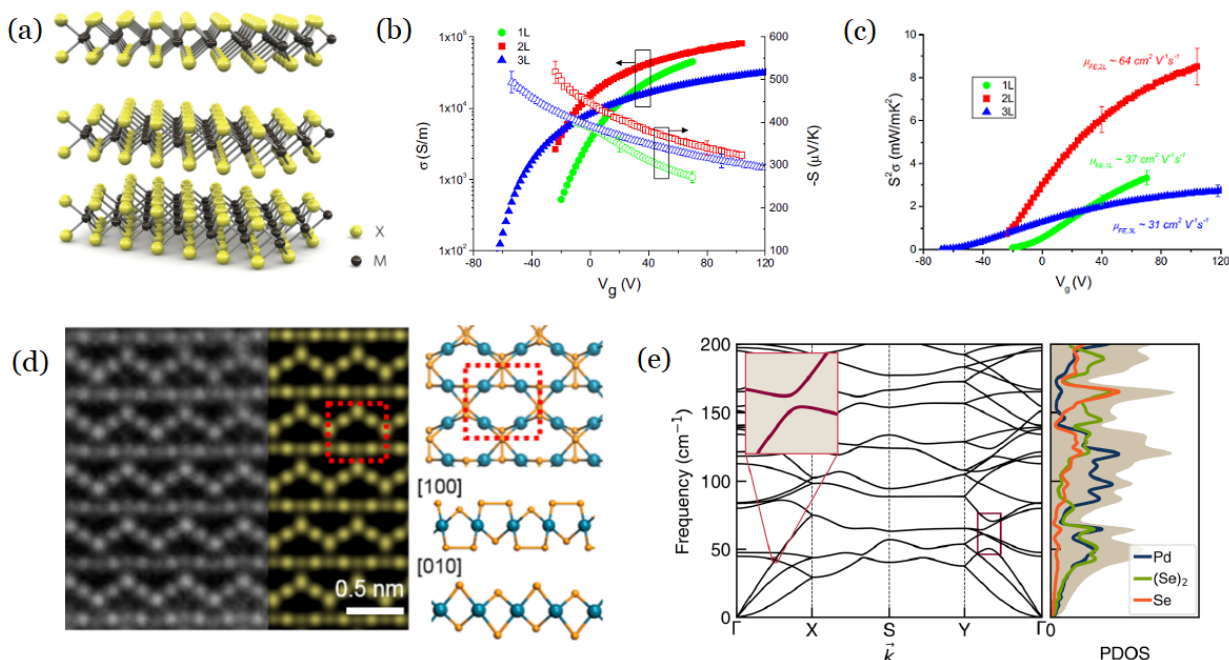


Figure 4 (a) Three-dimensional schematic representation of typical hexagonal MX₂ structure. Reproduced with permission from ref. 77. Copyright 2012, NPG. (b) Electrical conductivities σ and Seebeck coefficients S at RT as functions of V_g for single layer MoS₂. (c) Power factor $S^2\sigma$ as a function of V_g . Reproduced with permission from ref. 87. Copyright 2017, APS. (d) High resolution TEM (grey) and simulated (yellow) image for monolayer Pd₂Se₃. Reproduced with permission from ref. 101. Copyright 2017, APS. (e) Phonon band structure and density of states of monolayer Pd₂Se₃. Reproduced with permission from ref. 102. Copyright 2018, ACS.

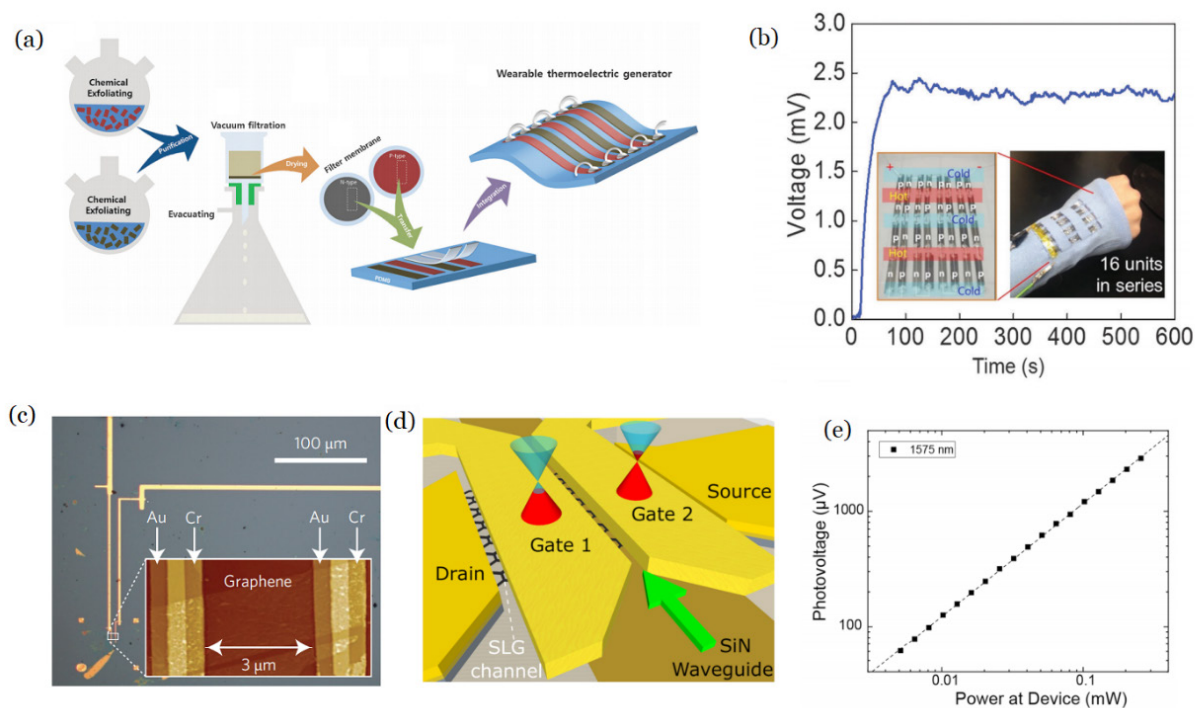


Figure 5 (a) Fabrication processes of wearable thermoelectric devices using TMDs nanosheets. (b) Output voltage from the human wrist's heat by thermoelectric generator. Reproduced with permission from Ref. 111. Copyright 2016, RSC. (c) Optical micrograph and atomic force microscopy of graphene photo detector. Reproduced with permission from Ref. 112. Copyright 2014, NPG. (d) Schematic illustration of the graphene photo detector with SiN waveguide. (e) The relation between photo voltage and optical power. Reproduced with permission from ref. 113. Copyright 2019, ACS.

Originally, the TE generator consisting of bulk Bi_2Te_3 and Sb_2Te_3 printed on a flexible glass fabric has been reported^[107]. A bend ability radius of up to 20 mm is shown in this kind of devices. This basically meets the demand of flexible wearables. Kim *et al.*^[110] have fabricated a novel wearable TE generator, which could attach to human skin and use the heat energy from body. Thus, it is expected to be with various potential applications. Because of unique electrical and mechanical properties, TMDs have given risen to great attention due to their potential in next-generation microelectronics and wearables. Oh *et al.*^[111] developed a method by combining chemical exfoliation and vacuum filtration to construct the TE generators directly which are parallel-connected on flexible substrates (seen in figure 5a). As shown in figure 5b, NbSe_2 and WS_2 nanosheets were used as the *p*-type and *n*-type materials, respectively. In this way, the TE generators were fabricated. This kind of devices has very high flexibility and durability. They can be used as the glove-type wrist-band thermal sensor.

Moreover, based on the Seebeck effect, the photo TE device can generate a photocurrent. With the adsorbed light, the temperature gradient between lighting region and dark region is built and thus the electric voltage is formed. This phenomenon has several advantages in designing the optoelectronics devices with high performance. The graphene TE terahertz photo detector has been investigated^[112] (figure 5c). This kind of device demonstrates an outstanding sensitivity more than 10 VW^{-1} at RT with noise-equivalent power less than $1100 \text{ pW Hz}^{-1/2}$, referenced to the incident power. If based on absorbed power, the sensitivity exceeds 700 VW^{-1} at RT with noise-equivalent power less than $20 \text{ pW Hz}^{-1/2}$. A photo-thermoelectric-based graphene photo detector has been designed to generate a photovoltage directly (seen in figure 5d)^[113]. It exhibits an external responsivity of about 12.2 V/W with a roll-off frequency up to 42 GHz and 3dB bandwidth. Figure 5e shows the relation between photovoltage and optical power. With TE effect, the voltage generated by temperature gradient due to the lighting has a linear response to optical power^[113].

4 Conclusion and Outlook

Over the last few decades, TE materials have made a great progress. In this review, we are focused on the TE properties of new two-dimensional materials and the possible applications. In particular, the relevant theoretical and experimental results for group IV-VI, group IV-V, group III-VI and layered transition metal dichalcogenides have been highlighted. We also compared the TE properties between new two-dimensional materials we considered and state-of-the-art layered structure materials. In these new two-dimensional materials, both low thermal conductivity and high power factor have been revealed. Finally, the current potential applications in TE device, including flexible generator and optoelectronics devices using two-dimensional film materials have also been presented.

Although the tremendous advances have been

achieved during the past decades, there are still problems and challenges for the practical applications. The phonon and electrical transport mechanism are still obscure. The mechanism of increasing the power factor has been proposed in two-dimension materials, but it still remains challenge to decouple the different transport coefficients. We also need a deeper understanding of transport mechanisms to help enhance TE properties and design new TE materials in the future.

Conflicts of interest: The authors declare no competing financial interest.

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References

- [1] Bell, L. E., Cooling, Heating, Generating Power, and Recovering Waste Heat with Thermoelectric Systems. *Science* 2008,321 (5895), 1457-1461.
- [2] Pichanusakorn, P.; Bandaru, P., Nanostructured thermoelectrics. *Mater. Sci. Eng., R* 2010,67, 19-63.
- [3] Rull-Bravo, M.; Moure, A.; Fernandez, J.; Martín-González, M., Skutterudites as thermoelectric materials: revisited. *RSC Adv.* 2015,5, 41653-41667.
- [4] Sundarraj, P.; Maity, D.; Roy, S. S.; Taylor, R. A., Recent advances in thermoelectric materials and solar thermoelectric generators—a critical review. *RSC Adv.* 2014,4, 46860-46874.
- [5] Tan, G.; Zhao, L.-D.; Kanatzidis, M. G., Rationally designing high-performance bulk thermoelectric materials. *Chem. Rev.* 2016,116, 12123-12149.
- [6] Snyder, G. J.; Toberer, E. S., Complex thermoelectric materials. *Nat. Mater.* 2008,7, 105-114.
- [7] Heremans, J. P.; Jovovic, V.; Toberer, E. S.; Saramat, A.; Kurosaki, K.; Charoenphakdee, A.; Yamanaka, S.; Snyder, G. J., Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states. *Science* 2008,321, 554-557.
- [8] Pei, Y.; LaLonde, A. D.; Heinz, N. A.; Shi, X.; Iwanaga, S.; Wang, H.; Chen, L.; Snyder, G. J., Stabilizing the optimal carrier concentration for high thermoelectric efficiency. *Adv. Mater.* 2011,23, 5674-5678.
- [9] Pei, Y.; Shi, X.; LaLonde, A.; Wang, H.; Chen, L.; Snyder, G. J., Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* 2011,473, 66.
- [10] Liu, W.; Tan, X.; Yin, K.; Liu, H.; Tang, X.; Shi, J.; Zhang, Q.; Uher, C., Convergence of conduction bands as a means of enhancing thermoelectric performance of *n*-type $\text{Mg}_{2-\text{x}}\text{Si}_{1-\text{x}}\text{Sn}_{\text{x}}$ solid solutions. *Phys. Rev. Lett.* 2012,108, 166601.
- [11] Heremans, J. P.; Wiendlocha, B.; Chamoire, A. M., Resonant levels in bulk thermoelectric semiconductors. *Energy Environ. Sci.* 2012,5, 5510-5530.

- [12] Tan, G.; Shi, F.; Hao, S.; Chi, H.; Zhao, L.-D.; Uher, C.; Wolverton, C.; Dravid, V. P.; Kanatzidis, M. G., Codoping in SnTe: Enhancement of thermoelectric performance through synergy of resonance levels and band convergence. *J. Am. Chem. Soc.* 2015,137, 5100-5112.
- [13] C.-W. Yau; T. T.-O. Kwok; C.-U. Lei; Kwok, Y.-K., in *Internet of everything: Algorithms, methodologies, technologies and perspectives*. Springer Singapore: (Eds: B. Di Martino, K.-C. Li, L. T. Yang, A. Esposito), Springer Singapore, Singapore, 2018.
- [14] Kanahashi, K.; Pu, J.; Takenobu, T., 2D Materials for Large-Area Flexible Thermoelectric Devices. *Adv. Energy Mater.* 2020,10, 1902842.
- [15] Li, D.; Gong, Y.; Chen, Y.; Lin, J.; Khan, Q.; Zhang, Y.; Li, Y.; Zhang, H.; Xie, H., Recent Progress of Two-Dimensional Thermoelectric Materials. *Nano-Micro Lett.* 2020,12, 36.
- [16] Dresselhaus, M. S.; Chen, G.; Tang, M. Y.; Yang, R.; Lee, H.; Wang, D.; Ren, Z.; Fleurial, J. P.; Gogna, P., New directions for low-dimensional thermoelectric materials. *Adv. Mater.* 2007,19 (8), 1043-1053.
- [17] Hicks, L.; Dresselhaus, M. S., Effect of quantum-well structures on the thermoelectric figure of merit. *Phys. Rev. B* 1993,47, 12727.
- [18] Heremans, J. P., Low-Dimensional Thermoelectricity. *Acta Phys. Polon. A* 2005,108, 609-634.
- [19] Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S., Detection of individual gas molecules adsorbed on graphene. *Nat. Mater.* 2007,6, 652-655.
- [20] Chang, C.; Wu, M.; He, D.; Pei, Y.; Wu, C.-F.; Wu, X.; Yu, H.; Zhu, F.; Wang, K.; Chen, Y.; Li, H.; Jing-Feng, L.; Jiaqing, H.; Li-Dong, Z., 3D charge and 2D phonon transports leading to high out-of-plane ZT in n-type SnSe crystals. *Science* 2018,360, 778-783.
- [21] Zhao, L.-D.; Lo, S.-H.; Zhang, Y.; Sun, H.; Tan, G.; Uher, C.; Wolverton, C.; Dravid, V. P.; Kanatzidis, M. G., Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature* 2014,508, 373.
- [22] Liu, Y.; Zhang, S.; He, J.; Wang, Z. M.; Liu, Z., Recent Progress in the Fabrication, Properties, and Devices of Heterostructures Based on 2D Materials. *Nano-Micro Lett.* 2019,11, 13.
- [23] Molle, A.; Goldberger, J.; Houssa, M.; Xu, Y.; Zhang, S.-C.; Akinwande, D., Buckled two-dimensional Xene sheets. *Nat. Mater.* 2017,16, 163-169.
- [24] Li, L.; Yu, Y.; Ye, G. J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X. H.; Zhang, Y., Black phosphorus field-effect transistors. *Nat. Nanotechnol.* 2014,9, 372-377.
- [25] Lee, C.; Wei, X.; Kysar, J. W.; Hone, J., Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* 2008,321, 385-388.
- [26] Yang, J.; Lü, T.; Myint, Y. W.; Pei, J.; Macdonald, D.; Zheng, J.-C.; Lu, Y., Robust Excitons and Trions in Monolayer MoTe₂. *ACS Nano* 2015,9, 6603-6609.
- [27] Lai, J.; Liu, X.; Ma, J.; Wang, Q.; Zhang, K.; Ren, X.; Liu, Y.; Gu, Q.; Zhuo, X.; Lu, W.; Wu, Y.; Li, Y.; Feng, J.; Zhou, S.; Chen, J.-H.; Sun, D., Anisotropic Broadband Photoresponse of Layered Type-II Weyl Semimetal MoTe₂. *Adv. Mater.* 2018,30, 1707152.
- [28] Nie, C.; Yu, L.; Wei, X.; Shen, J.; Lu, W.; Chen, W.; Feng, S.; Shi, H., Ultrafast growth of large-area monolayer MoS₂ film via gold foil assisted CVD for a highly sensitive photodetector. *Nanotechnol.* 2017,28, 275203.
- [29] Venkatasubramanian, R.; Siivola, E.; Colpitts, T.; O'quinn, B., Thin-film thermoelectric devices with high room-temperature figures of merit. *Nature* 2001,413, 597.
- [30] Wu, C.-W.; Wu, Y.-R., Optimization of thermoelectric properties for rough nano-ridge GaAs/AlAs superlattice structure. *AIP Adv.* 2016,6, 115201.
- [31] Ohta, H.; Kim, S.; Mune, Y.; Mizoguchi, T.; Nomura, K.; Ohta, S.; Nomura, T.; Nakanishi, Y.; Ikuhara, Y.; Hirano, M.; Hideo, H.; Kunihito, K., Giant thermoelectric Seebeck coefficient of a two-dimensional electron gas in SrTiO₃. *Nat. Mater.* 2007,6, 129.
- [32] Liu, Y.; Wang, W.; Yang, J.; Li, S., Recent Advances of Layered Thermoelectric Materials. *Adv. Sustainable Syst.* 2018,2, 1800046.
- [33] Singh, A. K.; Mathew, K.; Zhuang, H. L.; Hennig, R. G., Computational Screening of 2D Materials for Photocatalysis. *J. Phys. Chem. Lett.* 2015,6, 1087-1098.
- [34] Singh, A. K.; Hennig, R. G., Computational prediction of two-dimensional group-IV mono-chalcogenides. *Appl. Phys. Lett.* 2014,105, 042103.
- [35] Wang, F. Q.; Zhang, S.; Yu, J.; Wang, Q., Thermoelectric properties of single-layered SnSe sheet. *Nanoscale* 2015,7, 15962-15970.
- [36] Volykhov, A.; Shtanov, V.; Yashina, L., Phase relations between germanium, tin, and lead chalcogenides in pseudobinary systems containing orthorhombic phases. *Inorg. Mater.* 2008,44, 345-356.
- [37] Hu, Z.-Y.; Li, K.-Y.; Lu, Y.; Huang, Y.; Shao, X.-H., High thermoelectric performances of monolayer SnSe allotropes. *Nanoscale* 2017,9, 16093-16100.
- [38] Morales-Ferreiro, J.; Diaz-Droguett, D.; Celentano, D.; Luo, T., First-Principles Calculations of Thermoelectric Properties of IV-VI Chalcogenides 2D Materials. *Front. Mech. Eng.* 2017,3, 15.
- [39] Guo, S.-D.; Wang, Y.-H., Thermoelectric properties of orthorhombic group IV-VI monolayers from the first-principles calculations. *J. Appl. Phys.* 2017,121, 034302.
- [40] Xu, L.; Yang, M.; Wang, S. J.; Feng, Y. P., Electronic and optical properties of the monolayer group-IV monochalcogenides M X (M = Ge, Sn; X = S, Se, Te). *Phys. Rev. B* 2017,95, 235434.
- [41] Shafique, A.; Shin, Y.-H., Thermoelectric and phonon transport properties of two-dimensional IV-VI

- compounds. *Sci. Rep.* 2017,7, 506.
- [42] Qin, G.; Qin, Z.; Fang, W.-Z.; Zhang, L.-C.; Yue, S.-Y.; Yan, Q.-B.; Hu, M.; Su, G., Diverse anisotropy of phonon transport in two-dimensional group IV–VI compounds: A comparative study. *Nanoscale* 2016,8, 11306–11319.
- [43] Ding, G.; Gao, G.; Yao, K., High-efficient thermoelectric materials: The case of orthorhombic IV-VI compounds. *Sci. Rep.* 2015,5, 9567.
- [44] Yang, J.-H.; Yuan, Q.; Deng, H.; Wei, S.-H.; Yakobson, B. I., Earth-abundant and non-toxic SiX (X= S, Se) monolayers as highly efficient thermoelectric materials. *J. Phys. Chem. C* 2017,121, 123–128.
- [45] Nissimagoudar, A. S.; Ma, J.; Chen, Y.; Li, W., Thermal transport in monolayer InSe. *J. Phys. Condens. Matter* 2017,29, 335702.
- [46] Bahuguna, B. P.; Saini, L.; Sharma, R. O.; Tiwari, B., Hybrid functional calculations of electronic and thermoelectric properties of GaS, GaSe, and GaTe monolayers. *Phys. Chem. Chem. Phys.* 2018,20, 28575–28582.
- [47] Huang, H.; Xing, G.; Fan, X.; Singh, D. J.; Zheng, W., Layered TI 2 O: a model thermoelectric material. *J. Mater. Chem. C* 2019,7, 5094–5103.
- [48] Han, G.; Chen, Z. G.; Drennan, J.; Zou, J., Indium selenides: structural characteristics, synthesis and their thermoelectric performances. *Small* 2014,10, 2747–2765.
- [49] Hogg, J.; Sutherland, H.; Williams, D., The crystal structure of tetraindium triselenide. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1973,29, 1590–1593.
- [50] Popović, S.; Tonejc, A.; Gržeta-Plenković, B.; Čelustka, B.; Trojko, R., Revised and new crystal data for indium selenides. *J. Appl. Crystallogr.* 1979,12 (4), 416–420.
- [51] Nagpal, K.; Ali, S., X-Ray Crystallographic Study of InSe. *Indian J. Pure Appl. Phys.* 1976,14, 434–440.
- [52] Hogg, J., The crystal structure of In₆Se₇. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 1971,27, 1630–1634.
- [53] Han, G.; Chen, Z.-G.; Yang, L.; Cheng, L.; Jack, K.; Drennan, J.; Zou, J., Thermal stability and oxidation of layer-structured rhombohedral In₃Se₄ nanostructures. *Appl. Phys. Lett.* 2013,103, 263105.
- [54] Bandurin, D. A.; Tyurnina, A. V.; Geliang, L. Y.; Mishchenko, A.; Zólyomi, V.; Morozov, S. V.; Kumar, R. K.; Gorbachev, R. V.; Kudrynskyi, Z. R.; Pezzini, S.; D., K. Z.; Uli, Z.; S., N. K.; Amalia, P.; Laurence, E.; V., G. I.; I., F. k. V.; K., G. A.; Yang, C., High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe. *Nat. Nanotechnol.* 2017,12, 223.
- [55] Rhyee, J.-S.; Lee, K. H.; Lee, S. M.; Cho, E.; Kim, S. I.; Lee, E.; Kwon, Y. S.; Shim, J. H.; Kotliar, G., Peierls distortion as a route to high thermoelectric performance in In₄Se_{3-δ} crystals. *Nature* 2009,459, 965.
- [56] Zolyomi, V.; Drummond, N.; Fal'Ko, V., Band structure and optical transitions in atomic layers of hexagonal gallium chalcogenides. *Phys. Rev. B* 2013,87, 195403.
- [57] Zólyomi, V.; Drummond, N.; Fal'Ko, V., Electrons and phonons in single layers of hexagonal indium chalcogenides from ab initio calculations. *Phys. Rev. B* 2014,89, 205416.
- [58] Hu, P.; Wang, L.; Yoon, M.; Zhang, J.; Feng, W.; Wang, X.; Wen, Z.; Idrobo, J. C.; Miyamoto, Y.; Geohegan, D. B.; Kai, X., Highly responsive ultrathin GaS nanosheet photodetectors on rigid and flexible substrates. *Nano Lett.* 2013,13, 1649–1654.
- [59] Das, P.; Wickramaratne, D.; Debnath, B.; Yin, G.; Lake, R. K., Charged impurity scattering in two-dimensional materials with ring-shaped valence bands: GaS, GaSe, InS, and InSe. *Phys. Rev. B* 2019,99, 085409.
- [60] Lei, S.; Ge, L.; Liu, Z.; Najmaei, S.; Shi, G.; You, G.; Lou, J.; Vajtai, R.; Ajayan, P. M., Synthesis and photoresponse of large GaSe atomic layers. *Nano Lett.* 2013,13, 2777–2781.
- [61] Lei, S.; Ge, L.; Najmaei, S.; George, A.; Kappera, R.; Lou, J.; Chhowalla, M.; Yamaguchi, H.; Gupta, G.; Vajtai, R.; D., M. A.; M., A. P., Evolution of the electronic band structure and efficient photo-detection in atomic layers of InSe. *ACS nano* 2014,8, 1263–1272.
- [62] Hu, P.; Wen, Z.; Wang, L.; Tan, P.; Xiao, K., Synthesis of few-layer GaSe nanosheets for high performance photodetectors. *ACS nano* 2012,6, 5988–5994.
- [63] Late, D. J.; Liu, B.; Luo, J.; Yan, A.; Matte, H. R.; Grayson, M.; Rao, C.; David, V. P., GaS and GaSe ultrathin layer transistors. *Adv. Mater.* 2012,24, 3549–3554.
- [64] Wickramaratne, D.; Zahid, F.; Lake, R. K., Electronic and thermoelectric properties of van der Waals materials with ring-shaped valence bands. *J. Appl. Phys.* 2015,118, 075101.
- [65] Hung, N. T.; Nugraha, A. R.; Saito, R., Two-dimensional InSe as a potential thermoelectric material. *Appl. Phys. Lett.* 2017,111, 092107.
- [66] T. Hung, N.; Nugraha, A. R.; Yang, T.; Zhang, Z.; Saito, R., Thermoelectric performance of monolayer InSe improved by convergence of multivalley bands. *J. Appl. Phys.* 2019,125, 082502.
- [67] Zeng, J.; He, X.; Liang, S.-J.; Liu, E.; Sun, Y.; Pan, C.; Wang, Y.; Cao, T.; Liu, X.; Wang, C.; Lili, Z.; Shengnan, Y.; Guangxu, S.; Zhenlin, W.; Kenji, W.; Takashi, T.; J., S. D.; Lijun, Z.; Feng, M., Experimental identification of critical condition for drastically enhancing thermoelectric power factor of two-dimensional layered materials. *Nano Lett.* 2018,18, 7538–7545.
- [68] Balendhran, S.; Walia, S.; Nili, H.; Sriram, S.; Bhaskaran, M., Elemental analogues of graphene: silicene, germanene, stanene, and phosphorene. *Small* 2015,11, 640–652.
- [69] Zhang, S.; Yan, Z.; Li, Y.; Chen, Z.; Zeng, H., Atomically thin

- arsenene and antimonene: semimetal–semiconductor and indirect–direct band-gap transitions. *Angew. Chem. Int. Ed.* 2015,54, 3112-3115.
- [70] Huang, H.; Fan, X.; Singh, D. J.; Zheng, W., The thermal and thermoelectric transport properties of SiSb, GeSb and SnSb monolayers. *J. Mater. Chem. C* 2019,7, 10652-10662.
- [71] Barreteau, C.; Michon, B.; Besnard, C.; Giannini, E., High-pressure melt growth and transport properties of SiP, SiAs, GeP, and GeAs 2D layered semiconductors. *J. Cryst. Growth* 2016,443, 75-80.
- [72] Lee, K.; Kamali, S.; Ericsson, T.; Bellard, M.; Kovnir, K., GeAs: Highly anisotropic van der Waals thermoelectric material. *Chem. Mater.* 2016,28, 2776-2785.
- [73] Wang, F. Q.; Guo, Y.; Wang, Q.; Kawazoe, Y.; Jena, P., Exceptional thermoelectric properties of layered GeAs₂. *Chem. Mater.* 2017,29, 9300-9307.
- [74] Zhao, L.-D.; Tan, G.; Hao, S.; He, J.; Pei, Y.; Chi, H.; Wang, H.; Gong, S.; Xu, H.; Dravid, V. P.; Ctirad, U.; Jeffrey, S. G.; Chris, W.; G., K. M., Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe. *Science* 2016,351, 141-144.
- [75] Zhao, T.; Sun, Y.; Shuai, Z.; Wang, D., GeAs₂: A IV–V group two-dimensional semiconductor with ultralow thermal conductivity and high thermoelectric efficiency. *Chem. Mater.* 2017,29, 6261-6268.
- [76] Zhang, W.; Huang, Z.; Zhang, W.; Li, Y., Two-dimensional semiconductors with possible high room temperature mobility. *Nano Res.* 2014,7, 1731-1737.
- [77] Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S., Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* 2012,7, 699-712.
- [78] Ghosh, K.; Singiseti, U., Thermoelectric transport coefficients in mono-layer MoS₂ and WSe₂: role of substrate, interface phonons, plasmon, and dynamic screening. *J. Appl. Phys.* 2015,118, 135711.
- [79] Kumar, S.; Schwingschlogl, U., Thermoelectric response of bulk and monolayer MoSe₂ and WSe₂. *Chem. Mater.* 2015,27, 1278-1284.
- [80] Li, W.; Carrete, J.; Mingo, N., Thermal conductivity and phonon linewidths of monolayer MoS₂ from first principles. *Appl. Phys. Lett.* 2013,103, 253103.
- [81] Zhang, G.; Zhang, Y.-W., Thermoelectric properties of two-dimensional transition metal dichalcogenides. *J. Mater. Chem. C* 2017,5, 7684-7698.
- [82] Yan, R.; Simpson, J. R.; Bertolazzi, S.; Brivio, J.; Watson, M.; Wu, X.; Kis, A.; Luo, T.; Hight Walker, A. R.; Xing, H. G., Thermal conductivity of monolayer molybdenum disulfide obtained from temperature-dependent Raman spectroscopy. *ACS nano* 2014,8, 986-993.
- [83] Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F., Atomically thin MoS₂: a new direct-gap semiconductor. *Phys. Rev. Lett.* 2010,105, 136805.
- [84] Fan, X.; Chang, C.-H.; Zheng, W.; Kuo, J.-L.; Singh, D. J., The electronic properties of single-layer and multilayer MoS₂ under high pressure. *J. Phys. Chem. C* 2015,119, 10189-10196.
- [85] Dou, X.; Ding, K.; Jiang, D.; Sun, B., Tuning and Identification of Interband Transitions in Monolayer and Bilayer Molybdenum Disulfide Using Hydrostatic Pressure. *ACS Nano* 2014,8, 7458-7464.
- [86] Fan, X.; Singh, D. J.; Zheng, W., Valence band splitting on multilayer MoS₂: mixing of spin–orbit coupling and interlayer coupling. *J. Phys. Chem. Lett.* 2016,7, 2175-2181.
- [87] Hippalgaonkar, K.; Wang, Y.; Ye, Y.; Qiu, D. Y.; Zhu, H.; Wang, Y.; Moore, J.; Louie, S. G.; Zhang, X., High thermoelectric power factor in two-dimensional crystals of MoS₂. *Phys. Rev. B* 2017,95, 115407.
- [88] Wickramaratne, D.; Zahid, F.; Lake, R. K., Electronic and thermoelectric properties of few-layer transition metal dichalcogenides. *J. Chem. Phys.* 2014,140, 124710.
- [89] Huang, W.; Luo, X.; Gan, C. K.; Quek, S. Y.; Liang, G., Theoretical study of thermoelectric properties of few-layer MoS₂ and WSe₂. *Phys. Chem. Chem. Phys.* 2014,16, 10866-10874.
- [90] Yumnam, G.; Pandey, T.; Singh, A. K., High temperature thermoelectric properties of Zr and Hf based transition metal dichalcogenides: A first principles study. *J. Chem. Phys.* 2015,143, 234704.
- [91] Ding, G.; Gao, G.; Huang, Z.; Zhang, W.; Yao, K., Thermoelectric properties of monolayer MSe₂ (M= Zr, Hf): low lattice thermal conductivity and a promising figure of merit. *Nanotechnol.* 2016,27, 375703.
- [92] Jin, Z.; Liao, Q.; Fang, H.; Liu, Z.; Liu, W.; Ding, Z.; Luo, T.; Yang, N., A revisit to high thermoelectric performance of single-layer MoS₂. *Sci. Rep.* 2015,5, 18342.
- [93] Sahoo, S.; Gaur, A. P.; Ahmadi, M.; Guinel, M. J.-F.; Katiyar, R. S., Temperature-dependent Raman studies and thermal conductivity of few-layer MoS₂. *J. Phys. Chem. C* 2013,117, 9042-9047.
- [94] Hellman, O.; Broido, D. A., Phonon thermal transport in Bi₂Te₃ from first principles. *Phys. Rev. B* 2014,90, 134309.
- [95] Qiu, B.; Bao, H.; Ruan, X.; Zhang, G.; Wu, Y. In *Molecular dynamics simulations of lattice thermal conductivity and spectral phonon mean free path of PbTe: Bulk and nanostructures*, *Comput. Mater. Sci.*, 2012; pp 278-285.
- [96] Sun, J.; Shi, H.; Siegrist, T.; Singh, D. J., Electronic, transport, and optical properties of bulk and mono-layer PdSe₂. *Appl. Phys. Lett.* 2015,107, 153902.
- [97] Chow, W. L.; Yu, P.; Liu, F.; Hong, J.; Wang, X.; Zeng, Q.; Hsu, C. H.; Zhu, C.; Zhou, J.; Wang, X.; Juan, X.; Jiaxu, Y.; Yu, C.; Di, W.; Ting, Y.; Zexiang, S.; Hsin, L.; Chuanhong, J.; Kang, T. B.; Zheng, L., High mobility 2D palladium diselenide field-effect transistors with tunable ambipolar

- characteristics. *Adv. Mater.* 2017,29, 1602969.
- [98] Oyedele, A. D.; Yang, S.; Liang, L.; Poretzky, A. A.; Wang, K.; Zhang, J.; Yu, P.; Pudasaini, P. R.; Ghosh, A. W.; Liu, Z., PdSe₂: Pentagonal two-dimensional layers with high air stability for electronics. *J. Am. Chem. Soc.* 2017,139, 14090-14097.
- [99] Wang, Y.; Li, Y.; Chen, Z., Not your familiar two dimensional transition metal disulfide: structural and electronic properties of the PdS 2 monolayer. *J. Mater. Chem. C* 2015,3, 9603-9608.
- [100] Qin, D.; Yan, P.; Ding, G.; Ge, X.; Song, H.; Gao, G., Monolayer PdSe₂: A promising two-dimensional thermoelectric material. *Sci. Rep.* 2018,8, 2764.
- [101] Lin, J.; Zuluaga, S.; Yu, P.; Liu, Z.; Pantelides, S. T.; Suenaga, K., Novel Pd₂Se₃ Two-Dimensional Phase Driven by Interlayer Fusion in Layered PdSe₂. *Phys. Rev. Lett.* 2017,119, 016101.
- [102] Naghavi, S. S.; He, J.; Xia, Y.; Wolverton, C., Pd₂Se₃ monolayer: a promising two-dimensional thermoelectric material with ultralow lattice thermal conductivity and high power factor. *Chem. Mater.* 2018,30, 5639-5647.
- [103] Gandi, A. N.; Schwingenschlögl, U., Thermal conductivity of bulk and monolayer MoS₂. *EPL* 2016,113, 36002.
- [104] Zhang, J.; Liu, X.; Wen, Y.; Shi, L.; Chen, R.; Liu, H.; Shan, B., Titanium trisulfide monolayer as a potential thermoelectric material: a first-principles-based Boltzmann transport study. *ACS Appl. Mater. Interfaces* 2017,9, 2509-2515.
- [105] Park, S. H.; Jo, S.; Kwon, B.; Kim, F.; Ban, H. W.; Lee, J. E.; Gu, D. H.; Lee, S. H.; Hwang, Y.; Kim, J.-S.; Dow-Bin, H.; Sukbin, L.; Jin, C. K.; Wook, J.; Sung, S. J., High-performance shape-engineerable thermoelectric painting. *Nat. Commun.* 2016,7, 1-10.
- [106] Suemori, K.; Watanabe, Y.; Hoshino, S., Carbon nanotube bundles/polystyrene composites as high-performance flexible thermoelectric materials. *Appl. Phys. Lett.* 2015,106, 113902.
- [107] Kim, S. J.; We, J. H.; Cho, B. J., A wearable thermoelectric generator fabricated on a glass fabric. *Energy Environ. Sci.* 2014,7, 1959-1965.
- [108] Lu, Z.; Layani, M.; Zhao, X.; Tan, L. P.; Sun, T.; Fan, S.; Yan, Q.; Magdassi, S.; Hng, H. H., Fabrication of flexible thermoelectric thin film devices by inkjet printing. *Small* 2014,10, 3551.
- [109] Kim, S. J.; Choi, H.; Kim, Y.; We, J. H.; Shin, J. S.; Lee, H. E.; Oh, M.-W.; Lee, K. J.; Cho, B. J., Post ionized defect engineering of the screen-printed Bi₂Te₂.₇Se_{0.3} thick film for high performance flexible thermoelectric generator. *Nano Energy* 2017,31, 258-263.
- [110] Kim, C. S.; Lee, G. S.; Choi, H.; Kim, Y. J.; Yang, H. M.; Lim, S. H.; Lee, S.-G.; Cho, B. J., Structural design of a flexible thermoelectric power generator for wearable applications. *Appl. Energy* 2018,214, 131-138.
- [111] Oh, J. Y.; Lee, J. H.; Han, S. W.; Chae, S. S.; Bae, E. J.; Kang, Y. H.; Choi, W. J.; Cho, S. Y.; Lee, J.-O.; Baik, H. K.; Il, L. T., Chemically exfoliated transition metal dichalcogenide nanosheet-based wearable thermoelectric generators. *Energy Environ. Sci.* 2016,9, 1696-1705.
- [112] Cai, X.; Sushkov, A. B.; Suess, R. J.; Jadidi, M. M.; Jenkins, G. S.; Nyakiti, L. O.; Myers-Ward, R. L.; Li, S.; Yan, J.; Gaskill, D. K.; E., M. T.; Dennis, D. H.; S., F. M., Sensitive room-temperature terahertz detection via the photothermoelectric effect in graphene. *Nat. Nanotechnol.* 2014,9, 814.
- [113] Muench, J. E.; Ruocco, A.; Giambra, M. A.; Miseikis, V.; Zhang, D.; Wang, J.; Watson, H. F.; Park, G. C.; Akhavan, S.; Sorianello, V.; Michele, M.; Andrea, T.; Camilla, C.; Marco, R.; C., F. A.; Ilya, G., Waveguide-integrated, plasmonic enhanced graphene photodetectors. *Nano Lett.* 2019,19, 7632-7644.

Design of Large Injection Mould for Car Dashboard

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Abstract:

The dashboard is the most important part of the large inner decoration of cars; it should not only have enough strength and rigidity, but also have a harmonious body model which can unify the theme. Besides, it needs to reach the goal of lightweight. In order to achieve these three goals, the car dashboard is made by engineering-plastics and adopts the technology of injection moulding. This paper introduces the keys of design and the advanced technology of large injection moulding for car dashboard.

Keywords: automobile instrument panel; injection mould; sequential valve gate

1 Structural Analysis of Plastic Parts

Plastic part is an example of a car dashboard. The materials are PP + EPDM- TD25, and shrinkage is 1.0095^[1]. EPDM can be improved elasticity, T20 can improve the rigidity of the bumper, and it refers to the material plus 20% talc.

The average wall-thickness of the plastic parts is 3.5mm. The maximum size of the shape is 1308.00 × 526.00 × 476.00 (mm). The detailed structure is shown in figure 1, its features are as follow: Firstly, there are a lot of holes, melt flow resistance is high, and they are difficult to fill. Mould gating The size of the plastic parts is enormous, as well as the structure is very complicated because system, exhaust system and guide positioning system design are the first key technology. Secondly, The plastic parts of seven lateral concave hole structure (shown in figure 1. S1to S7) are plenty and irregular, the side core-pulling mechanism and parting system design are the second key technology.

2 Structural Analysis of the Mould

Injection mould uses hot runner gating system. The core side and the cavity side of this mould are a union-body. The mould guide-positioning system uses square guide pillar and the internal model tube. The largest dimension of mould is 2200×1100×1425mm, detailed structure is shown in figure 2.

3 Design of Forming Parts

The principle of forming-part design is to achieve a minimum size while to ensure the strength and durability of the premise of the mould in order to reduce the

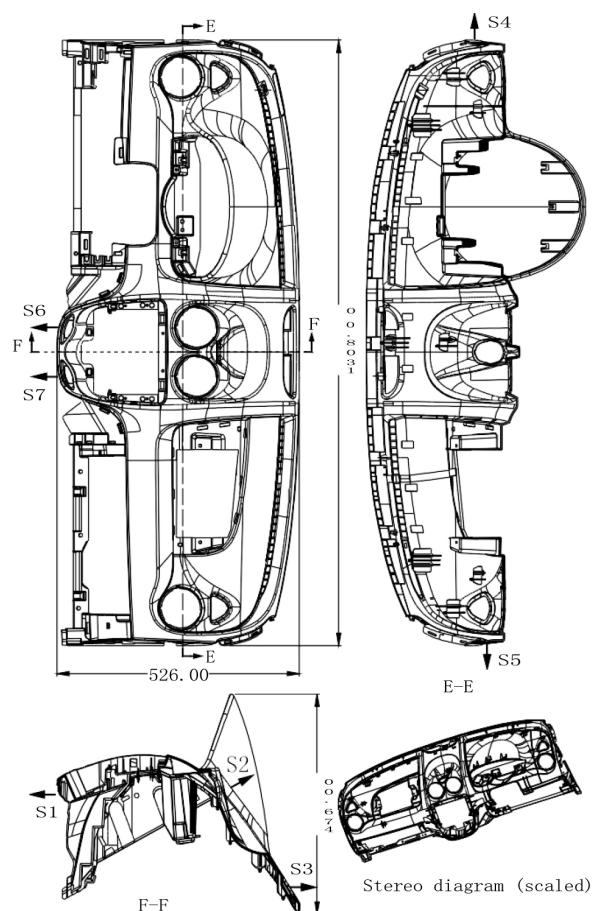


Figure 1 Car dashboard structure.

manufacturing cost and production costs [2].

Dashboard is a large plastic part with a complex structure. Mould is a large injection mould, and the parting surfaces are complex. In order to improve the stiffness and strength and to reduce the size, the mould template and moulded parts are designed to be integrated and inserted through all the holes which are greater than the angle of 7°. Given to the four corners of the template in the template notch protruding insert move, aimed at preventing a given template dislocation deformation, increasing the rigidity and strength of the mould.

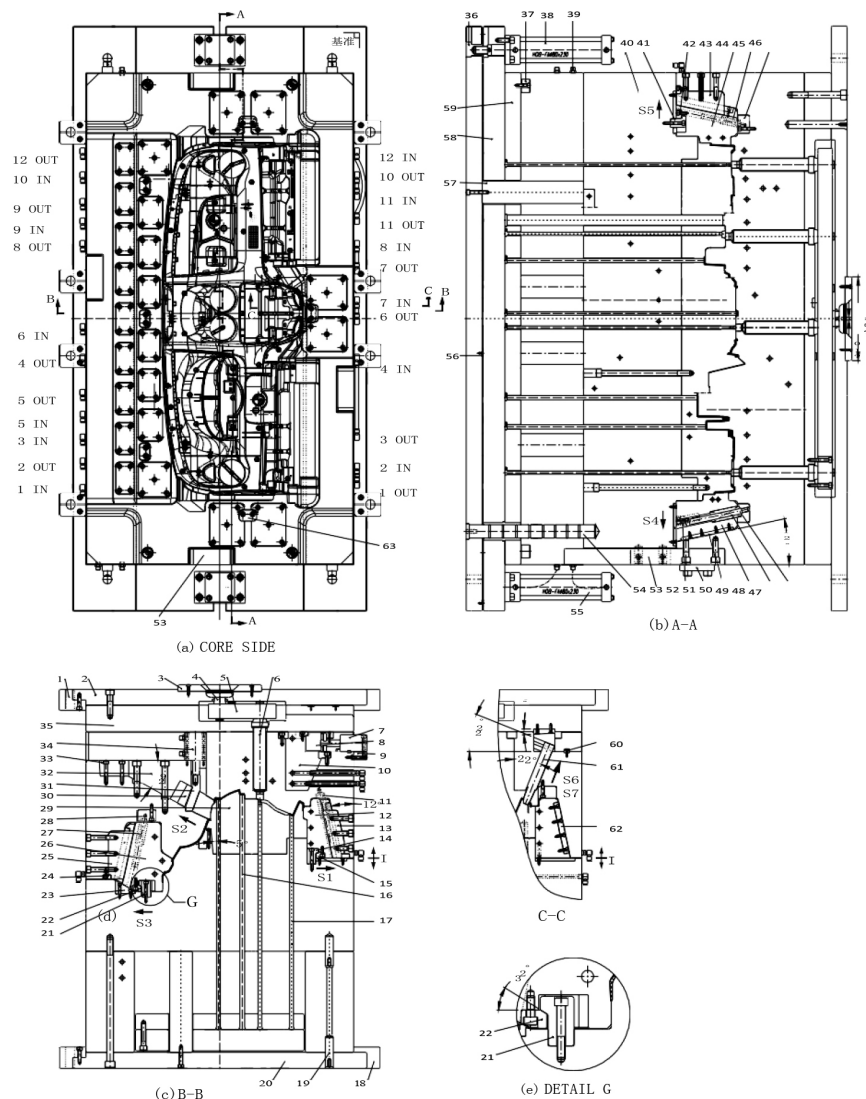
Appearance of the dashboard surface must be processed striae, and drafts of the product side must be greater than or equal to 5°, otherwise the plastic parts

cannot be out of the mould.

The fixed mould material is 2311, and the core material is P20. All cavity surface nitriding treatment should be carried out in order to improve the precision plastic parts and service life.

4 Design of Core Pulling Mechanism of Lateral

The side core pulling mechanism of the mould structure is most important and complex. Dashboard has seven lateral concave-convex structures and it needs 6 side core-pulling mechanisms. The lateral concave S6 and S7 are completed by the same side core-pulling mechanism (Shown in figure 2).



1. Cavity side fixed plate; 2. Top clamp plate; 3. Locating ring; 4. First Class nozzle; 5. Hot runner plate; 6. Second stage hot nozzle; 7. Thin cylinder; 8. T-type buckle; 9. Cylinder fixing seat; 10. Guide block; 11, 27, 45, 48. Spring; 12. Oblique slider; 13. Guide block; 14, 21, 41, 63. Hook; 15. Toggle block; 16, 17. Push rod; 18. Core side fixed plate; 19. Dowel pin; 20. Bottom clamp plate; 22. Toggle block; 23. Wear resistant block; 24. limit block; 25. Guide block; 26. Oblique slider; 28, 50. Wear resistant block; 29. Core insert; 30. Oblique core drawing; 31. Bending pin; 32. Briquetting; 33. Block; 34. Cylinder; 35. "A" plate; 36. Fixed block; 37. The limiting block; 38. Cylinder of push rod; 39. Oil pipe; 40. "B" plate; 42. Toggle block; 43. Guide block; 44. Oblique slider; 46. Spring mounts; 47. Spring guide rod; 49. Oblique slider; 51. Lock module; 52. Block; 53. The square guide column; 54. The round guide column; 55. Cylinder; 56. Stopper; 57. Support columns; 58. Ejector retainer plate; 59. Ejector plate; 60. Stop pin; 61. Oblique core drawing; 62. Wear resistant block.

Figure 2 The large injection mould of car dashboard

In this mould, inverted S1, S3, S4 and S5 are the "lateral oblique slider + spring + hook" core pulling mechanism, power source of oblique slide block core pulling is the hook and the spring. Here we should pay special attention to because if the spring did not receive mechanical impact, it will cause fatigue failure. Therefore, for large injection mould, oblique slide block core pulling must not only adopts a spring as power source. Hook structure is shown in figure 2 (e).

S2 is using the side core pulling mechanism with "inverted bending pin + block", which is composed of oblique core drawing30, bending pin31, core pulling pressing block 32 and block33. The power source of inclined core pulling30 is hydraulic cylinder 34 (Shown in figure 2 (c)).

Inverted S6 and S7 are using the "lateral hydraulic cylinder +T-type buckle" core pulling mechanism, composed of an inclined core pulling in 61 (2 pieces), thin cylinder 7, T-type buckle 8, oil cylinder base 9 and oblique core drawing guide block10. The power source of core pulling is the hydraulic cylinder (Shown in figure 2 (c) and (d)).

In the injection mould for car dashboard, it is better to use nitrogen gas spring and try to avoid using ordinary spring, because spring will be failure and damage the mould after a long time^[1].

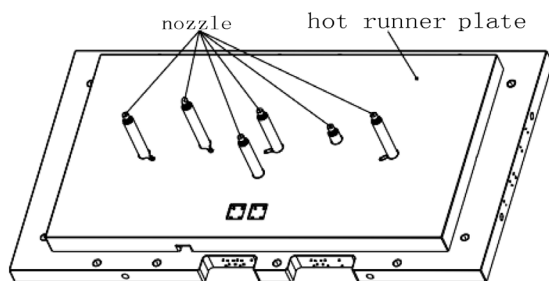


Figure 3 Sequential valve gating system.

5 Design of Gating System

In order to improve the melt filling, and to ensure the quality of the plastic parts moulding, mould casting used a hot runner system entirely, as is shown in figure 3.

The dashboard is the appearance, so weld lines must be formed on the non- appearance of the surface, or eliminate weld lines. This is the emphasis and difficulty in the mould design.

The traditional multi-point synchronization feed is difficult to achieve the desired quality requirements because of the presence of weld lines, even though making fill the entire cavity melt ^[3].

Therefore, this mould is using an advanced technology of sequence valve gate (SVG), and six hot nozzles are driven by the cylinder to control open and close that according to the requirements of order.

SVG is the recent development of a new hot runner

technology to meet the needs of the automotive industry for large flat plastic parts, as well as the demand for micro-electronics industry, thin-walled parts ^[4]. Using this key technology can not only eliminate weld lines or weld lines formed in the non-critical surface, but also get a smooth melt flow, reduce moulding pressure and residual stress, and ensure consistency throughout the plastic shrinkage. Thus it greatly improves the dimensional accuracy.

6 Design of Temperature Control System

The cooling system is significant in the automobile mould. Reliable cooling system can improve the forming quality of product and shorten the moulding time.

In the injection mould for car dashboard, there are 12 shares of "straight type cooling waterway + wells" cooling loop in the core side, and 20 shares "straight type cooling waterway + wells" cooling loop in the cavity side, as are shown in figure 4. The channel spacing distance is between 50 ~ 60mm, channel from the cavity surface is 20~ 25mm, channel arrangement is with the cavity surface shape. Channel crosses distributively, and the formation of waterway meshes uniform, not only enhances the mould labor productivity, but also avoids the buckling deformation of products. And it ensures the forming quality of plastic parts effectively.

7 Design of the Guiding and Positioning System

The guiding and positioning system directly affects the precision of product and mould service life, especially for large automobile injection mould. The mould is guided by four square pillar 53, which are arranged symmetrically in the mould of the four sides, and their size is: 174 × 60 × 612 (mm).

It should be noted that the parties cannot prejudice the position of the guide post robot that removed the plastic parts. In addition, the square pillar must be higher than the highest point of the mould core at least 30mm, which can ensure that the guide pin is inserted first when the movable mould clamping, and give effective protection of the core and cavity.

In order to ensure the safe and smooth launch of ejector pin, the fixed plate parts also used 4 round guide column 54, and their size is: $\phi 50 \times 480$ mm.

In the design of the positioning mechanism, there is one conical positioning structure in each corner, the size is 200 × 200mm, and the cone angle is 10 degrees, as is shown in figure 2 (a) and (b).

8 Design of Demoulding System

Stripping parts includes 50 pieces push rod and 21pieces ejector sleeve in this mould, because multi-pusher, ejection force and push the reset force pieces are larger, the ejection system uses two hydraulic cylinders as a power source. The cylinder Specifications Model is : HOB-FA□80×230. The position of cylinder is shown in figure 2 and figure 5.

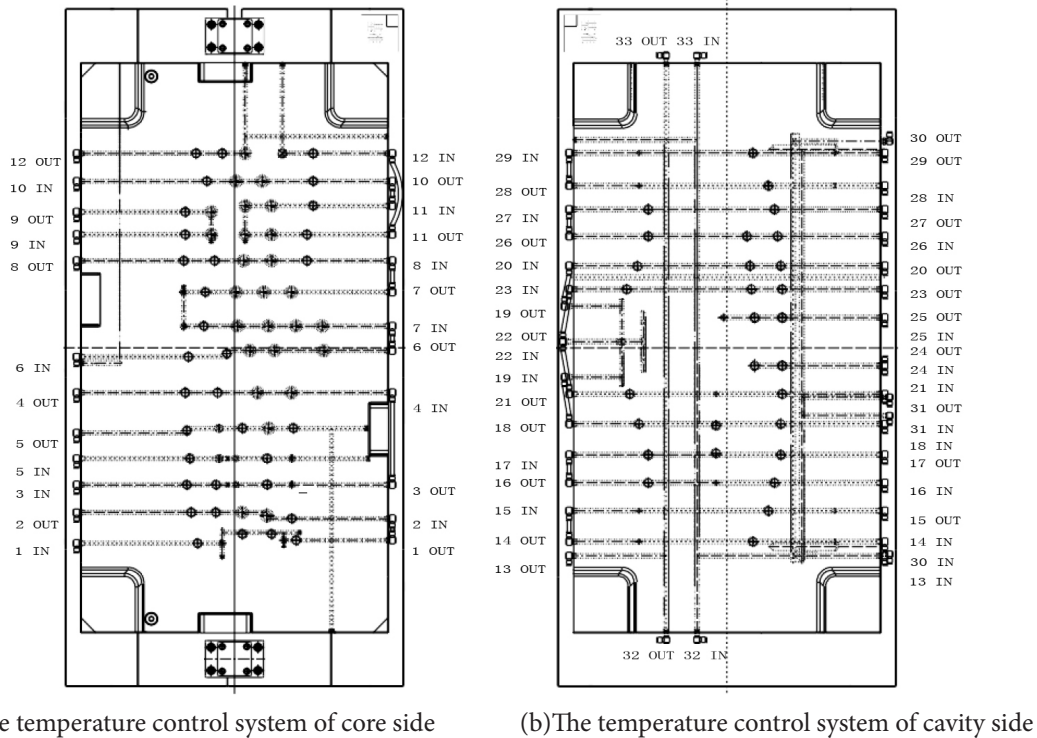


Figure 4 The temperature control system.

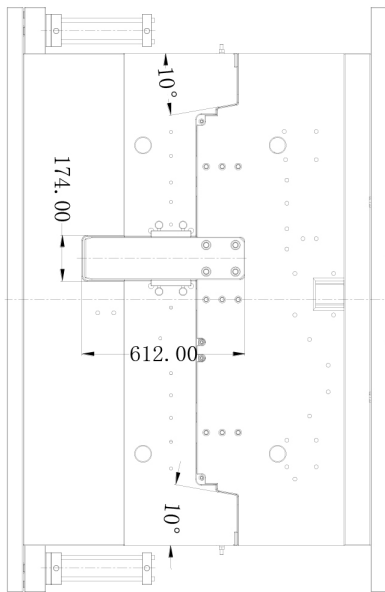


Figure 5 The position of cylinder for demoulding system

Due to the mould core uneven surface, all of the fixed end of the push rod and the push tube must design the structure to prevent rotation.

9 The Working Process of the Mould

(1) The plastic melts through the first class nozzle 4 into the hot runner plate 5 under the pressure of injection moulding machine. Then predetermined order into the mould cavity by the second stage hot nozzle 6 controlled by the sequence valve.

(2) The cavity is filling, packing, cooling and

solidifying.

(3) Cylinder 7 and 34 start when cured to rigid enough, and angle core 61 and 30 are pulling out of plastic parts by T-type buckle 8 and a square pin 31.

(4) Injection moulding machine pulls mould opening, after the completion of the fixed mould oblique core drawing. The mould is opened from the parting surface 1. In the retractor 14, 21, 41, 63 and spring 11, 27, 45, 48 action, the oblique slider 12, 26, 44 and 49 move from plastic parts, namely simultaneous lateral mould core pulling. That is, at the same time in the mould opening of side core pulling.

(5) After the completion of opening stroke 800mm, hydraulic cylinder 38 pushed rod plate 58 and put the fixed plate 5, then pushed rod. The dashboard were pushed away from the dynamic model of steady core, followed the dashboard removed by the robot will.

(6) The oil cylinder 7 and 34 push the angle core and reset 61 and 30, as well as hydraulic cylinder 38 and 35 to push the reset 16 and 17. Finally, injection moulding machine pushed the movable mould reposition, and then started the next injection moulding.

10 Conclusion

In recent years, the development of the automobile industry is just unfolding. Engineer and technical personnel pay more and more attention to the research and development of automobile mould. The large injection mould for dashboard is the most typical automobile mould, which is not only large in size, but also complicated in structure, has high precision and high moulding difficulty. Using a series of advanced technology in the mould would achieve good moulding effect. After the operation, the mould

action security coordination and the quality of plastic parts reached the requirement of design. The mould of the labor productivity has been improved obviously.

References

- [1] Zhang Weihe. Injection mould design practical guide [M]. Beijing: Chemical industry press, 2011, 112-148.
- [2] Zhang Weihe. Injection mould design Practical tutorial [M]. Beijing: Chemical industry press, 2011, 26-143.
- [3] Yangbin, liyanjie. Application of CAE technology in automobile dashboard in mould design [J]. Engineering Plastics Application, 2005, 33(3):61-63.
- [4] Guan zheng-qiang. sequential valve gate technology and its application[J].Manufacturing automation, 2010, 32(10), 206-207.
- [5] ZHANG Wei-he. Design of Large-sized Injection moulds for Main Bo s of Auto Central Channels[J]. China Plastics.2017:31(05): 92-97.
- [6] SUN Xiaoxia, TANG Youliang, ZHANG Jun. Design of Injection mould for Rearview Mirror Bracket of Automobile with Differential Combined Core-pulling[J]. China Plastics .2018, 32(6): 141-146.
- [7] ZHANG Wei-he. Design of injection mould of SVG and secondary ejection for automotive central decoration[J]. Engineering Plastics Application.2017, 46(7): 87-91.
- [8] Shen Zhongliang, Zheng Zijun, Xiao Guohua¹, Huang Jijun, You Jianguo .Design of IMD Group Mould for Central Control Panel in Automobile[J]. Engineering Plastics Application.2017, 45(1): 70-75.
- [9] ZHANG Wei-he. Design of injection mould of SVG and secondary ejection for automotive central decoration[J]. Engineering Plastics Application.2017, 46(7): 87-91.
- [10] Caozheng.The Design of Precision Injection mould of Mobile Shell base on mouldflow[J].China Plastic Industry. 2017, 45(05): 65-73.
- [11] Cheng Jianling.Design of injection moulds with core-pulling mechanism and Hotrunner system for screwed-bowl-covers[J]. China Plastics , 2015,29(9): 92-96.

High Temperature Flexural Deformation Properties of Engineered Cementitious Composites (ECC) with Hybrid Fiber Reinforcement

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Abstract:

Engineered Cementitious Composites (ECC) is a class of high-performance fiber reinforced composites with ultra-ductility designed based on micromechanics, and it has been developed for increasing application in the construction industry during recent decades. The properties of ECC at room temperature have been tested and studied in depth, however, few studies focus on its performance after high temperature that is one of the worst conditions to ECC. To investigate the change tendency and mechanism for the high temperature flexural properties of hybrid fiber reinforced ECC and the feasibility of calcium carbonate whisker to reduce the cost of ECC materials, polyvinyl alcohol fiber (PVA) reinforced strain hardening cementitious composites (PVA-ECC), steel fiber + PVA fiber reinforced ECC (defined as HyFRECC-A) and steel fiber + PVA fiber + CaCO₃ whisker reinforced ECC (defined as HyFRECC-B) subject to room temperature and 200 °C, 400 °C, 600 °C, 800 °C elevated temperature exposure were experimentally compared. The results indicate that equally replacing PVA fibers by steel fibers degraded the flexural hardening ability of PVA-ECC at room temperature, while the addition of appropriate amount of CaCO₃ whisker improved the flexural strength, toughness and flexural hardening behavior. The elevated temperature posed a significant effect on the flexural strength and toughness of the three types of ECCs. Flexural deflection hardening behavior of the three types of ECCs was eliminated after high temperature exposure. Flexural strength and toughness of PVA-ECC presented an exponential decay along with the increase of temperature. The addition of steel fiber slowed down the decay rate. Although the use of CaCO₃ whisker increased the post-temperature flexural strength and toughness of HyFRECC-B, the decay rate was not further decreased.

Keywords: engineered cementitious composites; hybrid fiber; high temperature; flexural behavior

1 Introduction

Based on fracture mechanics and micromechanics, Engineered Cementitious Composite (ECC) designed by adjusting fiber, matrix and interfacial properties of fiber/matrix significantly improved the inherent high brittleness and low toughness of cementitious materials [1-3]. ECC is a type of composite materials with high ultimate tensile strain (usually exceeds 1%) and obvious multiple crack cracking characteristics which makes it increasingly used in civil engineering, such as structural strengthening, Beam-column joints, lining tunnel and so on [4, 5]. However, the high cost of ECC has always been an engineering dilemma. The subject of application of ECC in construction consists of a set of problems that are central to effectively reduce the cost of it.

It is generally accepted that fiber blending is one of

the most important methods to reduce the cost of ECC so far [6-8]. The mix proportion and fundamental properties of hybrid fiber ECC materials (HyFRECC), which was added to fibers with different elastic modulus, was studied by domestic and foreign scholars in recent years. And based on the performance price ratio consideration, currently the attention of academic community and engineering community focus on steel fiber + PVA fiber reinforced ECC (HyFRECC-A). The tensile property, flexural property and anti-impact property of HyFRECC-A were investigated by scholars like Khin^[9, 10], Alessandro^[11], Zhang^[12], Xu^[13], etc. However, it must be emphasized that high temperature is one of the most adverse conditions that ECC may encounter in service [14, 15]. To date, several experimental studies conducted by Mechtcherine^[16], Bhat^[17], Magalhaes^[18] and Lin^[3] show that the tensile property of PVA-ECC is obviously degraded by high temperature. Especially when

the temperature exceeds 150 °C, PVA-ECC starts to lose its ductility. ECC loses almost all of its strain hardening characteristics and multi-slit cracking behavior due to PVA fiber, which is used to confect ECC widely up to now, would be melting and failure completely at 250 °C. However, limited effective investigations have been conducted to study the high-temperature behavior of steel fiber + PVA fiber reinforced ECC (HyFRECC-A). In terms of research findings of the high-temperature behavior of steel fiber reinforced concrete, the incorporation of steel fiber can effectively improve the basic mechanical properties of concrete after high temperature action. But the effect of steel fiber on the mechanical properties of PVA-ECC after high temperature is not clear at present, that's why it remains to be further explored.

Based on previous research results [19-21], the primary aim of this paper is to critically analyze the effects of cheap CaCO_3 whisker on the properties of ECC materials. In order to further reduce the cost of hybrid fiber ECC materials, steel fiber + PVA fiber + CaCO_3 whisker reinforced ECC (HyFRECC-B) was fabricated in our group. Then the flexural tensile properties of PVA-ECC, HyFRECC-A and HyFRECC-B at room temperature and after 200 °C, 400 °C, 600 °C, 800 °C elevated temperature exposure were experimental compared.

2 Test Materials and Methods

2.1 Matrix

Cement mortar matrix was selected, which contains P•O 42.5 cement, fly ash, fine quartz sand (particle size 100~210 μm , mean size 150 μm) and mixed according to cement, fly ash, quartz sand =1:4:1.8 ratio, water-binder ratio is 0.34. Polycarboxylic acid superplasticizer (water reduction rate 28.3%) and plasticizer (thickening type)

were used to adjust the workability of fresh mortar. Table. 1 shows the mass fraction of each mixture in the matrix.

2.2 Fibers

Steel fiber and CaCO_3 whisker were employed as the extra fibers of conventional ECC and the key point in the experimental study. Steel fiber selected from Shanghai Zhen Qiang Fiber Limited Company has end hooks. The melting point of PVA fiber selected from Japan kuraray Company is 244 °C~250 °C. The decomposition temperature of CaCO_3 whisker selected from Shanghai Feng Zhu Whisker Limited Company is 780 °C. Table. 2 lists the main parameter of fibers. From the table. 2, it can be seen that the price of CaCO_3 whisker and steel fiber is much cheaper than PVA, but both the tensile strength and elastic modulus of the other two fibers are much higher compared with PVA. In addition, CaCO_3 whisker, belonging to microfibers, provides effective reinforcement at the micro cracking level, restrain the generation and coalescence of micro cracks into unstable macro cracks, and bring great improvement of strength.

Up to now, common fiber volume dosage of HyFRECC-A in study on performance at room temperature is steel fiber 0.25%, PVA fiber 1.75%. Based on this dosage and combined with the previous research results, CaCO_3 whisker was added to confect HyFRECC-B. Previous research results [19-21] indicate that CaCO_3 whisker can improve the microstructure and fracture morphology of HyFRECC-A matrix by means of crack deflection, bridging and whisker pull-out. So as to improve the tensile strain hardening ability and multi-crack cracking ability of HyFRECC-A material, and further reduce the cost of HyFRECC-A by replacing PVA fiber with CaCO_3 whisker appropriately. Volume fraction of different fibers are listed in Table. 3.

Table 1 Mass fraction of each mixture

Powder (Cement + Fly ash + Sand)	Water	Water reducer	Plasticizer
1	0.248	2.62×10^{-3}	4.52×10^{-4}

Table 2 The main parameters of fibers

Types	Length/mm	Diameter/ μm	Tensile strength/ MPa	Elastic modulus/ GPa	Density/(g/ cm^3)	Price/ (thousand yuan/ton)
steel fiber	13	200	2000	200~210	7.8	20
PVA fiber	12	39	1100	42.8	1.3	140
CaCO_3 whisker	0.02~0.03	0.5~1	3000~6000	410~710	2.8	1.5

Table 3 Volume fraction of different fibers

Types	Groups	Steel fiber/%	PVA fiber/%	CaCO_3 whisker/%	Compressive strength /MPa
PVA-ECC	PVA2	0	2	0	41.7
HyFRECC-A	SF0.25PVA1.75	0.25	1.75	0	46.0
HyFRECC-B	SF0.25PVA1.7CW0.5	0.25	1.7	0.5	50.8
	SF0.25PVA1.65CW1	0.25	1.65	1	53.2

2.3 Specimen details

With reference to ISO 679^[22], the mixed materials were put into standard cement curing box (Temperature: $20 \pm 2^\circ\text{C}$, humidity: 95%) for 24h after they were formed, then take the specimen out of the mold and put it into the curing box for 28d. Finally, the specimens were removed and placed in an oven at 105°C for drying to a constant weight followed by high-temperature test. With reference to ASTM C348^[23], ASTM C1609^[24] and JCI-SF4^[25], the specimens with the dimension of $40\text{ mm} \times 40\text{ mm} \times 160\text{ mm}$ were tested to investigate the flexural behaviors. Each group has 15 proportioned specimens, which are used for flexural mechanical properties test under five temperature conditions. The preparation process of specimens adopted in the test are shown in figure 1.

2.4 High-temperature test

SX-10-12 box type resistance furnace was used to provide a high temperature environment. During the forming process of the specimens, WRNK-191 probe thermocouple was embedded and XMZ-101 temperature instrument was connected externally to monitor the temperature change in the center of the specimen to determine the difference

between the internal temperature of the specimen and the ambient temperature of the resistance furnace. Figure 2 shows the high temperature instrument.

The heating program is shown in figure 3, the heating rate is $10^\circ\text{C}/\text{min}$. Five temperature conditions (room temperature 20°C , 200°C , 400°C , 600°C and 800°C) were designed totally. In order to make the temperature inside and outside the specimen uniform, the temperature was maintained for 60 min under each high-temperature working condition. The specimens, which were naturally cooled to room temperature, were tested to investigate the flexural behaviors after high temperature action.

2.5 Loading configuration

Each specimen was loaded under four-point flexural by MTS E44 electronic universal testing machine with a span of 120mm between supports. Load transducer and clip type extensometer were employed to monitor the relationship between flexural load and mid-span deflection of specimen. Displacement loading control was adopted, and the loading rate was $0.1\text{ mm}/\text{min}$. The loading configuration is shown in figure 4.



Figure 1 Preparation process of specimens

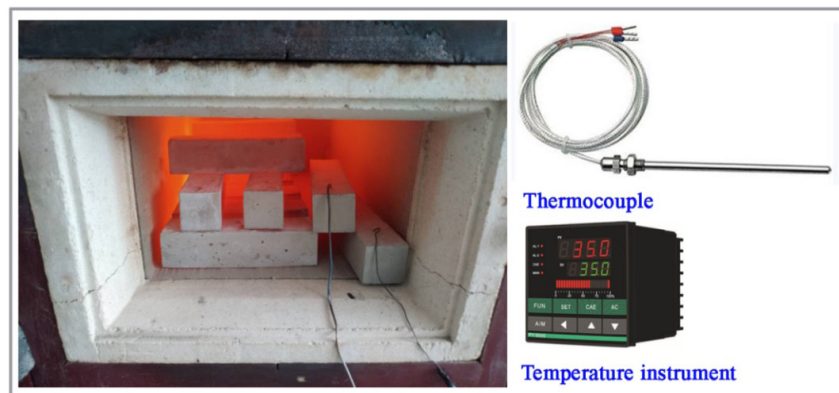


Figure 2 Instrument for high temperature test

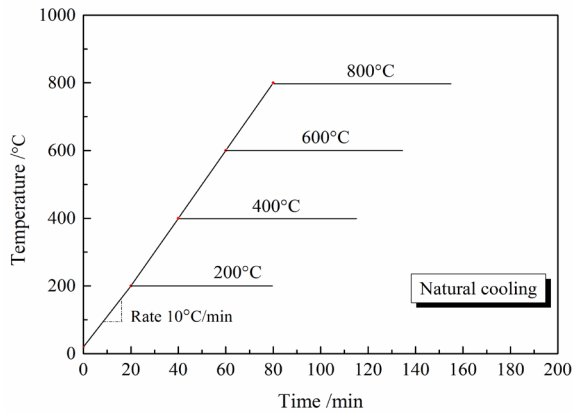


Figure 3 Heating Program for high temperature test



Figure 4 Loading instrument for flexural test

3 Experimental Results and Discussion

3.1 Appearance color change

Figure 5 shows the appearance color of PVA-ECC and HyFRECC-B specimens after natural cooling changes with the temperature experienced. It can be observed from figure 5 that the appearance color of all specimens is dark grey at room temperature, and the color of the specimen gradually fades to light brown with the increase in experienced temperature, that is no difference in the rule of color change of ordinary cement mortar and concrete at high temperature. With the increase in temperature, there are also the processes of evaporation of free water (30~105°C), decomposition of gypsum and ettringite (110~170°C), decomposition of calcium silicate hydrate, loss of binding water (180~300°C), mass decomposition of calcium silicate hydrate and calcium

hydroxide (450~550°C), and decomposition of calcium carbonate (700~900°C) in PVA-ECC and HyFRECC-B specimens^[26]. It is worth mentioning that since 400°C, the appearance color of specimens changed apparently which indicates the water loss process has basically ended, and the cement hydration products begin to decompose in large quantities. This process is very unfavorable to steel fiber and calcium carbonate whiskers due to the decomposition of calcium silicate hydrate will weaken the interfacial bond between the fiber and the matrix. In addition, the specimens of PVA-ECC and HYFRECC-B did not burst at high temperature, indicating that PVA fiber could restrain or alleviate the burst behavior of cement matrix composite at high temperature, as a consequence PVA fiber would melt at about 250 °C result in increasing the release channel of steam pressure inside the material^[27].

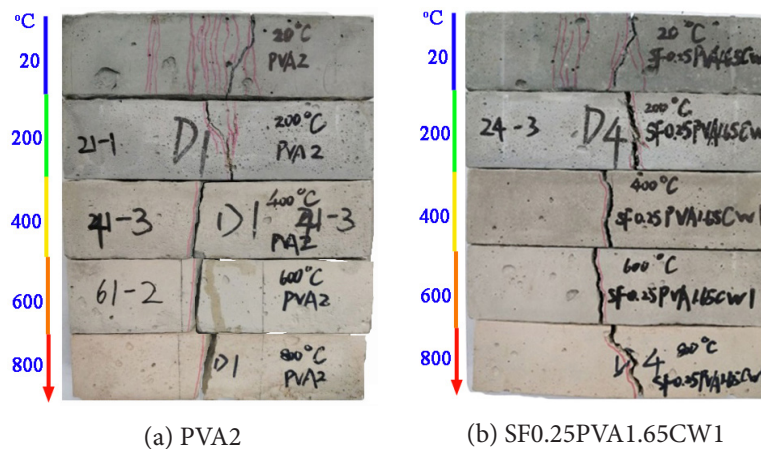


Figure 5 Effect of temperature on the color change of specimen

3.2 Load-deflection relationships

Three specimens were tested at room temperature for each mix proportion, and the median value of the flexural load-midspan deflection relationship is taken as the representative curve as seen in figure 6. It can be observed from figure 6a that the flexural specimens of PVA2 group showed obvious characteristics of deflection hardening. However, compared with PVA2 group, the

deflection hardening ability of SF0.25PVA1.75 (equivalent substituting PVA fiber with 0.25% steel fiber) specimens was significantly weakened. With the incorporation of CaCO₃ whisker (SF0.25PVA1.7CW0.5 and SF0.25PVA1.65CW1), compared with SF0.25PVA1.75 group, the flexural deflection hardening ability of specimens was significantly enhanced, although the ultimate deflection value was still lower than PVA2 group, the peak flexural load of

the specimen was significantly higher than PVA2 group, which further demonstrated the feasibility of replacing the relatively expensive PVA fiber with cheap CaCO_3 whisker. What's more, as shown in figure 6b, the initial crack of each specimen occurred at a deflection of $25\mu\text{m}$, and due to the addition of CaCO_3 whisker, its micro-crack resistance can make great contributions to increasing the initial crack load of specimens^[19].

Three specimens subjected to the temperature of 200°C were tested for each mix proportion, and the median value of the flexural load-midspan deflection relationship is taken as the representative curve as seen in figure 7. As shown in figure 7a, the specimens of PVA-ECC, HyFRECC-A and HyFRECC-B had basically lost the deflection hardening behavior after the temperature of 200°C , reflecting that PVA fiber plays a decisive role in the flexural deflection hardening behavior. Considering the fact that PVA fiber would soften significantly under the temperature of 200°C , which will destroy the interface bond between PVA fiber and cement matrix, and degrade the flexural deflection hardening behavior of specimens. In addition, the specimens in each group still retained a small amount of deflection hardening behavior, because the softened PVA fibers recovered some of their mechanical properties after natural cooling. Compared with PVA2 and SF0.25PVA1.75 groups, the addition of CaCO_3 whisker did not significantly

improve the flexural deflection hardening behavior of specimens but improved the flexural load of specimens with fuller post-peak curve, reflecting that the whisker is still beneficial to the toughness of the specimen. It can be observed from figure 7b, the initial crack of each specimen occurred at a deflection of $40\mu\text{m}$, and the first cracking load of specimen was improved due to the addition of whisker.

Figure 8, 9 and 10 show the typical flexural load-deflection relationships of tested specimen subjected to the temperature of 400°C , 600°C , 800°C respectively. It could be concluded by comparison that, when the temperature exceeds 400°C , all specimens in each group have completely lost the flexural deflection hardening behavior and changed into obvious softening characteristics. The reason lies in that the PVA fiber began to melt and decompose at about 250°C , which caused the PVA2 group specimens degraded into ordinary cement mortar specimens, showing obvious brittle failure behavior. In addition, it can be found that the peak flexural load of each group gradually decreases with the increase of temperature. The specimens of HyFRECC-A and HyFRECC-B subjected to the temperature of 400°C , 600°C and 800°C still had high load carrying capacity due to end hooks of steel fiber employed in the experiment. It can be found that the whisker, whose decomposition temperature is about 780°C , is still beneficial to improve the post-peak carrying capacity of the HyFRECC-B specimen

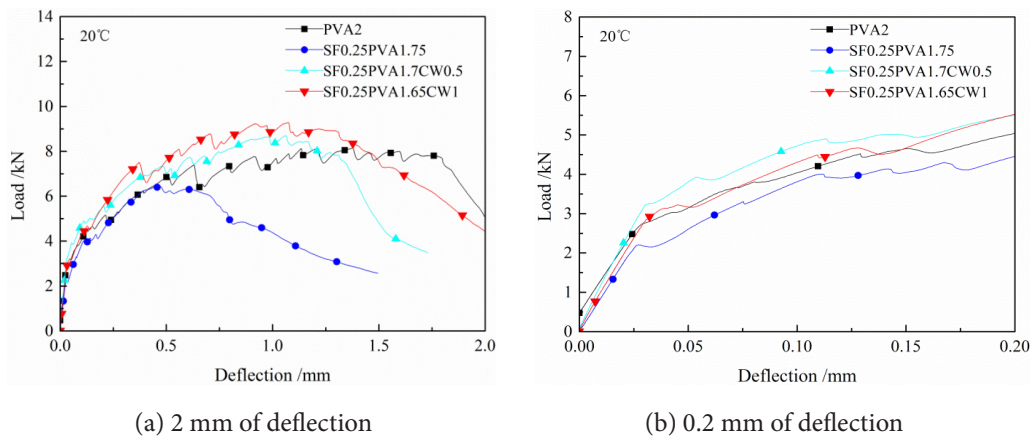


Figure 6 Flexural load-deflection curve of tested specimen at room temperature

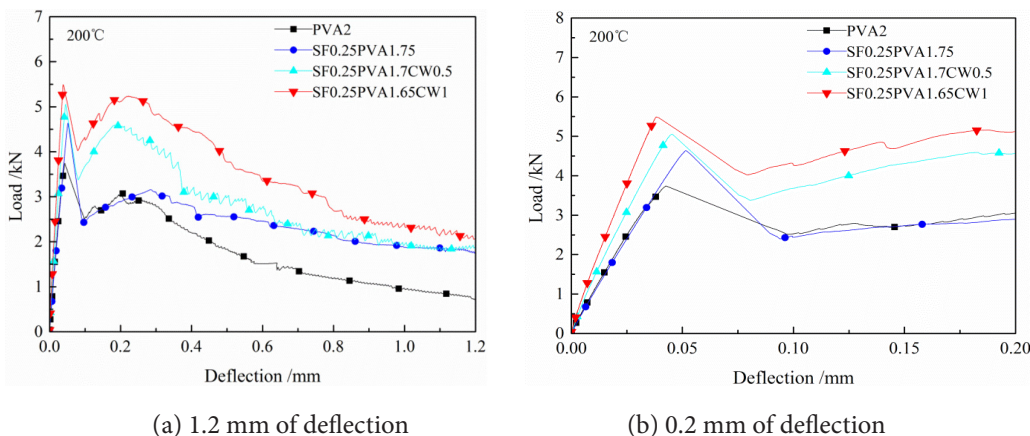


Figure 7 Flexural load-deflection curve of tested specimen after 200°C

after the temperature of 400 °C and 600 °C, and the carrying capacity tends to be further improved with the increase of whisker content, reflecting the superiority of the whisker properties. However, it can be observed from figure 10 that at 800 °C, the effect of whisker on the post-peak bearing capacity basically disappeared, and there was no obvious difference in the flexural load-deflection relationships between HyFRECC-A and HyFRECC-B specimens. By

comparing figure 8b, 9b and 10b, it can be found that due to the high-temperature deterioration of cement matrix, the initial crack deflection of each specimen increases with the increase of temperature. Compared with HyFRECC-A, the addition of CaCO_3 whisker improved the initial crack load and deflection of ECC materials, while the function of whiskers is no longer obvious after 800 °C.

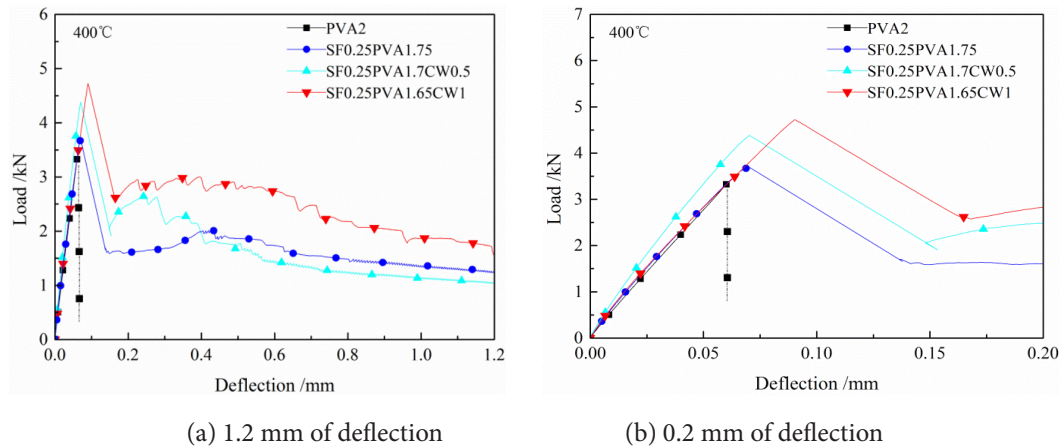


Figure 8 Flexural load-deflection curve of tested specimen after 400 °C

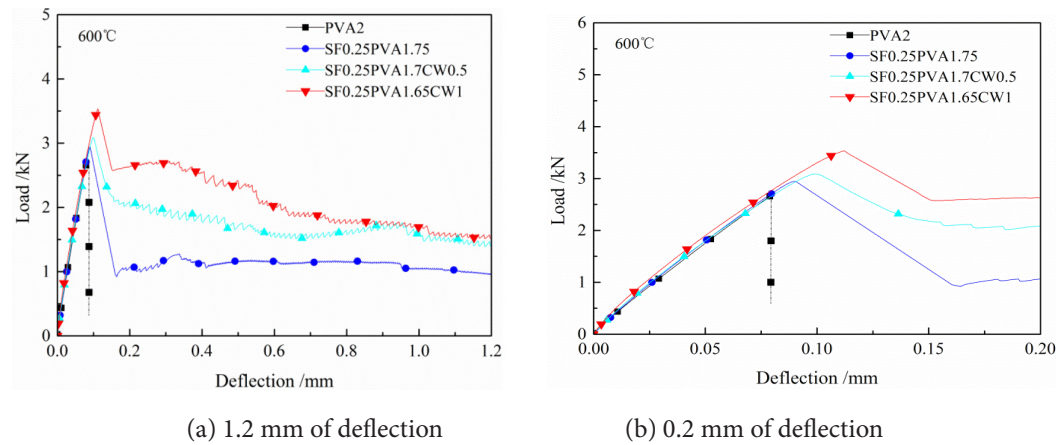


Figure 9 Flexural load-deflection curve of tested specimen after 600 °C

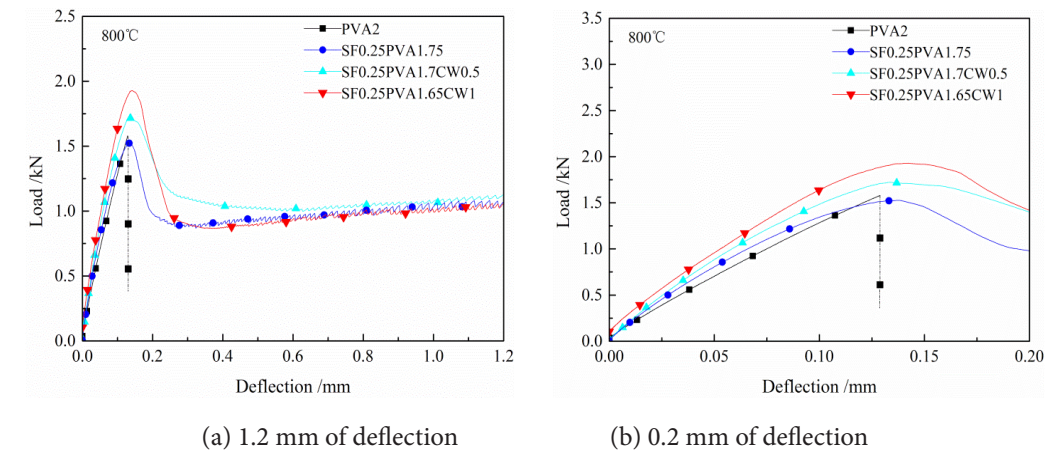


Figure 10 Flexural load-deflection curve of tested specimen after 800 °C

3.3 Flexural strength

Figure 11a plots the relationship between flexural strength and temperature of each group. The flexural strength of each specimen decreases significantly with the increase of temperature. At the same temperature, the flexural strength of HyFRECC-A was higher than that of PVA-ECC, and the incorporation of CaCO_3 whisker can further improve the flexural strength of specimens subjected to various temperatures. The relationship between the flexural strength of PVA2 group specimens and temperature as shown in figure 11b. The flexural strength of the specimen decreases exponentially with temperature in a situation where only PVA fiber is employed, and after 200 °C, the flexural strength of the specimen decreased by nearly 50%, while after 800 °C, the flexural strength of the specimen was less than 20% of the normal temperature, reflecting that the high temperature has a significant deterioration effect on the flexural strength of PVA-ECC. The relationship between the flexural strength of SF0.25PVA1.75 group specimens and temperature as shown in figure 11c. The flexural strength of the specimen decayed linearly with temperature due to steel fiber employed in the test. Compared with the PVA2 group, the flexural strength decayed more slowly. After 200 °C the flexural strength of the specimen decreased by 25%, and after 800 °C, the flexural strength of the specimen was about 23% of that at room temperature, indicating that the end hooks shaped steel fiber had a significant improvement

on the flexural strength of the specimen after high temperature. The relationship between the flexural strength of HyFRECC-B group specimens mixed with CaCO_3 whisker and temperature as shown in figure 11d. It can be found that the attenuation tendency of flexural strength with temperature keeps basically consistent between SF0.25PVA1.7CW0.5 and SF0.25PVA1.65CW1 group, while the attenuation tendency of SF0.25PVA1.7CW0.5 group is different from that of SF0.25PVA1.75 significantly. Compared with HyFRECC-A, the attenuation of flexural strength of HyFRECC-B is more obvious between 200 °C and 400 °C. The reason lies in that after 180 °C, calcium silicate hydrate begins to decompose, which weakens the interface bond between whisker and cement matrix and reduces the bridging effect of whisker, which is an important mechanism for whisker to exert its reinforcing effect [28]. Moreover, by comparing figure 11c with figure 11d, it can be found that despite the fact that CaCO_3 whiskers can improve the flexural strength of specimens after 400 °C, they have little significant influence on the attenuation rate of flexural strength with temperature.

3.4 Flexural toughness

Toughness reflects the ability of material to absorb energy and undergo plastic deformation before fracture. The flexural toughness of each group is obtained by integrating the load-deflection curve, which is calculated to $L/100$

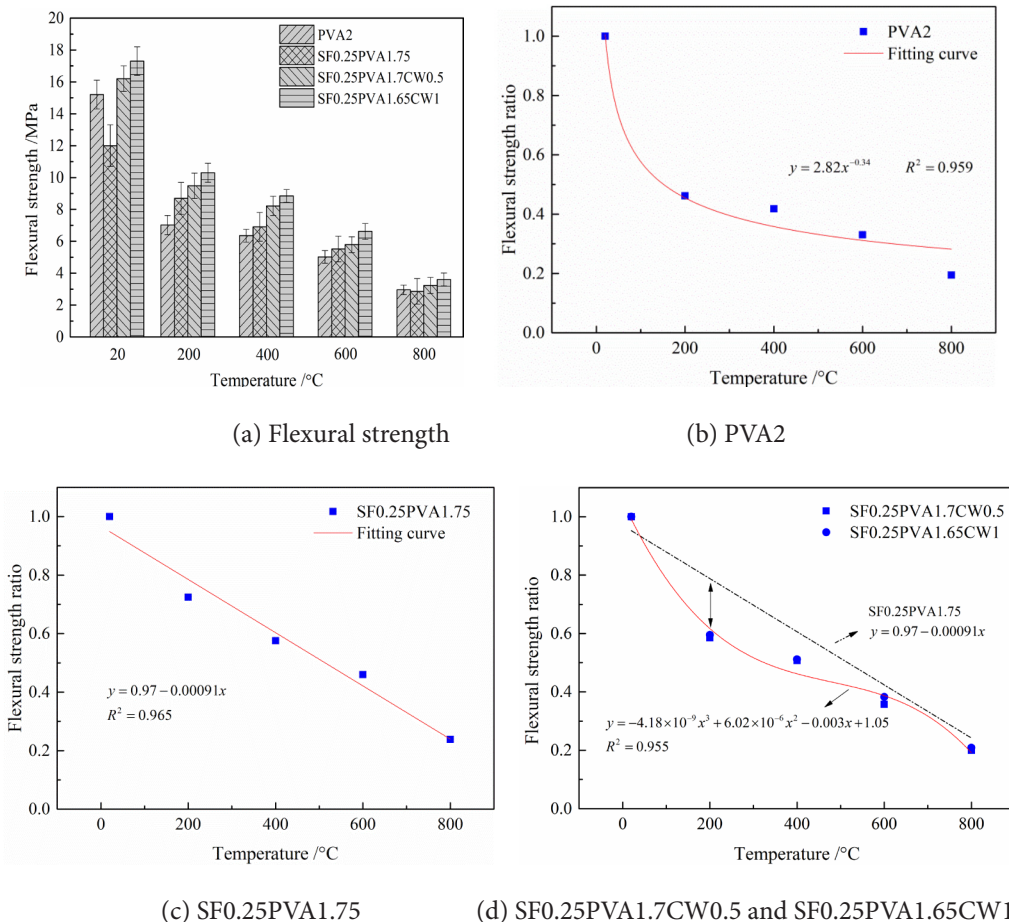
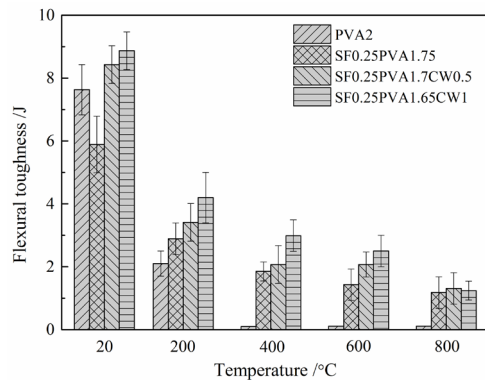


Figure 11 Effect of temperature on (a) flexural strength and (b) ~ (d) flexural strength ratio

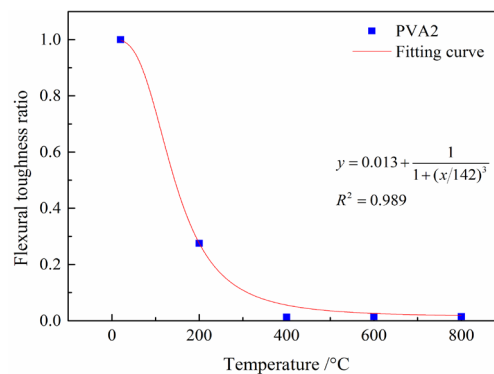
(referred to ASTM C1609^[24]), i.e., the deflection of 1.2mm. Figure 12a shows the relationship between the flexural toughness of each group of specimens and temperature. With the increase of temperature, the flexural toughness of each sample decreased obviously. At normal temperature, the flexural toughness of PVA2 group was significantly higher than that of SF0.25PVA1.75 group, reflecting that the use of steel fiber to substitute PVA fiber equivalently degraded flexural energy absorption capacity of ECC materials, while the addition of CaCO₃ whisker further improves the flexural toughness of ECC. Since whisker can improve the microstructure and fracture morphology of cement matrix by means of microcosmic effect such as crack deflection, bridging and whisker pull-out, the flexural deflection hardening and multi-crack cracking ability of steel fiber /PVA fiber HyFRECC-A material can be improved. In addition, it can be seen that when the temperature exceeds 400 °C, PVA2 materials are not significantly different from ordinary cement mortar, and the flexural toughness value is only about 0.1J. At the same temperature, the flexural toughness of HyFRECC-A is higher than that of PVA-ECC, and the introduction of CaCO₃ whisker can further improve the flexural toughness of specimens subjected to different high temperatures.

The flexural toughness value of each group of specimens at room temperature was taken as unit 1, and the comparison of the flexural toughness value at high

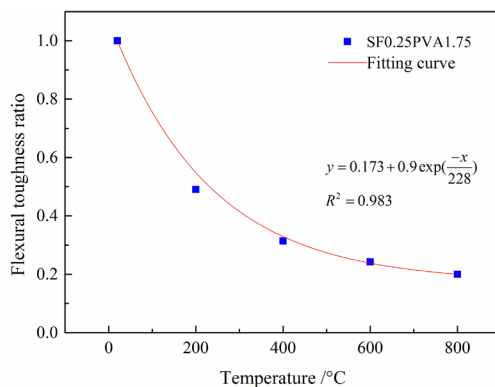
temperature was defined as the flexural toughness ratio. Figure 12b plots the relationship between the flexural toughness ratio of PVA2 specimens and temperature. The flexural toughness ratio of PVA2 group specimen decays exponentially with the increase of temperature. At 200 °C, the material's energy absorption capacity was less than 30% of the normal temperature, and after 400 °C, it was only about 1% of the normal temperature, proving that PVA-ECC could not service normally under high temperature environment. It can be concluded from figure 12c that the incorporation of steel fiber reduces the attenuation rate of flexural toughness. The flexural toughness of HyFRECC-A decays about 50% after 200 °C, while at 800 °C, the flexural energy absorption capacity of HyFRECC-A remained 20% compared with normal temperature. The relationship between the flexural toughness ratio of HyFRECC-B group specimens mixed with CaCO₃ whisker and temperature as shown in figure 12d. Compared with HyFRECC-A group (see figure 12c), it can be observed that the whisker failed to further retard the attenuation rate of the flexural toughness of the specimen, but only increased the flexural toughness of the specimen under various temperature conditions. The reason lies in that the bonding ability between whisker and cement matrix decreases with the increase of temperature, however, the toughening mechanism of whisker such as crack deflection and pull out is beneficial to improve the energy absorption capacity of ECC material^[28].



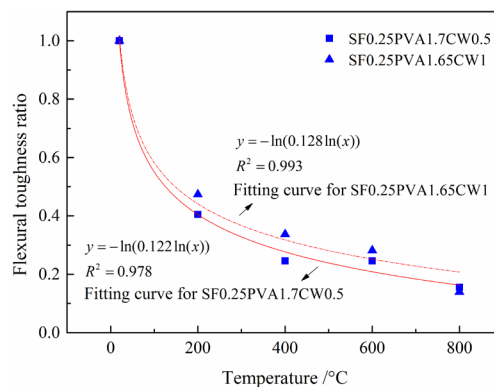
(a) Flexural toughness



(b) PVA2



(c) SF0.25PVA1.75



(d) SF0.25PVA1.7CW0.5 and SF0.25PVA1.65CW1

Figure 12 Effect of temperature on (a) flexural toughness and (b) ~ (d) flexural toughness ratio

4 Conclusion

In this paper, the effects of temperature on flexural performance in terms of flexural strength, flexural toughness of PVA-ECC, HyFRECC-A and HyFRECC-B were analyzed, demonstrating the feasibility of using calcium carbonate whisker to partially replace PVA fiber to reduce the cost of ECC materials. The following conclusions can be drawn:

At room temperature, the flexural deflection hardening ability of PVA-ECC is degraded by replacing PVA fiber with steel fiber, while it can improve the flexural strength, flexural toughness and deflection hardening ability in a situation where calcium carbonate whisker replaces PVA fiber. It is feasible to reduce the cost of PVA-ECC and steel fiber /PVA fiber HyFRECC-A by replacing PVA fiber with calcium carbonate whisker moderately.

Rather significant is the effect of high temperature action on the flexural strength of PVA-ECC, HyFRECC-A and HyFRECC-B specimens. After 200 °C exposure, all the materials in each group had lost the flexural deflection hardening ability basically, while after 400 °C, they had completely lost the flexural deflection hardening behavior and changed into obvious softening characteristics.

The flexural strength and toughness of PVA-ECC decrease exponentially with the increase of temperature, but the incorporation of steel fiber can slow down the attenuation rate of the flexural strength and toughness of specimens. Despite the fact that calcium carbonate whiskers can improve the flexural strength and flexural toughness of materials under high temperature, they are useless to slow down the attenuation rate of flexural strength and flexural toughness with temperature.

Author Contributions: Zhihui YU performed the experiment and wrote this manuscript; Zhen YUAN contributed significantly to manuscript preparation; Chaofan XIA performed the data analyses; Cong ZHANG helped perform the analysis with constructive discussions, he will be responsible for this article.

Conflict of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Li VC. Progress and application of Engineered Cementitious Composites [J]. Journal of the Chinese Ceramic Society, 2007, 35(4): 531-536.
- [2] Li VC. On Engineered Cementitious Composites (ECC) [J]. Journal of Advanced Concrete Technology, 2003, 1(3): 215-230.
- [3] LIU Zejun, LI Yan, WEN Congge. Experimental study on strength and deformation performance of PVA-ECC under splitting tension [J]. Journal of Building Materials, 2016, 19(4): 746-751.
- [4] Qudah S, Maalej M. Application of Engineered Cementitious Composites (ECC) in interior beam-column connections for enhanced seismic resistance [J]. Engineering Structures, 2014, 69: 235-245.
- [5] Choi W, Yun H, Cho C. Attempts to apply high performance fiber-reinforced cement composite (HPFRCC) to infrastructures in South Korea [J]. Composite Structures, 2014, 109: 211-223.
- [6] WANG Zhenbo, ZHANG Jun, WANG Qing. Mechanical behavior and crack width control of hybrid fiber reinforced ductile cementitious composites [J]. Journal of Building Materials, 2018, 21(2): 216-221.
- [7] Maalej M, Quek ST, Ahmed SFU, et al. Review of potential structural applications of hybrid fiber Engineered Cementitious Composites [J]. Construction and Building Materials, 2012, 36: 216-227.
- [8] WANG Zhenbo, ZUO Jianping, ZHANG Jun. Mechanical properties of hybrid fiber reinforced Engineered Cementitious Composites under uniaxial compression [J]. Journal of Building Materials, 2018, 21(4): 639-644.
- [9] Khin TS, Zhang YX, Zhang LC. Material properties of a new hybrid fibre-reinforced Engineered Cementitious Composites [J]. Construction and Building Materials, 2013, 43: 399-407.
- [10] Khin TS, Zhang YX, Zhang LC. Impact resistance of hybrid-fibre Engineered Cementitious Composite panels [J]. Composite Structures, 2013, 104: 320-330.
- [11] Alessandro PF, Hirozo M, Tomoya N. Tailoring hybrid strain-hardening cementitious composites [J]. ACI Materials Journal, 2014, March-April: 211-218.
- [12] Jun Zhang, Zhenbo Wang, Qing Wang. Simulation and test of flexural performance of polyvinyl alcohol-steel hybrid fiber reinforced cementitious composite [J]. Journal of Composite Materials, 2016, 0: 1-15.
- [13] Li QH, Gao X, Xu SL. Multiple effects of nano-SiO₂ and hybrid fibers on properties of high toughness fiber reinforced cementitious composites with high volume fly ash [J]. Cement and Concrete Composites, 2016, 72: 201-212.
- [14] Sahmaran M, Lachemi M, Li VC. Assessing mechanical properties and microstructure of fire-damaged Engineered Cementitious Composites [J]. ACI Materials Journal, 2010, 107(3): 1-8.
- [15] Sahmaran M, Lachemi M, Li VC. Effect of fly ash and PVA fiber on microstructural damage and residual properties of Engineered Cementitious Composites exposed to high temperatures [J]. ASCE Journal of Materials in Civil Engineering, 2011, 23(12): 1735-1745.
- [16] Mechtcherine V, Andrade S, Muller S. Coupled strain

- rate and temperature effects on the tensile behavior of strain-hardening cement-based composites (ECC) with PVA fibers [J]. *Cement and Concrete Research*, 2012, 42(11): 1417-1427.
- [17] Bhat PS, Chang V, Li M. Effect of elevated temperature on strain-hardening engineered cementitious composites [J]. *Construction and Building Materials*, 2014, 69: 370-380.
- [18] Magalhaes M, Toledo Filho R, Fairbairn E. Thermal stability of PVA fiber strain hardening cement-based composites [J]. *Construction and Building Materials*, 2015, 94: 437-447.
- [19] ZHANG Cong, CAO Ming-li. Mechanical property test of a multi-scale fiber reinforced cementitious composites [J]. *Acta Materialiae Composite Sinica*, 2014, 31(3): 661-668.
- [20] Ma H, Cai JM, Lin Z. CaCO_3 whisker modified Engineered Cementitious Composite with local ingredients [J]. *Construction and Building Materials*, 2017, 151: 1-8.
- [21] ZHANG Cong, CAO Ming-li. Using calcium carbonate whisker in hybrid fiber reinforced cementitious composites [J]. *ASCE Journal of Materials in Civil Engineering*, 2015, 27(4): 1-13.
- [22] International Organization for Standardization. ISO 679 Cement-Test methods-Determination of strength [S]. Switzerland: ISO, 2009.
- [23] American Society for Testing and Materials. ASTM C348 Standard test method for flexural strength of hydraulic-cement mortars [S]. Philadelphia: ASTM International, 2008.
- [24] American Society for Testing and Materials. ASTM C1609 Standard test method for flexural performance of fiber-reinforced concrete [S]. Philadelphia: ASTM International, 2010
- [25] Japan Concrete Institute. JCI-SF4 Methods of tests for flexural strength and flexural toughness of fiber reinforced concrete [S]. Japan: Japan Concrete Institute, 1983.
- [26] Lucia A, Gerard P, Etienne M. The use of thermal analysis in assessing the effect of temperature on a cement paste [J]. *Cement and Concrete Research*, 2005, 35: 609-613.
- [27] Liu JC, Tan KH. Mechanism of PVA fiber in mitigating explosive spalling of engineered cementitious composite at elevated temperature [J]. *Cement and Concrete Composites*, 2018, 93: 235-245.
- [28] ZHANG Cong, CAO Ming-li. Microscopic reinforcement for cement based composite materials [J]. *Construction and Building Materials*, 2013, 40: 14-25.

Isothermal and Non-Isothermal Crystallization Kinetics of PVDF and PVDF/PMMA Blends

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Abstract:

Background: poly(vinylidene fluoride) PVDF and PVDF/PMMA blends have been investigated with a focus on the crystal structure, immiscibility and mechanical properties. However, few reports were found on the crystallization behaviors of PVDF and PVDF/PMMA blends, especially on crystallization kinetics. The article is to report the research on isothermal and nonisothermal crystallization kinetics for PVDF and PVDF/PMMA blends using differential scanning calorimetry (DSC). Results: Besides crystallization temperature and isothermal crystallization activation energy, the Avrami equation exponent of PVDF in blends decreased compared with pure PVDF. The nonisothermal crystallization kinetics of PVDF and PVDF/PMMA (70:30) blends were investigated by Ozawa equation, Jeziorny method and crystallization rate constant (CRC) in detail. The nonisothermal crystallization energy of pure PVDF and its blends were determined by the Kissinger and Vyazovkin's method. Conclusion: The nucleation and growth mechanism of PVDF in blends changed compared with pure PVDF. The Ozawa equation is not applicable in nonisothermal crystallization kinetics of PVDF and PVDF/PMMA blends. The decreasing of crystallization ability of PVDF in blends were found and confirmed by CRC and the decline of crystallization rate constant in Jeziorny method. Such is opposite to the results of Kissinger's and Vyazovkin's method, chances are that these two methods were not used to calculate the nonisothermal crystallization activation energy where the nucleation process was influenced.

Keywords: PVDF; PMMA; crystallization; isothermal

1 Introduction

The investigation of isothermal and non-isothermal crystallization kinetics is very important to ultimate properties of polymer products. This is because many macroscopic properties of polymer largely depend on their crystal structure and spherulite morphology which in turn is determined by the crystallization conditions. So the research in this field is very useful for polymer industry.

PVDF, with excellent resistance to chemistry erosion, high temperature, oxidation and irradiation, especially good piezoelectricity, pyroelectricity, has been extensively studied in recent years^[1]. Many researchers have done a lot of works centered on the crystal structure, crystallization, grafting and blending^[2-6]. It has been reported that PVDF could be blended with many polymers and exhibited excellent properties^[7-10]. Recently, the physical blending of polymer thanks to its convenience and easy processing has been popular in polymer modification fields. PVDF and PMMA within the whole ratio could be miscible by melt blending or by solution blending. The reference^[11] has reported that PVDF with 30 wt% PMMA held good

balance of optical properties, solvent resistance, hardness, mechanical strength and weathering resistance, whereas relevant crystallization kinetics data is devoid, which are important meaning to the materials processing.

Therefore, the aim of this article is to obtain more information with respect to the crystallization behaviors of PVDF and PVDF/PMMA (the mass ratio is 70:30) using DSC. The dimethyl sulphoxide (DMSO) solvent was used to dissolve the PVDF and PMMA resin.

2 Experimental part

2.1 Materials and Sample Preparation

PVDF (FR902), with melt index 10g/min, is purchased from Shanghai 3F New Materials Co. Ltd. (China). PMMA resin (HT1000L) is bought from Kuraray Co. Ltd. (Japan).

PVDF and PVDF/PMMA with mass ratio of 70:30 are dissolved in the DMSO solvent at 70°C, agitated until the completion of dissolving yielding 20 wt% condensable solutions. The solution was casted on the glass plate, and then dried in a vacuum oven at 80°C for 24h in order to

remove the residual DMSO solvent.

2.2 DSC measurement

The Perkin-Elmer Diamond apparatus are used to investigate the crystallization kinetics of PVDF and PVDF/PMMA blends. The weights of samples are 3~4 mg to the transmission of quantity of heat. All the DSC runs are performed in the nitrogen atmosphere.

For isothermal crystallization process, at first, the samples are quickly heated to 210°C at a heating rate of 150°C /min in DSC, held for 5min to eliminate thermal history, and then quickly cooled to designated temperature which ranged from 159°C to 155°C at intervals of 1°C for PVDF and from 147°C to 143°C at intervals of 1°C for PVDF/PMMA blends, and maintained until the completion of crystallization. In the nonisothermal crystallization the PVDF and PVDF/PMMA blends, samples are heated to 210°C, and then cooled to room temperature at cooling rate of 2.5°C /min, 5°C /min, 10°C /min, 20°C /min and 40°C /min, respectively.

3 Results and Discussion

3.1 Avrami Equation Analysis of Isothermal Crystallization

The macroscopic isothermal crystallization kinetics are usually described in terms of the Avrami equation [12, 13], which has been successfully applied in many polymer systems:

$$X(t) = 1 - \exp(-kt^n) \quad (1)$$

This equation may be rewritten further,

$$\ln(-\ln(1-X(t))) = \ln k + n \ln t \quad (2)$$

Where $X(t)$ is relative crystallinity at time t , n represents the Avrami exponent that is correlated to the crystallization mechanism and k is overall crystallization rate constant. According to Eq. 2 we can obtain the Avrami exponent and crystallization rate constant from the slope and interception of plots of $(-\ln(1-X(t)))$ versus $\ln t$ at various crystallization temperatures (shown in figure 1 and 2).

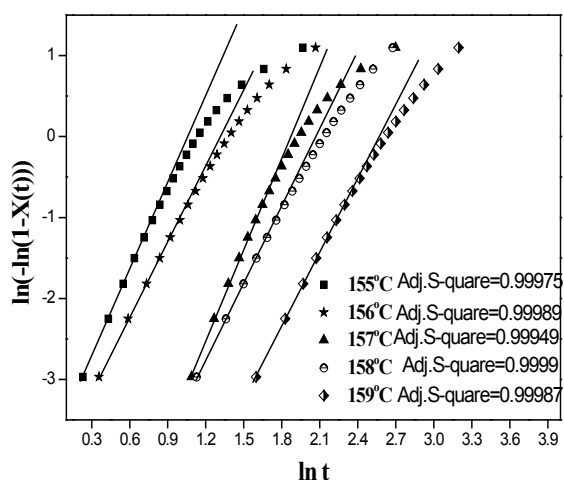


Figure 1 The plots of $\ln(-\ln(1-X(t)))$ and $\ln t$ for PVDF at various crystallization temperature T_c

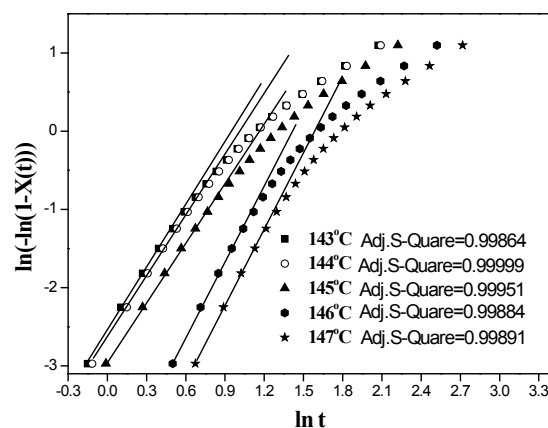


Figure 2 The plots of $\ln(-\ln(1-X(t)))$ and $\ln t$ for PVDF/PMMA blends at various crystallization temperature T_c

Obviously, in figure 1 for PVDF and 2 for PVDF/PMMA blends, each curve exhibited a beeline at preliminary crystallization which meant the experimental data agreed well with the Avrami equation at low relative crystallinity, and at later crystallization the curves showed a little deviation due to the impingement of spherulites. By fitting to the linear portion at preliminary crystallization of every curve, the Avrami parameters n and crystallization rate constant k can be obtained and the results are shown in Table 1.

Table 1 The isothermal crystallization kinetics parameters for PVDF and PVDF/PMMA blends

	T_c (°C)	n	k	$t_{1/2}$ (min)	t_{max} (min)
pure PVDF	155	3.56	2.27×10^{-2}	2.61	2.64
	156	3.04	1.75×10^{-2}	3.36	3.32
	157	3.85	7.95×10^{-1}	5.82	5.90
	158	3.09	1.575×10^{-3}	7.16	7.11
	159	3.07	3.85×10^{-4}	11.51	11.39
PVDF/PMMA	143	2.62	7.83×10^{-2}	2.30	2.20
	144	2.66	7.08×10^{-2}	2.36	2.27
	145	2.51	5.33×10^{-2}	2.78	2.63
	146	3.15	1.10×10^{-2}	3.74	3.71
	147	3.13	6.437×10^{-3}	4.46	4.43

Another two important kinetics parameters is half-time of crystallization $t_{1/2}$ and t_{max} . $t_{1/2}$ is defined as the time at which the crystallization is 50% complete, is determined by

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{1/n} \quad (3)$$

t_{max} represents the maximum crystallization rate corresponds to the point at which $dQ(t)/dt = 0$, with $Q(t)$ being the heat-flow rate. t_{max} can be calculated by the Avrami equation, as follows:

$$t_{max} = \left(\frac{n-1}{nk} \right)^{1/n} \quad (4)$$

The $t_{1/2}$ and t_{max} may be used to characterize the

crystallization rate, which increases as crystallization temperature increases (in Tab 1). It was interesting that the change extent of $t_{1/2}$ or t_{max} for pure PVDF was larger than that for PVDF in PVDF/PMMA blends, which is correlated to higher crystallization temperature of pure PVDF. At the same time this also suggested that PVDF crystallization was more sensitive to temperature changes than PVDF in blends.

From Tab 1 we can also see that after PVDF blending with PMMA the crystallization temperature of PVDF shifted prominently toward to the lower temperature. This indicated that the PVDF crystallization ability turned weak since the movement of PVDF molecular chains were limited by more PMMA. In Tab 1 the Avrami exponents for pure PVDF changed from 3.04 to 3.85 and from 2.51 to 3.15 for PVDF in blends. This indicated that the nucleation and growth mechanism have change from three-dimensional growth to two-dimensional growth. Reference [14] has reported that the noncrystalline component would influence nucleation mechanism and growth geometry of crystalline component.

3.2 Isothermal Crystallization Activation Energy (ΔE)

The isothermal crystallization activation energy ΔE is determined by the Arrhenius equation [15], which presumes that the isothermal crystallization process of polymer is to be thermally activated,

$$k^{1/n} = k_0 \exp\left(-\frac{\Delta E}{RT_c}\right) \quad (5)$$

$$\frac{\ln k}{n} = \ln k_0 - \frac{\Delta E}{RT_c} \quad (6)$$

Where k is the crystallization rate constant, n the Avrami exponent, k_0 is the temperature-independent pre-exponential factor, T_c is the crystallization temperature, R is the gas constant and ΔE is isothermal crystallization activation energy.

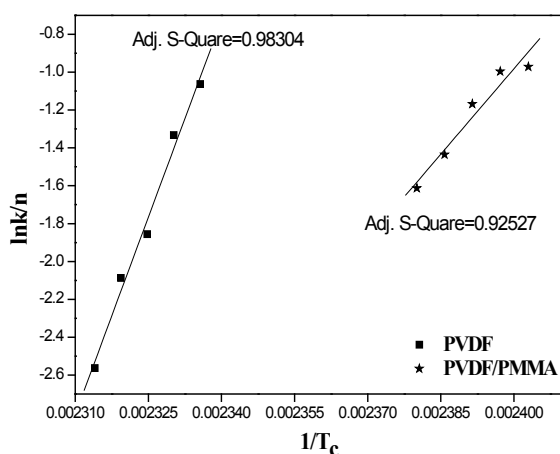


Figure 3 The isothermal crystallization activation energy ΔE for PVDF and PVDF/PMMA blends determined by the plots of $\ln k/n$ and $1/T_c$

By fitting the plots of $\frac{\ln k}{n}$ versus $\frac{1}{T_c}$ (shown in

figure 3), the isothermal crystallization activation energy ΔE for pure PVDF and PVDF in PVDF/PMMA blends are determined to be -577.6kJ/mol and -250.0kJ/mol, respectively. After PVDF blending with PMMA the isothermal crystallization activation energy dramatically decreased, but it must be noted that the values of ΔE were not applied to elucidate difficulty extent of crystallization in the present experiments owing to the difference of crystallization temperature. In light of the Eq.5 we know that PVDF with higher ΔE will be more sensitive to temperature variation than PVDF in blends with lower ΔE during nonisothermal crystallization process. This accorded with the changes of $t_{1/2}$ or t_{max} in Avrami equation.

3.3 Ozawa Equation of Nonisothermal Crystallization

In order to apply the Avrami equation to the nonisothermal crystallization process, Ozawa [16] proposed a method which assumes the polymer system cooled at a constant rate and the Ozawa exponent m is independent on temperature, which can be prescribed in the following form:

$$1 - X(T) = \exp[-P(T)/\phi^m] \quad (7)$$

$$\log[-\ln(1 - X(T))] = \log P(T) - m \log \phi \quad (8)$$

Where $X(T)$ is relative degree of crystallinity at crystallization temperature T , m the Ozawa exponent, related to the nucleation mechanism and growth geometry, $P(T)$ is the cooling function of nonisothermal crystallization. By calculating the slope and intercept of $\log[-\ln(1 - X(T))]$ versus $\log \phi$ we can easily the values of m and $P(T)$. Figure 4 and 5 showed the plots of $\log[-\ln(1 - X(T))]$ and $\log \phi$ for PVDF and PVDF/PMMA blends at different crystallization temperature. From the two figures we know that the $\log[-\ln(1 - X(T))]$ present curves with $\log \phi$, instead of straight line, and the Ozawa exponents also varied with crystallization temperature. The results suggested that the Ozawa equation was not adaptive to analyze the nonisothermal crystallization behaviors of PVDF and its blends due to ignoring the seconding crystallization.

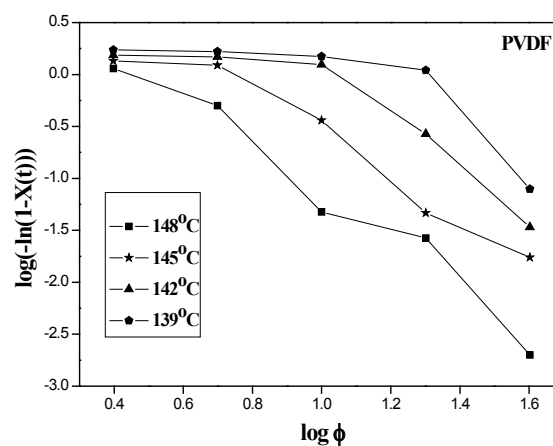


Figure 4 The nonisothermal crystallization of PVDF analyzed by the Ozawa equation

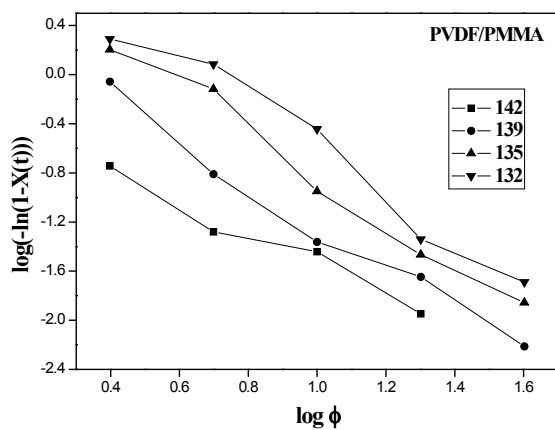


Figure 5 The nonisothermal crystallization of PVDF analyzed by the Ozawa equation

3.4 The Avrami Equation Modified by Jeziorny

Mandelkern^[17, 18] proposed that the nonisothermal crystallization kinetics could be described by the Avrami equation, as follows:

$$\log\{-\ln[1-X(t)]\} = n \log t + \log Z_t \quad (9)$$

Where Z_t is the crystallization rate constant. Considering the effect of cooling or heating rate, Jeziorny^[19] assumed ϕ to be constant or approximately constant.

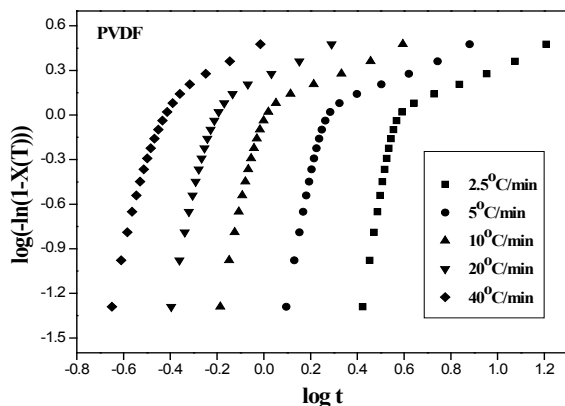


Figure 6 The plots of $\log(-\ln(1-X(T)))$ and $\log t$ for PVDF at various cooling rate

The final form of the rate parameter (Z_c), characterizing the nonisothermal crystallization kinetics is given as follows:

$$\log Z_c = \frac{\log Z_t}{\phi} \quad (10)$$

Figure 6 and 7 showed the plots of $\log\{-\ln[1-X(t)]\}$ versus $\log t$ for PVDF and PVDF/PMMA blends at various cooling rate. The values of n and Z_c could be obtained from the slope and intercepts, respectively, the results were exhibited in Tab 2. Similar to isothermal crystallization the whole nonisothermal crystallization process may be also divided into two stages: primary and secondary crystallization stages. Dissimilarly, whether in PVDF or PVDF/PMMA blends the Avrami exponent of primary crystallization stage far surpassed 3 at various cooling rate, which hinted spherulite nucleation and growth is very complicated. From Tab 2, we can see that at the same cooling rate the crystallization temperature and the crystallization rate constant of PVDF in blends were lower than that of pure PVDF, which implied the addition of PMMA weaken crystallization ability of PVDF. This is possible attributed to the two reasons: firstly, excess PMMA molecules must inhibit the movement of PVDF molecules during crystallization process. Secondly, the decrease of the concentration of PVDF molecules in blends at unit volume should not be ignored.

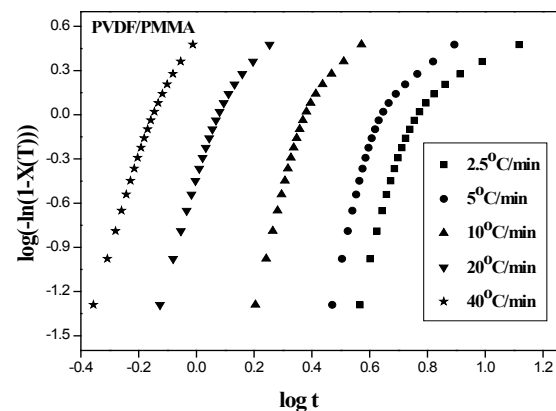


Figure 7 The plots of $\log(-\ln(1-X(T)))$ and $\log t$ for PVDF/PMMA blends at various cooling rate

Table 2 The nonisothermal crystallization kinetics parameters for PVDF and PVDF/PMMA blends

	Φ (°C/MIN)	T_c (°C)	Primary		Secondary	
			Crystallization Stage		Crystallization Stage	
			n_1	Z_{c1}	n_2	Z_{c2}
PVDF	2.5	150	9.6	7.3×10^{-3}	0.64	0.74
	5	148	8.1	0.39	0.66	0.94
	10	145	7.9	1.04	0.69	1.01
	20	141	7.7	1.23	0.71	1.03
	40	137	6.8	1.20	0.88	1.09
PVDF/ PMMA	2.5	141	7.7	5.5×10^{-3}	1.2	0.46
	5	137	8.7	0.085	1.6	0.64
	10	131	8.2	0.51	2.0	0.86
	20	124	6.8	0.96	2.2	0.99
	40	115	6.5	1.1	3.0	1.03

3.5 Crystallization Rate Coefficient (CRC)

Khanna ^[20] put forwarded a new parameter to describe crystallization ability, “crystallization rate coefficient $CRC = \Delta\phi / \Delta T_c$ ”. ϕ is the cooling rate and T_c the crystallization peaks temperature. The values of T_c at various Φ are exhibited in Tab 2. Here, the larger the values of CRC, the stronger the ability of polymers crystallization is. In the present works, we obtain the values of CRC for PVDF and PVDF/PMMA by fitting cooling rate ϕ versus crystallization peaks temperature T_c (shown in figure 8). In evidence, the slope of PVDF plots is higher than that of PVDF/PMMA blends, which suggested that crystallization ability of PVDF is weakened after blending with PMMA. This result is consistent with the outcomes of Jeziorny method. The CRC values of PVDF and PVDF/PMMA are 166 h^{-1} and 87 h^{-1} , respectively. The CRC of PVDF (166 h^{-1}) is very bigger among semi-crystalline polymers, which approaches to the PTFE, far above PE, nylon 66, nylon 46, PET, etc. however, when blending with PMMA the CRC of

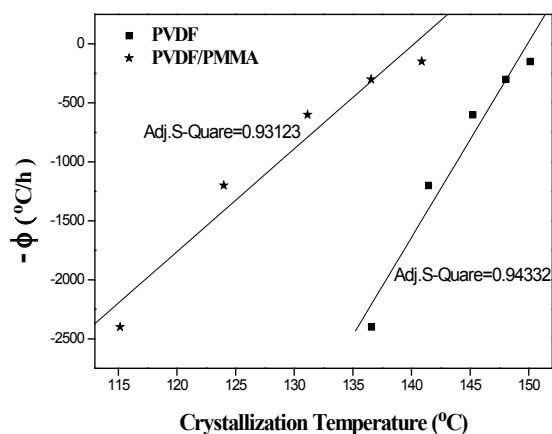


Figure 8 The crystallization rate constant CRC for PVDF and PVDF/PMMA blends at cooling process

3.7 Activation Energy of non-Isothermal Crystallization Proposed by Vyazovkin

Vyazovkin ^[22] believed that the Kissinger's method is not used to determined the nonisothermal crystallization activation energy on cooling from melt, therefore he proposed and adopted Friedman's ^[23] equation to calculate the nonisothermal crystallization activation energy ΔE , as follows:

$$\ln\left[\frac{dX(T)}{dt}\right] = \ln[Af(X(T))] - \frac{\Delta E}{RT} \quad (12)$$

Where $X(T)$ is the relative crystallinity, t is the time, A is the pre-exponential factor, and $f(X(T))$ is the crystallization model. At a certain relative crystallinity, $X(T)$, the slope of the plot of $\ln[dX(T)/dt]$ versus $1/T$ was used to measure ΔE , which displayed in figure 10. The application of this method to nonisothermal crystallization activation energy yields crystallinity-dependent activation energy. the ΔE of pure PVDF firstly decreased with relative crystallinity increasing, when dropped to minimum value at 60% relative crystallinity, ΔE increase suddenly above

PVDF dramatically decreased to 87 h^{-1} , which is close to the CRC of nylon 46 and nylon 66 ^[15].

3.6 Activation Energy of Non-Isothermal Crystallization

Considering the changes in the crystallization peak temperature with the cooling rate ϕ , we can derive ΔE for non-isothermal crystallization by the Kissinger method ^[21]:

$$\frac{d[\ln(\phi / T_c^2)]}{d(1/T_c)} = - \frac{\Delta E}{R} \quad (11)$$

Where T_c is the crystallization peaks temperature; ϕ is the cooling rate; R is the gas constant; ΔE nonisothermal crystallization activation energy. The plots of $\ln(\phi/T_c^2)$ and ΔE were shown in figure 9. The values of ΔE of PVDF and PVDF/PMMA blends were determined to be 295.3 kJ/mol and 148.1 kJ/mol through fitting the linear parts, respectively, the nonisothermal crystallization activation energy ΔE did not become bigger but smaller. The reason will be discussed in next section.

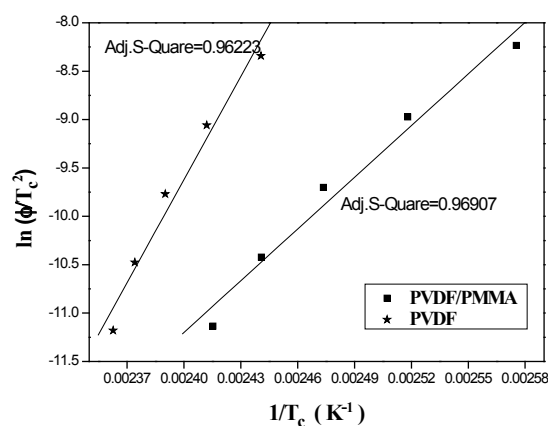


Figure 9 the nonisothermal crystallization activation energy determined by Kissinger method for PVDF and PVDF/PMMA blends

60% relative crystallinity. The changing trend for ΔE in pure PVD proved that at early crystallization stage the polymer system the crystallization rate increase rapidly with crystallization time prolonging, but crystallization rate is slow due to the spherulite impingement and the reduction of crystallizable molecules at later crystallization stage, therefore the nonisothermal crystallization activation ΔE increases. Conversely, the activation energy ΔE for PVDF in PVDF/PMMA blends by and large does not change on the whole relative crystallinity ranges and keeps at 123 kJ/mol or so, this is possibly correlated to PVDF diluted and dispersed by PMMA.

Note that in terms of CRC and Jeziorny method the PVDF in PVDF/PMMA blends crystallization should be weakened compared with pure PVDF, that is, the nonisothermal crystallization activation energy ΔE would increased after PVDF blended with PMMA. However, both the Kissinger's method and Vyazovkin's method showed the ΔE decreased after blending. Such phenomenon, some researchers considered, the Kissinger method is not suited in treating with nonisothermal crystallization on cooling

from melt ^[22], the others ^[24] figured the Kissinger method was not used in which the spherulite nucleation and growth were affected, in our situation the authors considered, similar to Kissinger method, the Vyazovkin's method was also not appropriate where spherulite nucleation and growth were affected.

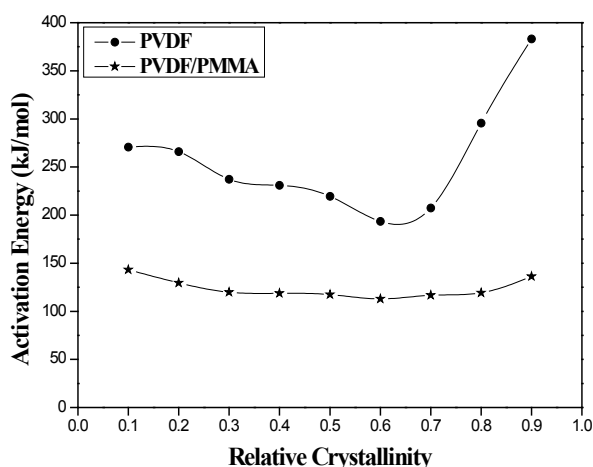


Figure 10 The nonisothermal crystallization activation energy as a function of relative crystallinity for PVDF and PVDF/PMMA blends on the basis of Vyazovkin's advice

4 Conclusions

Using the DSC we studied the isothermal and nonisothermal crystallization kinetics of PVDF and PVDF/PMMA blends with mass ratio 70:30, which were prepared by dissolving in DMSO. The isothermal crystallization kinetics were analyzed by the Avrami equation, and the results have indicated PVDF spherulite in blends have changed into two-dimensional growth, at the same time the decrease of crystallization temperature was found. The isothermal crystallization activation energy in PVDF was determined to be -577.6kJ /mol, higher than that PVDF in blends (-250.0kJ /mol). At the same cooling rate the PVDF/PMMA blends represented lower crystallization peaks temperature compared with PVDF, what's more the crystallization rate constants Z_c for PVDF at primary or secondary crystallization stage were higher than that for blends. The crystallization rate constant (CRC) was measured to be $166h^{-1}$ OF PVDF and $87h^{-1}$ of PVDF in blends, respectively. The results of Z_c and CRC implied that PVDF crystallization ability in PVDF/PMMA blends weakened under nonisothermal crystallization conditions. It was found that the Ozawa equation was not used to investigate nonisothermal crystallization kinetics for PVDF and PVDF/PMMA blends. The Kissinger method and Vyazovkin's method were not proper to calculate

nonisothermal crystallization activation energy in which the nucleation was influenced.

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References

- [1] Esterly DM and Love BJ. J Polym Sci Part B: Polym Phys 42:91 (2004).
- [2] Zhang GZ, Kitamura T, Yoshida H and Kawai T, J Therm Anal Calorim 69:939 (2002).
- [3] Gregorio JR and Cestari M, J Polym Sci Part B: Polym Phys 32:859 (1994).
- [4] Moussaif M, Pagnoulle C, Riga J and Jerome R, Polymer 41:3391 (2000).
- [5] Li G., Zhu B, Zhang C and Xu Y, J Appl Polym Sci 107:2109 (2008).
- [6] Holmberg S, Nasman J and Undholm F, Polym Advan Technol 9:121 (1996).
- [7] Nishi T and Wang TT, Macromolecules 8:909 (1975).
- [8] Kader MA, Kwak SK, Kang SL, Ahn JH and Nah C, Polym Int 57:1199 (2008).
- [9] Pramoda K, Mohamed A, Phang IY and Liu TX, Polym Int 54:226 (2005).
- [10] Benedetti E, Catanorchi S, Alessio AD and Vergamini P, Polym Int 45:373 (1998).
- [11] Lin S, Argasinski K, In:Hougham G, Cassidy Pe, Johns K, Davidson T, (Eds). Fluoropolymer Alloys Performance Optimization of PvdF Alloys, Plenum Press, New York, P121 (1999).
- [12] Avrami MJ, Chem Phys 7:1103 (1939).
- [13] Avrami MJ, Chem Phy 8:212 (1939).
- [14] Chiu HJ, J Polym Res 9:169 (2002).
- [15] Yin JH and Mo ZS, Modern Polymer Physics, Science Press, Beijing, 2001
- [16] Ozawa T, Polymer 12:150 (1971).
- [17] Fava RA, Methods of Experimental Physics Academic New York, 1980, 16.
- [18] Zhang QX, Zhang ZH, Zhang HF and Mo ZS, J Polym. Sci Part B: Polym Phys 40:1790 (2002).
- [19] Jeziomy A, Polymer 19:1142 (1978).
- [20] Kissinger HE, J Res Natl Bur Stand 57:217 (1956).
- [21] Vyazovkin S, Macromol Rapid Comm 23:771 (2002).
- [22] Friedman H, J Polym Sci Part C 6:183 (1964).
- [23] Liu MY, Zhao QX, Wang YD, Zhang CG, Mo ZS and Cao SK, Polymer 44:2537 (2003).

Effect of Carbides and γ/γ' Eutectic on Crack Initiation and Propagation in Ni-based Superalloy

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Abstract:

The Ni-based Udimet720Li superalloy tends to form large γ/γ' eutectic on grain boundaries (GBs) during solidification due to the addition of excessive Al and Ti elements, which provides convenience to study the effect of carbide and γ/γ' eutectic on crack initiation and propagation during tensile process. In this paper, Udimet720Li superalloy samples were prepared by induction melting casting method, arc melting and suction casting method. The microstructure, tensile properties and mechanism of crack initiation and propagation in Ni-based superalloy fabricated by two methods are investigated. The results exhibit γ/γ' eutectic accelerates the stress concentration at GB and thus leads to premature fracture failure. The samples with grain-boundary eutectic have higher strain hardening rate, but their cumulative and local misorientations are lower. For samples without eutectic at GB, the primary crack initiates at grain-boundary carbide along GB and extends along GB or into grain matrix, and exhibits better deformation performance and dislocation storage capacity within grains.

Keywords: Superalloy; Carbides; Eutectic; Crack

1 Introduction

Ni-based superalloy has excellent strength, creep, fatigue and corrosion resistance, which is widely used in high-temperature parts of gas turbine, such as turbine disk and combustion chamber [1,2]. The excellent high-temperature strength mainly arises from the precipitation of ordered and coherent γ' (Ni_3Al) phase in the solid solution matrix [3]. Udimet720Li (developed from Udimet720) alloy is a γ' reinforced alloy developed in the late 1970s [4] that operates at higher temperature ($\sim 730^\circ\text{C}$) than other nickel-base alloy turbine disk. The alloying method is the most widely used method in the microstructure and mechanical properties of Ni-based superalloy. Compared with Udimet720, carbon and boron contents are reduced in Udimet720Li to reduce carbide and boride stringers and improve the forgeability, thus avoiding the need for powder processing [5,6]. Moreover, chromium content decreases from 18 to 16 wt. % to enhance tissue stability and prevent the formation of σ phase, so there is less likely of mechanical properties degradation during high temperature service [7]. The additions of Al and Ti (up to 7.5 wt. %) cause the severe segregation and large precipitation of γ/γ' eutectic in the interdendritic region while significantly increasing

the volume fraction of γ' phase [8]. It was acknowledged from alloying experiments that the excellent mechanical properties of Udimet720Li superalloy are mainly come from the precipitation hardening effect of γ' phase (L12 ordered $\text{Ni}_3(\text{Al,Ti})$ particles) and $\text{M}(\text{C,N})$ (carbon-nitride precipitates) within grain and at GBs [9-11].

In general, the researches demonstrate that the factors affecting the mechanical properties of polycrystalline Ni-based superalloy include precipitates phase, grain size and GB, etc. Microstructures have different effects on the mechanical properties of polycrystalline nickel base superalloy [12,13]. Yan et al. [14] studied the microstructure and lateral properties of a directionally solidified (DS) superalloy with different amounts of boron added. It was found that after solution heat treatment, a γ' cladding was formed around the carbides in boron-containing alloys, which significantly improves transverse creep life and tensile properties at room temperature and 870°C . Chang et al. [15] found that γ/γ' eutectic preferentially consumed Al and Ti in the melt and pushed B and Zr into the final solidified melt, resulting in the formation of coarse γ/γ' eutectic structure, η phase and boride in the final solidification stage. Pang et al. [16] studied the influence of

initial microstructure on fatigue crack initiation and short crack propagation at room temperature and found that smaller grain size and coherent γ' phase particle size and higher volume fractions of γ' precipitates improved overall fatigue lifetimes in Udimet720Li superalloy. However, coarsening of grain and secondary γ' precipitates decreases strength and ductility both at room temperature and 400 °C^[17]. Previous researches focused on the precipitation of phase during the solidification of Udimet720Li superalloy^[8,15], the effect of grain size on properties^[16,18], and the tensile properties of heat treated state^[17,19]. Although carbide and γ/γ' eutectic have been determined to cause stress concentration which is a dominant factor for cracking, there is still no clear explanation on the role of carbides and γ/γ' eutectic in crack initiation and propagation.

In addition, researchers are committed to optimize the microstructure to simultaneously improve the strength and ductility of materials. Traditional methods to enhance strength are grain-refined strengthening, solution strengthening, dispersion strengthening and strain strengthening. For example, when the grain size is greater than 1 μm , grain refinement can often increase strength without causing a significant decrease in ductility^[20-22]. However, traditional strengthening methods can cause dislocations to interact with internal barriers (such as solution atoms, dispersed particles, and GBs) and often reduce plasticity^[20]. In particular, owing to the local concentration of internal stress, particles in micron size are the positions priority for crack nucleation, in particular to the particles segregated at GBs, thus considerably reducing ductility and fatigue strength^[23-26]. Reasonable ways for optimizing the trade-off between strength and ductility are to take into account the fact that features that not only impede dislocation but also to withstand plastic strain should be strengthened^[27,28]. Therefore, it is of great significance to explore and study the mechanism of its strengthening strength and ductility. Regulating the microstructure of material, such as a certain degree of grain refinement, precipitation refinement and the elimination of the brittle segregation is considered to be a reasonable approach for optimizing the strength and ductility trade-off.

The cooling rate is an important influence on the solidification process and microstructure of Ni-base superalloy^[29-31], and the evolution of microstructure with cooling rate is closely related to the precipitation behavior of the phases. As a superalloy, Udimet720Li tends to form large γ/γ' eutectic microstructure on GBs during solidification due to the addition of excessive Al and Ti elements, which provides convenience to study the effect of carbide and γ/γ' eutectic microstructure on crack initiation and propagation during tensile process. In this paper, induction melting casting method and arc melting suction casting method were used to fabricate Udimet720Li superalloy samples, respectively. Arc melting and suction casting method have fast cooling. By comparing the tensile properties of the microstructures in alloys fabricated by two method, and the local misorientation after stretching was analyzed by electron backscatter diffraction (EBSD)

technique, the effect of carbides and γ/γ' eutectic on crack initiation and propagation was determined.

2 Experimental procedures

The nominal compositions of Udimet720Li superalloy is listed in Table 1. In this study, cylindrical ingot of $\Phi 5070$ mm was produced by vacuum induction melting and casting in air-cooled steel mold, labeled as sample A; cuboid ingot of 151560 mm was produced by vacuum arc melting and suction casting in water-cooled copper mold, labeled as sample B. Induction melting and casting were conducted in medium frequency induction furnace with an ultimate vacuum level of 6.0×10^{-2} Pa. Pure Ni, Cr, Co, Mo, W (with a purity of 99.95%, 99.98%, 99.97%, 99.95%, 99.95%, respectively) were first introduced into a corundum crucible located in the vacuum chamber. It is noted that W and Mo were placed at the bottom of the crucible to accelerate diffusion melting. After being evacuated to 5 Pa, the chamber temperature was increased from room value to 1550 °C, and the temperature was maintained for 20 min. Then, argon was flow into the chamber to increase the chamber pressure to 0.07 MPa, and the bulk Al, Ti and the aluminum foil wrap B, Zr was then added to the melt. After homogenizing, the furnace temperature was reduced to 1450 °C and hold for 10 min. Finally, the melt was poured into the steel mold and natural cooling. The cooling rate of the alloy in steel mold was less than 100 K/s. In addition, arc melting and suction casting were processed by arc-melting furnace with an ultimate vacuum level of 5.0×10^{-3} Pa. 50 g bulk was cut from sample A for arc melting. Electromagnetic stirring was conducted during the melting process to ensure the uniformity of components. After melted, the alloy was drop-cast into the water-cooled copper mold and cooling rate more than 1000 K/s.

Table 1 Material compositions in wt%.

Composition	C	Cr	Co	W	Mo	Al	Ti	B	Zr	Ni
Content	0.015	16	14.75	1.25	3	2.5	5	0.015	0.03	Bal.

The metallographic and “dog-bone plate tensile were EDM (Electric Discharge Machining) wire cutting process from 1/2 radius of cylindrical ingot and 1/4 cuboid ingot as show in figure 1.

The tensile tests were carried out on a CMT4105 testing machine according to the GB/T 228.1-2010. The tensile speed and temperature was set as 1mm/min and 21 °C, respectively. After tensile testing, longitudinal section was cut from the fractured specimens. The specimens were ground, polished and chemical etched and then characterized by using SEM to observe the propagation path of crack and the evolution of crack in the longitudinal section. The as-cast microstructure, tensile fracture and longitudinal section of two samples were studied by optical microscopy (OM), scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). The metallographic specimens were ground through 400 to 2000 grit papers, polished with diamond paste, cleaned by ultrasonic device. And then the specimens were chemically

etched using a solution of 5g CuCl_2 + 100 ml $\text{C}_2\text{H}_5\text{OH}$ + 100ml HCl for OM examination or electro etched with 13 ml H_3PO_4 + 42 ml HNO_3 + 43 ml H_2SO_4 at 6V for 5~10s at room temperature for SEM examination. For EBSD samples, the specimens were electro-polished with 10 ml H_4ClO_4 +

90 ml $\text{C}_2\text{H}_5\text{OH}$ at 29V for 5s at room temperature, and the EBSD investigation was performed on the sample by using a LEO1450 scanning electron microscope equipped with HKL Channel 5, to observe the grain size, grain orientation and the plastic deformation distribution after tensile tests.

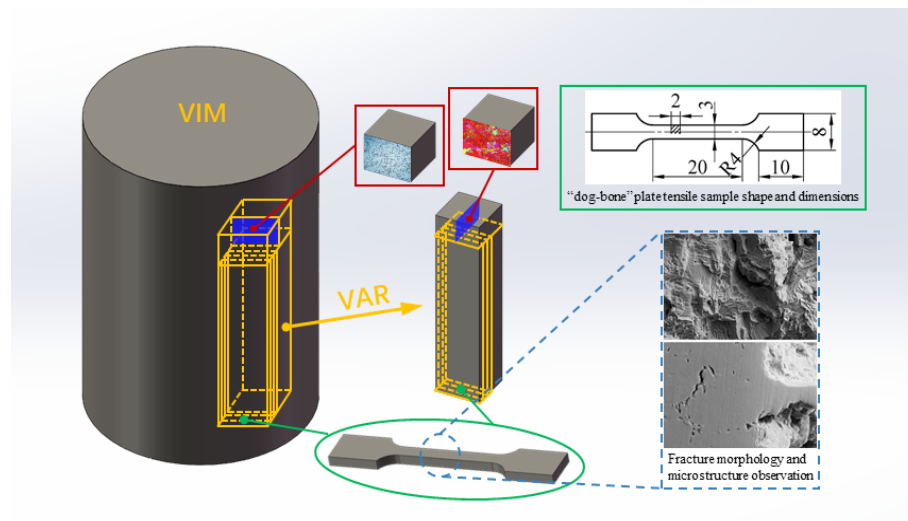


Figure 1 Schematic illustration of Udimet720Li metallographic and “dog-bone” plate tensile

3 Results and discussion

3.1 Microstructure of the as-cast Udimet720Li superalloy

Figure 2 displays the low magnification OM image of microstructure by two casting method. It is obvious that sample A shows larger grain size of equiaxed crystals accompanied by local dendrites, and fan-type γ/γ' eutectic,

block-shaped and strip-shaped $\eta\text{-Ni}_3\text{Ti}$ are distributed at GBs (figure 2a, c), consistent with the as-cast microstructure of Uidmet720Li [8]. The macrostructure images of sample B show extremely fine grain size and fine MC carbides discontinuously distributing at GB, with no common γ/γ' eutectic structure (figure 2b, d).

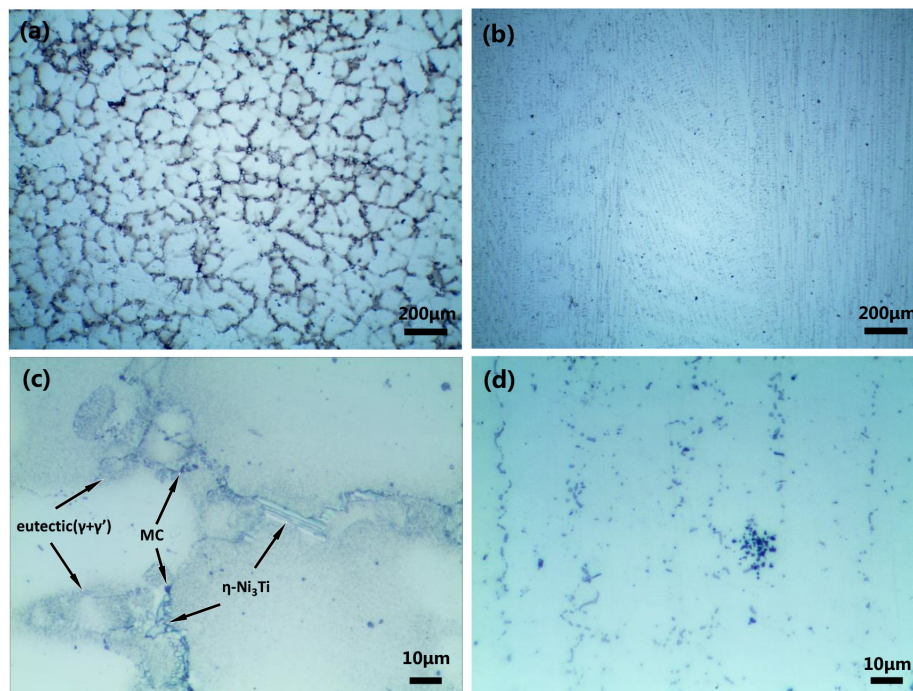


Figure 2 Low magnification OM image of alloying microstructure in (a) sample A and (b) sample B; (c) fan-type γ/γ' eutectic, block-shaped and strip-shaped $\eta\text{-Ni}_3\text{Ti}$ distributed at GB of sample A; (d) fine MC carbides discontinuously distributed at the GB of sample B.

In SEM images, the γ' particles are observed dispersed in the grain matrix of in samples A and B. As shown in figure 3b, the size of γ' precipitate increases from the grain center to the GB, and γ' particles in sample A are finer than those in sample B. In addition to the fan-type γ/γ' eutectic, block-shaped and strip-shaped η -Ni₃Ti, there are also a series of granular MC carbides at the GB of sample A (figure 3a). However, γ/γ' eutectic rarely appears at the GB of sample B, and it can be observed irregular phases are intermittently distributed at the GB (figure 3c). Trough EDS analysis (figure 4), it can be ascertained that the irregular phases is TiC (figure 3d). It is reported that the formation

of γ/γ' eutectic mainly depends on the segregation of titanium [32]. The few eutectic in as-cast microstructure of sample B, different from sample A, can be attributed to the rapid solidification of arc melting and suction casting method, which prevents the segregation of titanium at the GB to form γ/γ' eutectic. Furthermore, γ/γ' eutectic tends to aggregate at the triple GB junctions, in which more titanium is enriched. In contrast, the enrichment of titanium at general GBs is not enough to produce the γ/γ' eutectic.

The orientation image microscopy map of the two samples in figure 5 shows quite difference in grain size.

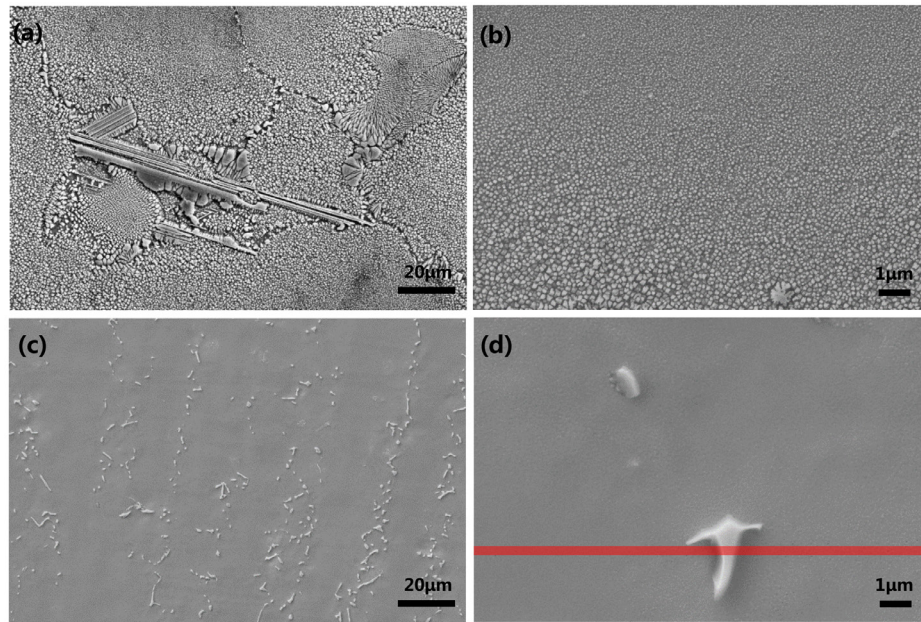


Figure 3 SEM image of two as-cast microstructures: (a) the phases and structure of GB in sample A; (b) the size of γ' distribution in grain of sample A; (c) irregular phase intermittently distributed at GB in sample B, (d) irregular phase in sample B determined by EDS as TiC.

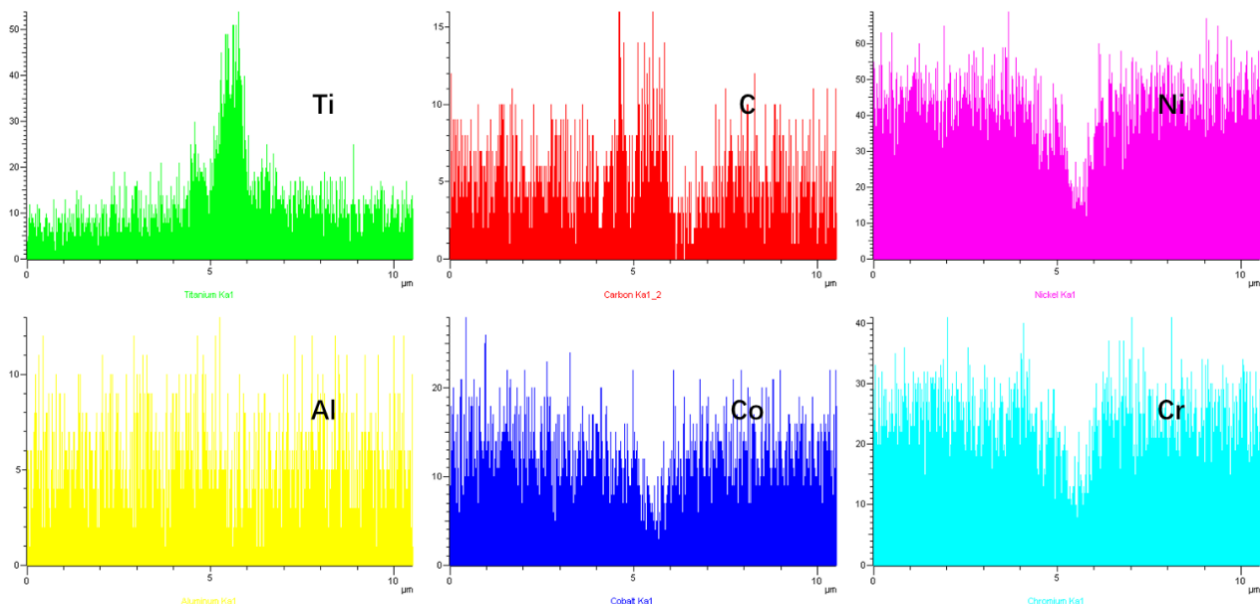


Figure 4 Element distribution along the red line marked in Fig 3d

By the line interception method, the average grain sizes in samples A and B are determined as 74.6 and 36.4 μm , respectively. Here, different color levels in the orientation

image micrograph represent different crystal orientations, thin-gray lines and thick-black lines represent LAGBs and HAGBs, respectively.

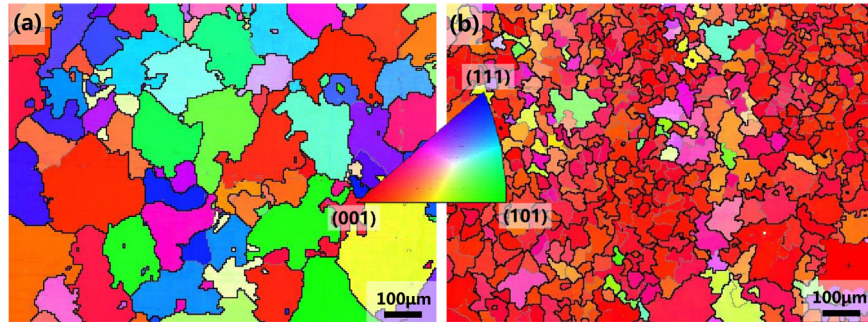


Figure 5 Orientation image microscopy map of (a) sample A and (b) sample B

3.2 Tensile behavior of the as-cast Udimet720Li superalloy

Tensile tests were performed on Udimet720Li superalloy at room temperature, and the results are shown in Table 2. It can be found, compared with sample A, the yield strength (σ_s), ultimate tensile strength (σ_{UTS}) and elongation (δ_u) of sample B are enhanced. Sample A displays the lower strength and ductility, which is most likely caused by its coarse and uneven microstructure in terms of grains and phases at GB (figure 3a and figure 5a). For sample B, attributed to suction casting in water-cooled copper mold, finer grains and particle phases at GB lead to substantial elevations in the σ_s from of 826-939 MPa, and in the δ_u from of 12-15%. In addition, the strain hardening rate of sample A is higher than that of sample B during tensile deformation (figure 6). Dislocations accumulate when they intersected or bypassed the γ' particles, which induces enhanced strain hardening. However, the uniform elongation of sample A is lower than sample B. Although sample A has a higher strain hardening rate than sample B, but premature fracture occurs.

Table 2 Mechanical performance of samples A and B

Samples	σ_s (MPa)	σ_{UTS} (MPa)	δ_u (%)
A	826	1156	12
B	939	1213	15

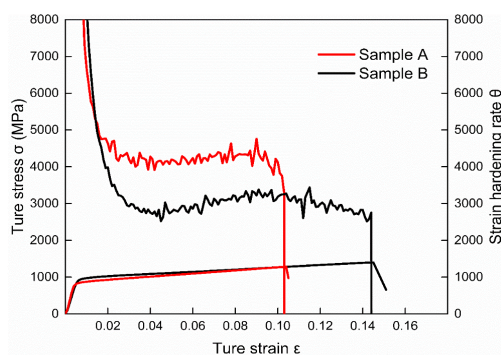


Figure 6 Comparison of room-temperature tensile behavior for the samples

red and black lines are tensile true stress-strain curves and hardening rate-strain curves of samples A and B, respectively. Strain hardening rate $\theta = d\sigma / d\epsilon$

3.3 Crack and deformed microstructure of Udimet720Li superalloy after tensile test

Samples A and B both demonstrate a combination of ductile and brittle fracture mechanisms, respectively with dimples and quasi-cleavage facets. The number of dimples in the fracture surface of sample A is significantly less than sample B. In SEM images of fracture surface (figure 7) and cross-section microstructure of fracture tips (figure 8), the crack is mainly generated at the GB at which brittle carbon act as a crack source. The crack growth and fracture mode are different between the two samples. For sample B (figure 7b, d and f), micro-fracture shows many dimple and tearing ridge basically dendrite fracture, and the proportion of dimple is dominant. The primary crack originates from carbide at GB due to intermittent existence of carbide, and secondary crack extends along the GB or into grain matrix, so that crack propagation is hindered by intragranular γ' precipitation^[33]. The strip tearing ridge of fracture surface is a sign of rapid crack growth. At the same time, the existence of massive phases can be observed at the end of each tearing ridge, which is the carbide at the GB through EDS analysis. It can be concluded, the brittle carbides distributed at the GB can act as the crack source, but can also hinder the dislocation slip between grains. For sample A (figure 7a, c and e), macro fracture is composed of fiber zone and shear lip zone. Fiber zone area has a lot of intergranular or transgranular fracture planes and some tearing dimples, and the proportion of dimple is inferior. Primary crack originate from carbide at GB tends to extend to γ/γ' eutectic (figure 8). Fan type γ/γ' eutectic has a petal or lamellar shape and always leads to phenomenon of delamination and peeling of eutectic because of poor deformation coordination between eutectic layers, as shown in figure 8a. This delamination will reduce the dislocation pinning ability of strengthening phase at GB and causing premature fracture, thus reduce the ultimate strength.

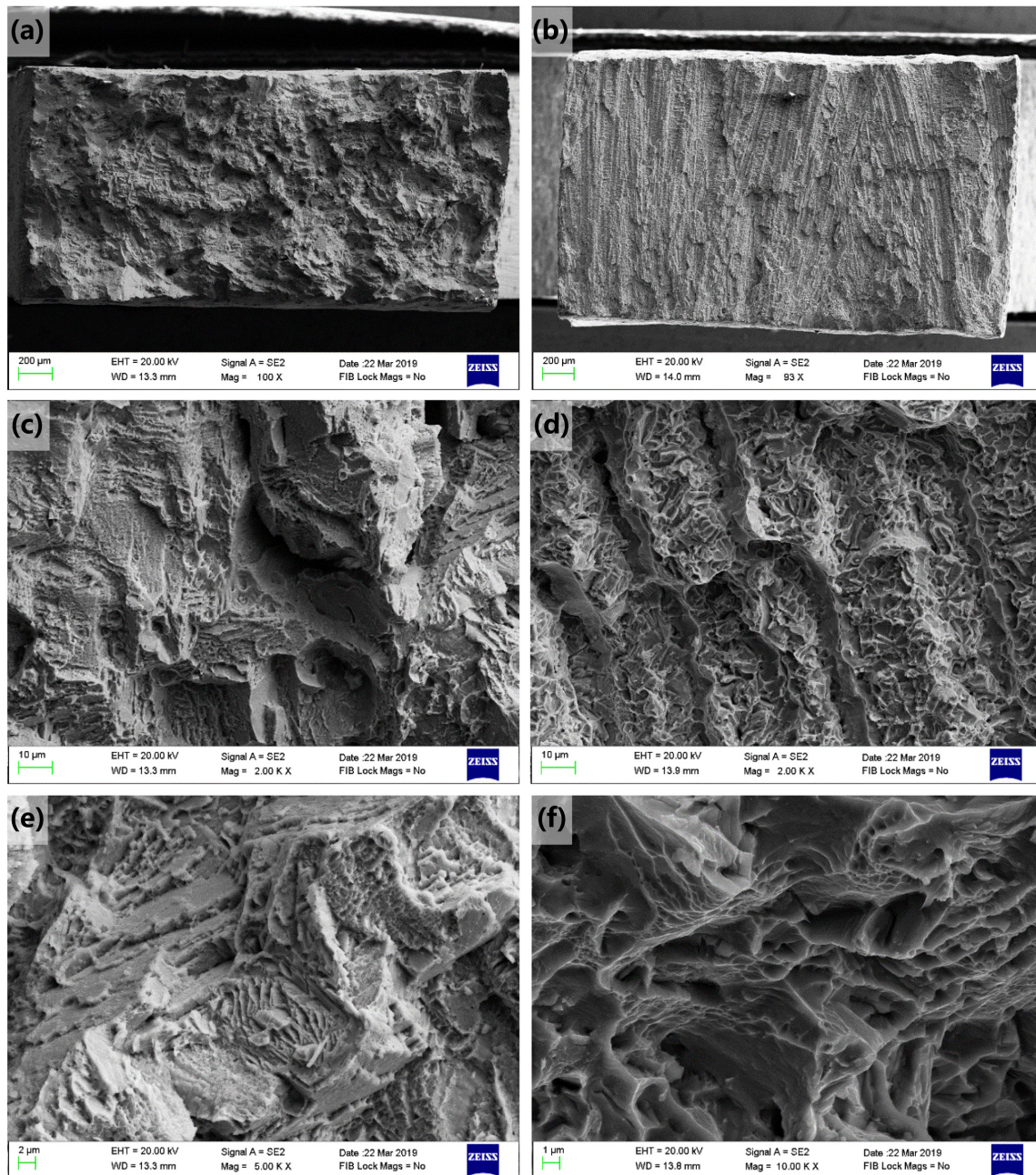


Figure 7 Fractographs of specimens under room-temperature tensile test: (a), (c) and (e) sample A; (b), (d) and (f) sample B

3.4 Electron backscatter diffraction of cross section of fracture tips

In order to study the tensile deformation mechanism, electron backscatter diffraction (EBSD) was used to analyze the plastic deformation of the cross section of fracture tips. EBSD can be used to study the relationship between microstructure and plastic deformation, and analyze the distribution of plastic deformation in polycrystalline alloy [34,35]. The applied stress causes dislocation migration and plastic deformation in the alloy, and inhomogeneous distribution of dislocation in grains will lead to inhomogeneous plastic deformation, resulting different

local misorientation within grains [36]. Local misorientation images can reflect the distribution of plastic deformation. The distribution of plastic deformation in polycrystalline alloy can be clearly revealed by comparing All Euler image and Local misorientation image.

The microstructure near the tensile fracture surface analyzed by EBSD plane scanning are shown in figure 9. The local misorientation of sample A tends to gather at the GB and the crystal is relatively small, which indicates that the plastic deformation mainly occurs at GB and the plastic deformation in crystal is relatively small (figure 9a, c). Meanwhile, triple GB junctions often has more large misorientation, at which the plastic deformation is greater

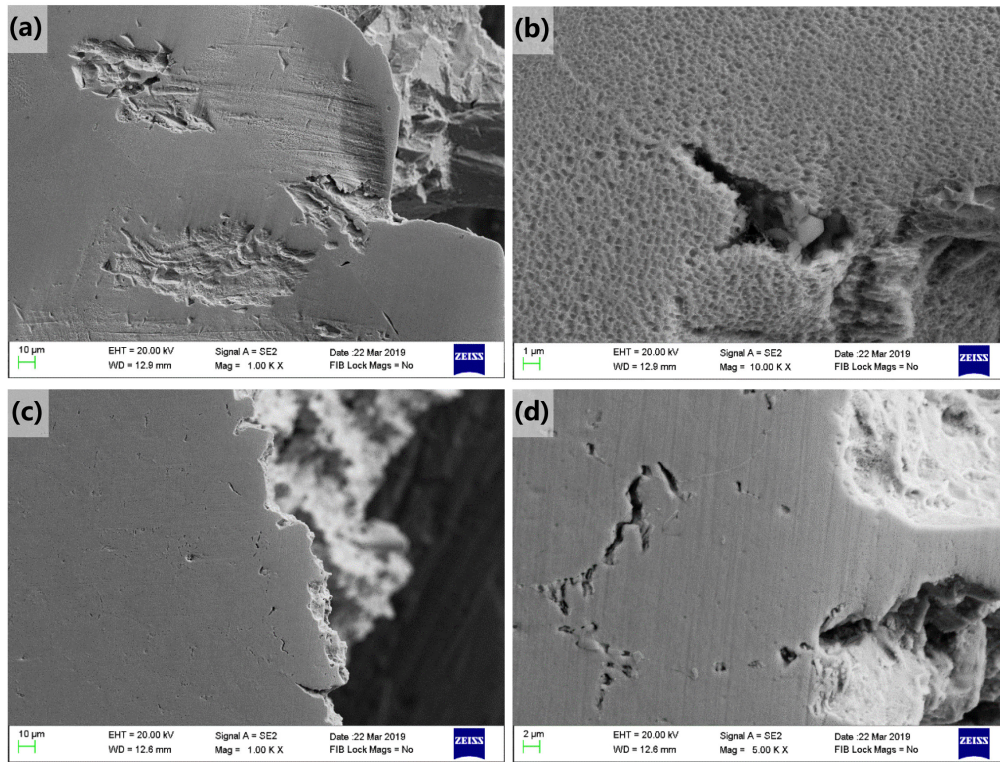


Figure 8 Micrographs of cross section of fracture tips for room-temperature tensile test (a) and (b) sample A; (c) and (d) sample B.

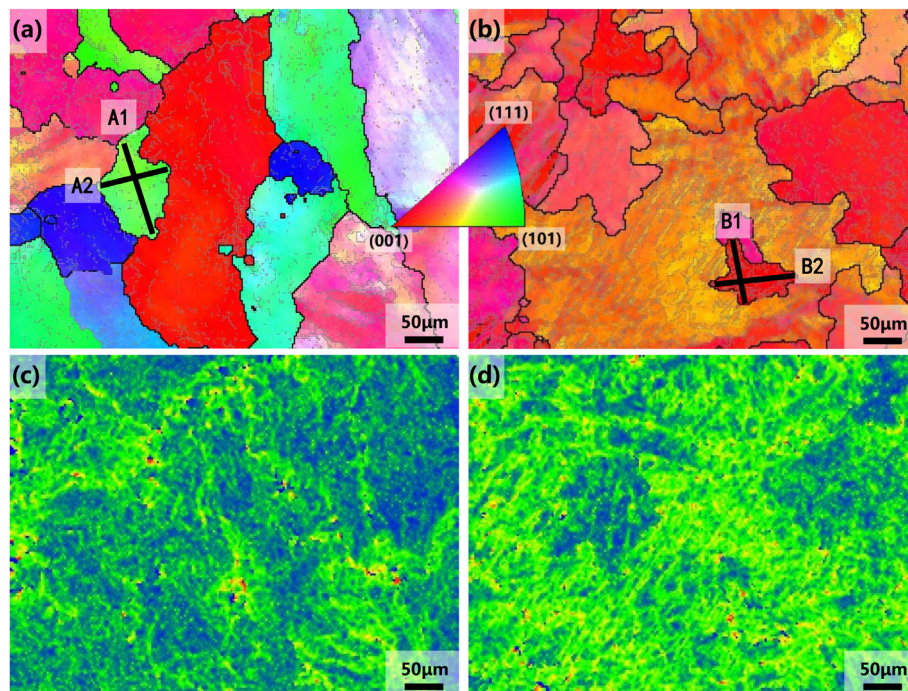


Figure 9 EBSD plane sweep scanning images near the tensile fracture: (a), (b) IPF image; (c), (d) Local Misorientation image. (The misorientation increases from blue to red).

and stress concentration is also more serious. In as-cast structure, the γ/γ' eutectic usually solidifies at the triple GB junctions. For sample B, there is a different situation. As shown in figure 9b, d, the misorientation is almost uniformly distributed in a single grain and no significantly different

between crystal and GB. These results confirm previous conclusion that γ/γ' eutectic at GB causes premature stress concentration and leads to premature fracture failure of the material.

To evaluate quantitatively the transformation of

orientation difference between two samples, the point to origin (cumulative) misorientation and point to point (local) misorientation are calculated along the lines marked in figure 9a, b. The misorientation profiles along the directions of lines A1 and A2 are illustrated in figure 10a, b. The cumulative misorientation is around 6 and average local misorientation is 1 of sample A. As shown in figure 10 c, d, an increased misorientation gradient near the GB is developed, and the cumulative misorientation along line B1 and B2 exceeds 8° for a distance about 100µm. Therefore, it can be concluded that the misorientation in the grain of sample A is less than that of sample B. In other words, sample B has better deformation performance and dislocation storage capacity in grains. However, as shown in figure 10, the distance from grain interior to GB, the local misorientation does not increase monotonically. The obvious misorientation jumps appear at all range. According previous study, this is related to the activation of different slip systems^[37]. Original grain has several orientation bands, and compatible deformation between adjacent grains

takes place by activating different slip systems.

Although sample B has a low strain hardening rate at large strains during deformations, but shows stronger work hardening stability. High strain rates led to a large number of dislocations during tensile tests at room temperature, while high hardness phase and carbide resulted in dislocation accumulation in the crystal channels and phase interfaces. In general, numerous dislocations segregated at the interface of matrix/carbide and matrix/eutectic cause stress concentration along these phase interface. For sample A, the cross section of fracture tips shows delamination and peeling of γ/γ' eutectic (figure 8a, b). Different from sample A, sample B cross section of fracture tips shows source of crack is carbide (figure 8c, d). As shown in the EBSD results in figure 9c, d, compared with sample B, the narrow and small strain concentration region near GB indicates that the stress required for GB cracking of sample A is small. As a result, the stress concentration caused by the GB would be large, and the microcrystalline crack of samples A and B tends to nucleate at carbide and γ/γ' eutectic at the GBs.

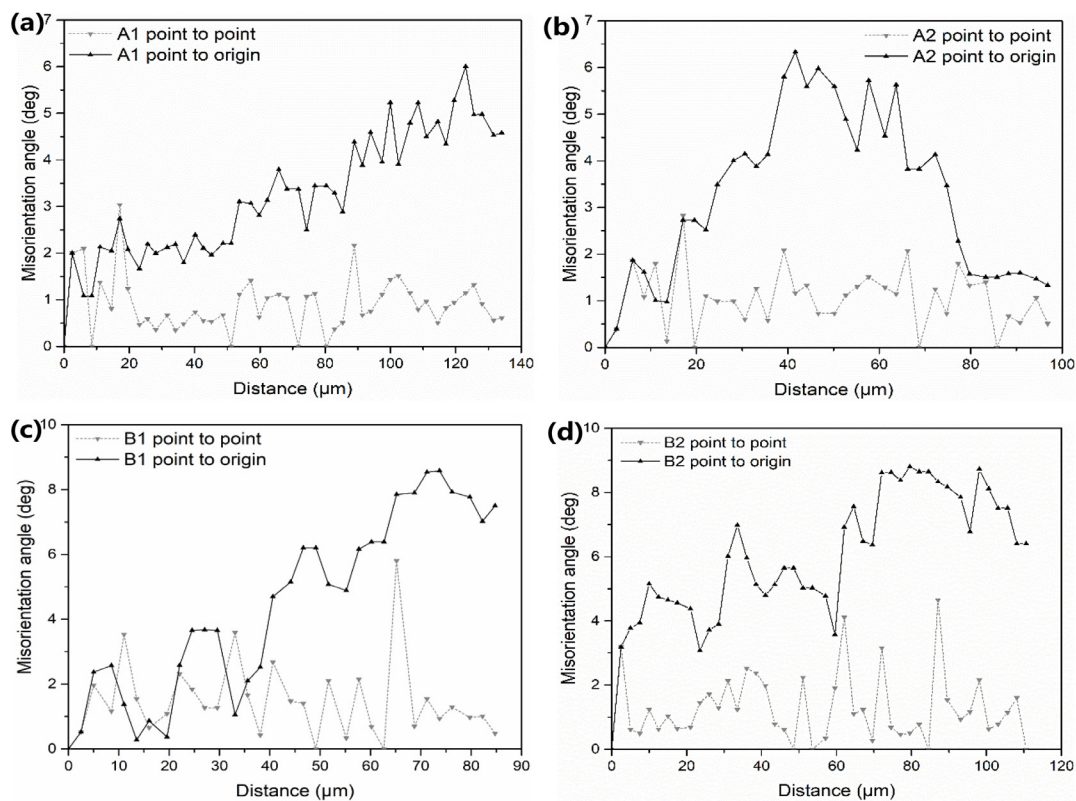


Figure 10 Change of misorientation angle along the lines marked in Figure 9 (a) A1; (b) A2; (c) B1; (d) B2

4 Conclusions

The microstructure and mechanisms of tensile cracks initiation and propagation in Ni-based superalloy fabricated by two methods are investigated. The results can be concluded as follows:

(1) Sample B has a finer grain size and less eutectic content due to its rapid solidification. Various phases are distributed at GBs for sample A, but only the single Ti-rich

carbide dispersed at GBs of sample B.

(2) The strain hardening rate of sample A is higher than sample B, but the uniform elongation is lower in the former due to the premature fracture during deformation.

(3) The cumulative and local misorientations in sample A are less than those in sample B, which indicates that sample B has better deformation performance and dislocation storage capacity in grains. In terms of crack initiation and propagation, γ/γ' eutectic accelerates the

stress concentration at GB and leads to premature fracture failure.

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References

- [1] Kim S E, Jackson M P, Reed R C, et al. Quantification of the minor precipitates in UDIMET™ alloy720(LI) using electrolytic extraction and X-ray diffraction 1[J]. *Materials Science & Engineering A*, 1998, 245(2):225-232.
- [2] Yongchang L, Qianying G, Chong L I, et al. Recent progress on evolution of precipitates in Inconel 718 superalloy [J]. *Acta Metallurgica Sinica*, 2016.
- [3] Mao J, Chang K M, Yang W, et al. Cooling precipitation and strengthening study in powder metallurgy superalloy U720LI[J]. *Metallurgical & Materials Transactions A*, 2001, 32(10):2441-2452.
- [4] F E Sczerzenie, G E Maurer. Development of Udimet 720 for High Strength Disk Applications[J]. *Special Metals Corporation*, 1984
- [5] P W Keefe, S O Mancuso, G E Maurer. Effect of heat treatment and chemistry on the long-term phase stability of a high strength nickel-based superalloy[J]. *Superalloys*, 1992, 487-496
- [6] Bain K R, Gambone M L, Hyzak J M, et al. Development of Damage Tolerant Microstructures in Udimet 720[C]// *Superalloys*. 1988.
- [7] Na Y S, Park N K, Reed R C. Sigma morphology and precipitation mechanism in udimet 720Li[J]. *Scripta Materialia*, 2000, 43(7):585-590.
- [8] Zhao G D, Yu L X, Qi F, et al. The Minor Precipitation at the Final Stage of U720Li Solidification[J]. *Acta Metallurgica Sinica*, 2016, 29(6):518-526.
- [9] Li F, Fu R, Yin F, et al. Impact of $\gamma'(\text{Ni}_3(\text{Al,Ti}))$ phase on dynamic recrystallization of a Ni-based disk superalloy during isothermal compression[J]. *Journal of Alloys & Compounds*, 2017, 693:1076-1082.
- [10] Joseph C, Persson C, Colliander M H. Influence of heat treatment on the microstructure and tensile properties of Ni-base superalloy Haynes 282[J]. *Materials Science and Engineering: A*, 2016:S0921509316312618.
- [11] Liu F, Chen J, Dong J, et al. The hot deformation behaviors of coarse, fine and mixed grain for Udimet 720Li superalloy[J]. *Materials Science and Engineering: A*, 2016, 651:102-115.
- [12] Du B, Sheng L, Cui C, et al. Precipitation and evolution of grain boundary boride in a nickel-based superalloy during thermal exposure[J]. *Materials Characterization*, 2017, 128:109-114.
- [13] Osada T, Gu Y, Nagashima N, et al. Optimum microstructure combination for maximizing tensile strength in a polycrystalline superalloy with a two-phase structure[J]. *Acta Materialia*, 2013, 61(5):1820-1829.
- [14] Yan B C, Zhang J, Lou L H. Effect of boron additions on the microstructure and transverse properties of a directionally solidified superalloy[J]. *Materials Science & Engineering A*, 2008, 474(1-2):39-47.
- [15] Chang L, Jin H, Sun W. Solidification Behavior of Ni-base Superalloy Udimet 720Li[J]. *Journal of Alloys & Compounds*, 2015.
- [16] Pang H T, Reed P A S. Effects of microstructure on room temperature fatigue crack initiation and short crack propagation in Udimet 720Li Ni-base superalloy[J]. *International Journal of Fatigue*, 2008, 30(10-11):2009-2020.
- [17] Zhipeng W, Lianxi H, Yu S, et al. Effect of solution treatment on microstructure and tensile properties of a U720LI Ni-based superalloy[J]. *Vacuum*, 2018, 156: 248-255
- [18] Villechaise P, Cormier J, Billot T, et al. Mechanical Behavior and Damage Processes of Udimet 720Li: Influence of Localized Plasticity at Grain Boundaries[M]// *Superalloys 2012*.
- [19] Rao G A, Satyanarayana D V V. Influence of HIP processing on microstructure and mechanical properties of superalloy Udimet 720LI[J]. *Materials Science & Technology*.
- [20] Lu K. The Future of Metals[J]. *Science*, 2010, 328:319-320.
- [21] M. A. Meyers, A. Mishra, D.J. Benson, Mechanical properties of nanocrystalline materials, *Progress in Materials Science*. 51: 427-556.
- [22] Lu K. Stabilizing nanostructures in metals using grain and twin boundary architectures[J]. *Nature Reviews Materials*, 2016, 1(5):16019.
- [23] Valiev R Z. Nanostructured alloys: Large tensile elongation[J]. *Nature Materials*, 2013, 12(4):289-291.
- [24] Liu G, Zhang G J, Jiang F, et al. Nanostructured high-strength molybdenum alloys with unprecedented tensile ductility[J]. *Nature Materials*, 2013, 12(4):344-350.
- [25] Launey M E, Ritchie R O. On the Fracture Toughness of Advanced Materials[J]. *Advanced Materials*, 2009, 21(21):2103-2110.
- [26] Kaixuan C, Xiaohua C, Zidong W, et al. Optimization of deformation properties in as-cast copper by microstructural engineering. Part I. microstructure[J]. *Journal of Alloys and Compounds*, 2018, 763:592-605.
- [27] Lu K, Lu L, Suresh S. Strengthening Materials by Engineering Coherent Internal Boundaries at the Nanoscale[J]. *SCIENCE*, 2009, 324(5925):349-352.
- [28] Chen K X, Chen X H, Ding D, et al. Effect of in-situ nanoparticle wall on inhibiting segregation of tin bronze alloy[J]. *Materials Letters*, 2016, 175:148-151.
- [29] Seo S M, Lee J H, Yoo Y S, et al. A Comparative Study of γ/γ' Eutectic Evolution During the Solidification of Ni-Base Superalloys[J]. *Metallurgical & Materials Transactions A*, 2011, 42(10):3150-3159.

- [30] Bingming G, Lin L, Xinbao Z, et al. Effect of Directional Solidification Methods on the Cast Microstructure and Grain Orientation of Blade Shaped DZ125 Superalloy[J]. Rare Metal Materials and Engineering, 2013, 42(11):2222-2227.
- [31] Liu L, Huang T W, Zhang J, et al. Microstructure and stress rupture properties of single crystal superalloy CMSX-2 under high thermal gradient directional solidification[J]. Materials Letters, 2007, 61(1):227-230.
- [32] Seo S M, Lee J H, Yoo Y S, et al. A Comparative Study of the γ/γ' Eutectic Evolution During the Solidification of Ni-Base Superalloys[J]. Metallurgical & Materials Transactions A, 2011, 42(10):3150-3159.
- [33] Wang Q, Ding H, Zhang H, et al. Variations of microstructure and tensile property of γ -TiAl alloys with 0~0.5 at% C additives[J]. Materials Science and Engineering A, 2017, 700:198-208.
- [34] Kuhn F, Zeismann F, Brueckner-Foit A. Crack growth mechanisms in an aged superalloy at high temperature[J]. International Journal of Fatigue, 2014, 65:86-92.
- [35] Miao J, Pollock T M, Jones J W. Microstructural Extremes and the Transition from Fatigue Crack Initiation to Small Crack Growth in a Polycrystalline Nickel-base Superalloy[J]. Acta Materialia, 2012, 60(s 6–7):2840–2854.
- [36] Jiashi Miao, Tresa M Pollock, J Wayne Jones. Crystallographic fatigue crack initiation in nickel-based superalloy René 88DT at elevated temperature[J]. Acta materialia, 2009, 5946-5974
- [37] Randle V , Hansen N , Jensen D J . The deformation behaviour of grain boundary regions in polycrystalline aluminium[J]. Philosophical Magazine A, 1996, 73(2):265-282.

Effect of Deformation Conditions on Mechanical Properties of Zr-based Metallic Glasses

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Abstract:

In this paper, the effects of different strain rate ($1 \times 10^{-5} \text{ s}^{-1}$, $5 \times 10^{-5} \text{ s}^{-1}$, $1 \times 10^{-4} \text{ s}^{-1}$, $5 \times 10^{-4} \text{ s}^{-1}$, $1 \times 10^{-3} \text{ s}^{-1}$) and aspect ratio (1:1, 1.5:1, 2:1, 2.5:1, 3:1) on mechanical properties of Zr-based metallic glasses at room temperature were investigated. The results indicate that as the strain rate increases, the plastic strain and compressive strength of the specimens gradually decrease. The specimen with the strain rate of $1 \times 10^{-5} \text{ s}^{-1}$ exhibits the higher plastic strain of 10.25 %, compressive strength of 2002 MPa and fracture strength of 1999 MPa. In addition, accompanied with the increase in aspect ratio, the plastic strain of the specimens declines from 25.42 % to 1.97 %, meanwhile, the compressive strength and fracture strength of the specimens also present declining trend.

Keywords: Zr-based Metallic glasses; mechanical properties; plastic strain; strain rate; aspect ratio

1 Introduction

Metallic glass is a novel type of metal material with long-range disorder, short-range or medium-range ordered structure^[1]. Metallic glasses are produced by the rapid solidification from liquid metals, which inhibit the crystallization process. Compared to traditional crystalline materials, metallic glasses hold a variety of unique advantages because of their special atomic structure, such as higher strength, higher hardness, higher elastic strain, and elastic limit, lower elastic modulus^[2-5], and good magnetism^[6]. However, metallic glass, a thermodynamic metastable atomic structure, can cause crystallization when the temperature and pressure reach a certain condition^[1,7]. At the same time, since there are no microstructure defects such as grain boundary and dislocation, the plastic deformation at room temperature is concentrated in the highly localized shear band, which can easily lead to adiabatic shear and non-uniform flow of materials. The non-uniform flow of materials further gives rise to brittle fracture metallic glasses, which is also one of the bottlenecks restricting the application of metallic glasses as engineering structural materials^[8]. The second phase plastic particles were first applied to metallic glasses by researchers, thus improving the plastic deformation of bulk metallic glasses at room temperature to a certain extent^[9]. Zhang S G et

al^[10]. studied the unidirectional compression deformation behavior of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ amorphous alloy under different strain rates in the temperature range of supercooled liquid region, and found that the flow stress was only 74 MPa at $2 \times 10^{-2} \text{ s}^{-1}$, which was more suitable for superplastic processing. Chen D M et al^[11] studied the change of mechanical properties of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ bulk amorphous alloy composite under different strain rates, which found that the plasticity of this kind of amorphous alloy composite increased greatly under quasi-static compression. Lewandowski^[12] pointed out that hydrostatic pressure has a certain influence on the plastic deformation of Zr-based Metallic glasses, and its plastic deformation ability can be more than 10 % under limited conditions. Yuan B^[13]. Studied the relationship between strain rate and serrated flow behavior of amorphous alloy, and pointed out that the number of standard serrations was linear with strain rate. With the decrease of strain rate, the number of standard serrations increases gradually. There is a strain rate correlation in plastic deformation at room temperature on account of the uneven deformation of metallic glasses. It is found that increasing of crystal phase content in metallic glass led to an increase in the strain rate sensitivity of metallic glass^[14]. In addition, the fracture strength of metallic glass also demonstrate decreasing trend as the compression strain rate of metallic glass increases^[15].

Zr-based Metallic glasses characterized by high strength, high elasticity, superplastic, high hardness, high wear resistance and high corrosion resistance, generates a broad application prospect^[16]. Moreover, Zr-based Metallic glasses has good dynamic compression properties, positive strain rate effect, good extensibility, excellent inherent low frequency vibration damping performance^[17], excellent electrocatalytic activity^[18], and good magnetic properties after adding iron^[19]. High hardness and fairly low elastic modulus make Zr-based Metallic glasses a candidate material for bioimplants^[20]. Based on the understanding of the mechanism of nanocrystalline reinforced Zr-based Metallic glasses, Zr-based metallic glasses have been widely used in structural materials^[21].

In this paper, the effects of different compression strain rate and aspect ratio on the mechanical properties of Zr-based metallic glasses at room temperature were explored. The compression deformation behavior of metallic glasses was investigated by analyzing the stress-strain curve, fracture microstructure and shear band evolution characteristics.

2 Experimental materials and methods

Master alloy with nominal composition of $\text{Zr}_{61.88}\text{Cu}_{18}\text{Ni}_{10.12}\text{Al}_{10}$ was chosen for this experiment, the experimental materials were high-purity zirconium (Zr 99.95%), copper (Cu 99.98%), aluminum (Al 99.98%) and nickel (Ni 99.98%). The master alloy ingots were prepared by magnetic suspension smelting process in highly pure argon atmosphere. The melting process of the master alloy needs to be repeated four times to ensure the uniform distribution of the chemical elements in the parent alloy. The alloy bars with diameters of 3 mm were fabricated by copper model suction casting method under argon atmosphere. The metal bars were cut by a diamond slicer to obtain the compression specimen with different aspect ratio of 1:1, 1.5:1, 2:1, 2.5:1 and 3:1. In order to eliminate the interference of other factors other than deformation conditions, compression specimens with the same amorphous rod were used for three repeated experiments. The specimen structure of was

identified by X-ray diffraction (XRD, Cu K α radiation). The diffraction angle range 2- θ is between 20° and 80°, and the step length of scanning is 0.02°. The glass transition and crystallization behavior of the specimens were evaluated by an STA449 thermal differential calorimeter (DSC) under the protection of argon with a heating rate of 20 K min⁻¹. The heating temperature range was from room temperature to 1200°C, and the weight of the specimen was 5 mg. Uniaxial compression tests of the specimens were carried out by WDW-100D universal testing machine with different strain rate of 1 $\times 10^{-5}$, 5 $\times 10^{-5}$, 1 $\times 10^{-4}$, 5 $\times 10^{-4}$ and 1 $\times 10^{-3}$ s⁻¹, and different aspect ratio of 1:1, 1.5:1, 2:1, 2.5:1 and 3:1. The fracture surface and shear band were observed by Quanta Feg450 field emission scanning electron microscope (SEM).

3 Result and discussion

3.1 Analysis of X-ray diffraction

Figure 1 illustrates the XRD diffraction pattern of $\text{Zr}_{61.88}\text{Cu}_{18}\text{Ni}_{10.12}\text{Al}_{10}$ alloy. It can be seen that the XRD pattern consists of one broad diffuse peak between diffraction angles 30° and 45°, and no significant diffraction peaks corresponding to a crystalline phase showing that the specimen has complete amorphous structure.

3.2 Analysis of DSC

In order to characterize the thermodynamic stability of the metallic glass, the specimens were analyzed by DSC, displayed in figure 2. The specific thermodynamic characteristic parameters are reflected in Tab.1, where T_g is glass transition temperature, T_x is crystallization start temperature, T_m is melting temperature and T_l is liquidus temperature. It can be found that the supercooled liquid region ΔT_x ($\Delta T_x = T_x - T_g$) of the specimen is 85 K, the reduced glass transition temperature T_{rg} ($T_{rg} = T_g / T_l$) and the parameter γ describing thermodynamic stability ($\gamma = T_x / (T_g + T_l)$) are 0.568 and 0.409 respectively. The results exhibit that the specimen holds a wide supercooled liquid region, larger T_{rg} and parameter γ , which state that specimen possesses good thermodynamic stability.

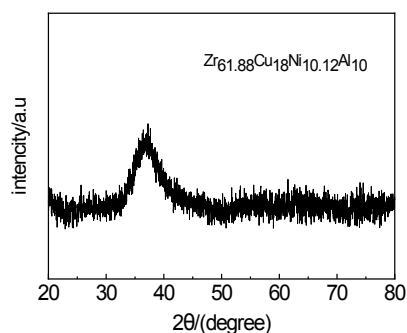


Figure 1 XRD pattern of specimen

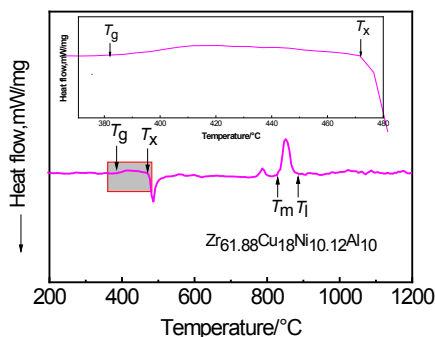


Figure 2 The DSC result of specimen

Table 1 The thermodynamic characteristic parameter of specimen

T_g/K	T_x/K	T_m/K	T_l/K	$\Delta T_x/\text{K}$	T_{rg}	γ
659	744	899	1159	85	0.568	0.409

3.3 Effect of strain rate on mechanical properties of Zr-based metallic glasses

3.3.1 Analysis of engineering stress-strain curve

The compression tests of specimens with the aspect ratio of 2:1 was carried out by using a universal mechanical testing machine with different strain rate of 1×10^{-5} , 5×10^{-5} , 1×10^{-4} , 5×10^{-4} and $1 \times 10^{-3} \text{ s}^{-1}$. The engineering stress-strain curves of the specimens are shown in figure 3 and other mechanical properties are summarized in Tab.2. Combined with Table 2 and figure 3, it reveals that the yield strength of the specimen has slight changes with the change of compression strain rate, which indicates that the yield strength of the specimen is scarcely affected by the strain rate. However, the compressive strength and plastic strain of the specimen display the correlation of strain rate, which embodies that the compressive strength and plastic strain of the specimen decreases with the strain rate increasing. With the raise of strain rate, the plastic strain of specimens manifests a falling trend. The plastic strain decreases from 10.25 % to 4.18 %. In addition, the compressive strength of the specimen reduces from 2002 MPa to 1767 MPa with the increase of strain rate. It can also be concluded that the elastic modulus of specimen fluctuates irregularly along with the change in strain rate while its variation range is small. At low strain rates, the plastic deformation of metallic glass can be more evenly distributed in each tiny volume unit of the glass, which is beneficial to the formation of multiple shear bands inside the metallic glass, and thus its plasticity is improved^[22].

From the local enlarged diagram of stress-strain curve (shown in figure 3), it can be seen that each curve has a certain sawtooth rheological behavior in the plastic

deformation stage, and the sawtooth rheological behavior is very similar at the same order of strain rate, indicating that the strain rate is related to the sawtooth rheological behavior. Studies have shown that the sawtooth rheological behavior is generally obvious at low temperature and low strain rate, and with the increase of temperature and strain rate, the serration will gradually disappear or even completely disappear^[23]. As shown in figure 3, at low strain rate, the sawtooth rheological behavior of sawtooth is mainly small sawtooth, and the stress change range of sawtooth is relatively uniform. With the increase of strain rate, the distribution of large and small sawtooth is mixed and the change range of stress is uneven. The smaller sawtooth is, the more interaction of shear bands in the plastic process is, that is, the stronger the plastic deformation ability is, and vice versa^[24]. This is consistent with the results of this paper.

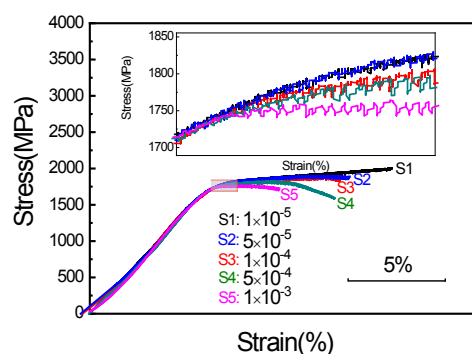


Figure 3 The compressive stress-strain curve of specimen with different strain rates at room temperature

Table 2 The mechanical performance parameter of specimen with different strain rates at room temperature

strain rate ϵ/s^{-1}	elastic modulus E/ MPa	plastic strain $\epsilon_p/\%$	yield strength σ_s/MPa	compressive strength σ_{bc}/MPa	fracture strength σ_c/MPa
1×10^{-5}	29884	10.25	1457	2002	1999
5×10^{-5}	32003	8.41	1470	1900	1888
1×10^{-4}	29762	8.12	1306	1888	1869
5×10^{-4}	30344	7.28	1538	1827	1557
1×10^{-3}	31552	4.18	1597	1767	1727

3.3.2 Analysis of fracture morphology

The fracture morphology of the specimens under different strain rates were shown in figure 4. From figure 4(a-e), it can be found that the fracture morphology of the specimens is composed of continuous vein patterns, which is a typical fracture morphology after fracture of metallic glasses. With the increase of strain rate, the size of vein patterns in the fracture morphology of specimens enlarges gradually, showing the characteristics of uneven distribution. The regularity of vein patterns size from small to large in the fracture morphology of specimen in figure 4(a-e) also confirms the change of plastic strain from large to small in figure 3. Therefore, the rule can be summarized that the fine and uniform distribution of vein patterns correspond

to larger plastic strain and higher strength, and the thick and uneven distribution of vein patterns reflects the smaller plastic deformation and lower strength of specimens^[25].

3.3.3 Analysis of surface shear band morphology

The formation and expansion of shear band is the main way of plastic deformation of bulk metallic glass at room temperature, so that the movement of shear band and the number of shear band in metallic glass will directly affect the plastic deformation mode and plastic strain of metallic glass. Based on the fact that the limited plastic strain of metallic glasses at room temperature is prone to be brittle fracture, it has become a challenge of how to improve the plasticity of metallic glasses at room temperature. Some researchers were keen to improve the plasticity of metallic

glasses by adjusting the composition or by controlling the evolution of shear bands of metallic glasses during deformation^[26,27].

A variety of shear bands observed on the side surface of the specimen after fracture are exhibited in figure 5. It is well known that the limited plastic strain of metallic glasses benefits from the generation and proliferation of shear bands and the interaction between shear bands during fracture^[28], such as figure 5(a), the lateral surface of the specimen is similar to the mountain shape and the morphology of the laminated shear band is extremely similar to that of the

surface formed after the mountain fracture. It is a precise result because of the existence of multiple shear bands that the energy generated by stress in the fracture process of specimens can be released, thus enhancing the plastic strain of metallic glasses and inhibiting the occurrence of brittle fracture. On the other hand, the interaction between shear bands can promote the proliferation of shear bands, so that the energy generated by stress can be dispersed into multiple shear bands for release, thus effectively avoiding brittle fracture of specimens.

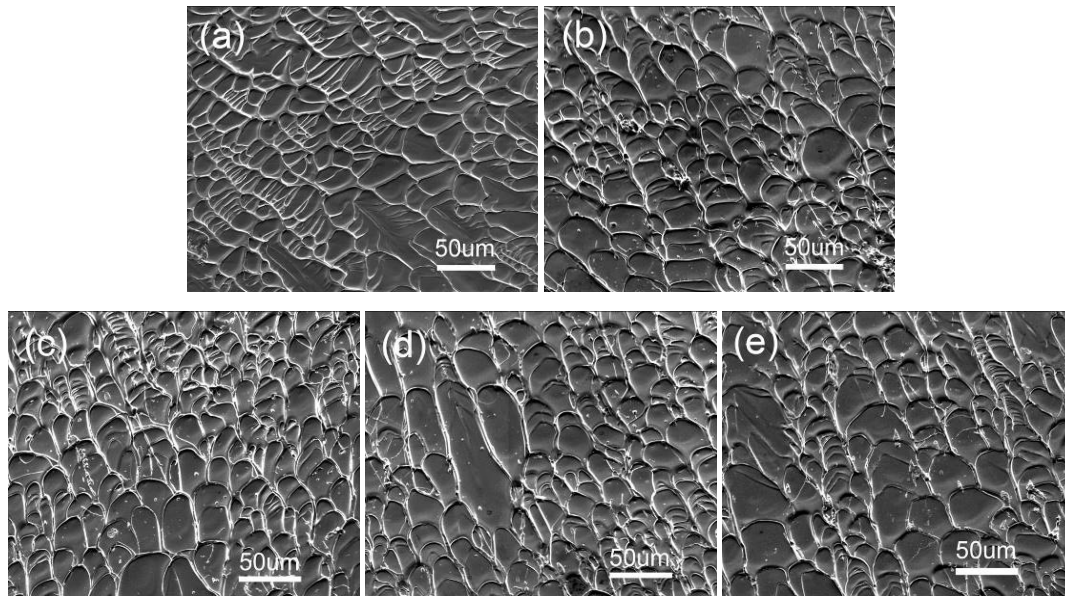


Figure 4 The compression fracture morphology of specimen with different strain rates at room temperature

(a) $1 \times 10^{-5} \text{ s}^{-1}$, (b) $5 \times 10^{-5} \text{ s}^{-1}$, (c) $1 \times 10^{-4} \text{ s}^{-1}$, (d) $5 \times 10^{-4} \text{ s}^{-1}$, (e) $1 \times 10^{-3} \text{ s}^{-1}$

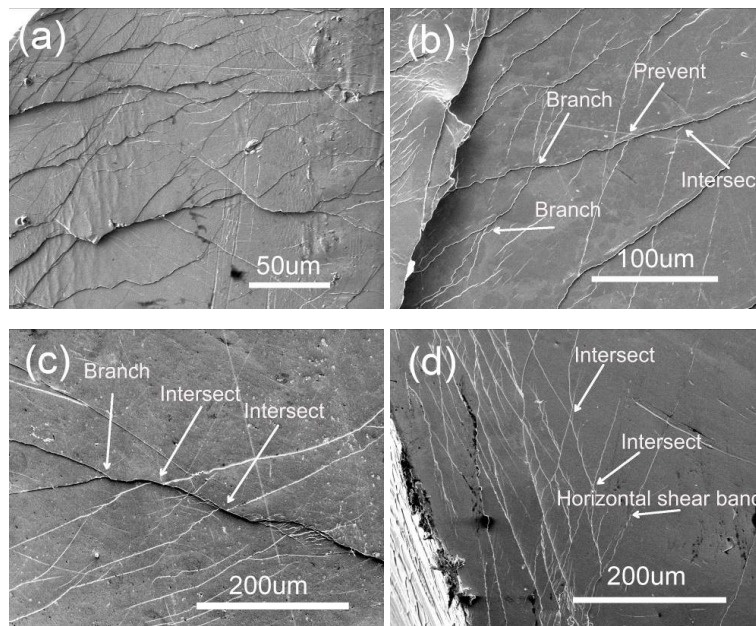


Figure 5 The shear band morphology of specimen under different strain rate.

(a) $1 \times 10^{-5} \text{ s}^{-1}$, (b) $5 \times 10^{-5} \text{ s}^{-1}$, (c) $1 \times 10^{-4} \text{ s}^{-1}$ and (d) $5 \times 10^{-4} \text{ s}^{-1}$

The morphology of the shear band under different strain rate were illustrated in figure 5. Obviously, there are three main forms of interaction between shear bands of metallic glasses, such as branch, prevent and intersect. It can be seen from figure 5(d) that the morphology of the shear band is mainly distributed in the direction parallel to the section. In addition, the horizontal shear band^[29] perpendicular to the direction of applied load is also observed from figure 5, which is bound to interact with the main shear band with the loading direction of 45°. These interactions will inevitably promote the proliferation of shear bands and the expansion of shear bands in other directions, thus improving the plastic strain of metallic glasses^[30]. Therefore, the appearance of horizontal shear band can promote the proliferation of shear band and further inhibit the brittle fracture of metallic glass to a certain extent. Furthermore, it can also be found that the shear bands, containing large number and more interaction between the shear bands, are observed on the surface of the specimens with the lower strain rate, that consistent with the specimen of it is presented as well plasticity. The sawtooth rheological behavior is caused by the extension of shear band, that is, the extension of shear band is discontinuous, and the reactivation of shear band will lead to serrated rheological phenomenon^[31]. At low strain rate, sawtooth with smaller size and uniform stress corresponds to the more shear band of the compressed specimens. This can also be explained that the shear band of metallic glass can be uniformly expanded and proliferated at low strain rate, thus improving the strength and plasticity of metallic glass. At high strain rate, the shear of the specimen is not enough to propagate and proliferate, and the crack propagates along a single shear band, which leads to fracture. In summary, the compressive strain rate at room temperature and shear bands on the surface of the specimen (the number, the distribution intensity and the extent of the interaction between them) are negatively correlated.

3.4 Effect of aspect ratio on mechanical properties of Zr-based metallic glass

Table 3 The mechanical performance parameter of specimen with different aspect ratio at room temperature

aspect ratios	elastic modulus E/ MPa	plastic strain ϵ_p /%	yield strength σ_s /MPa	compressive strength σ_{bc} /MPa	fracture strength σ_c /MPa
1:1	19280	25.42	1436	2381	2375
1.5:1	19852	15.19	1394	1832	1593
2:1	31001	7.73	1371	1900	1853
2.5:1	43503	4.78	1380	1866	1842
3:1	41440	1.97	1582	1741	1707

According to the influence of sample size and aspect ratio on the plasticity of amorphous alloy, Han^[32] proposed a parameter called shear band instability index. According to Han's analysis, the specimens with small aspect ratio have larger critical shear band instability parameter Scr , therefore, the specimens have better plasticity. From the local enlarged diagram (shown in figure 6) of local stress-

3.4.1 Analysis of stress-strain curve in engineering

In addition to strain rate, aspect ratio is also one of the main factors affecting compression deformation of metallic glasses. In this experiment, the specimens with various aspect ratios of 1:1, 1.5:1, 2:1, 2.5:1 and 3:1 were subjected to Uniaxial compression tests at room temperature. The engineering stress-engineering strain curves of the specimens are illustrated in figure 6. The specific mechanical properties parameters are obtained, as displayed in Tab.3. Combined with figure 6 and table 3, it can be clearly seen that the sawtooth flow occurs in the specimens during compression, and the plastic strain decreases with the increase of aspect ratio. The yield strength of the specimen changes as aspect ratio increases, which tends to decrease at first and then increase, but the range of variation is very slight. The specimen has a maximum plastic strain of up to 25.42 % when the aspect ratio is 1:1. In addition to large plasticity, the specimen also manifest obvious work-hardening phenomenon, and its strength is also obviously higher than that of the specimens with other aspect ratio. The smallest plastic strain occurs when the aspect ratio is 3:1, and the plastic strain is only 1.97 %.

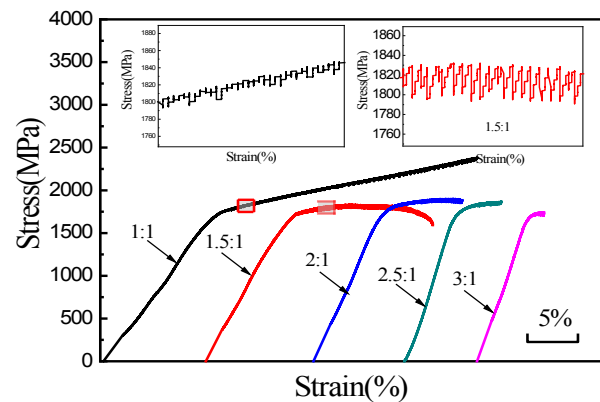


Figure 6 The compressive stress-strain curve of specimen with different aspect ratio at room temperature

strain curve, it can be seen that some curves show different sawtooth rheological behavior in the plastic deformation stage. Especially when the ratio of height to diameter is 1:1, the plasticity of the specimen with uniform stress range and small serration is significantly greater than that of the specimen with large aspect ratio.

The relationship among elastic modulus, strength,

plastic strain and aspect ratio of specimens is drawn by analyzing the compression mechanical properties parameters in Tab.3. The results are displayed in in figure 7 (P represents the aspect ratio of specimens). From figure 7 (a), when P varies from 1 to 2.5, the elastic modulus of the specimen raises with the increase of aspect ratio. Especially, the elastic modulus rockets sharply with the increase of aspect ratio from 1.5 to 2.5, and decreases when P changes from 2.5 to 3. In addition, the plastic strain of the specimen decreases with the increase of aspect ratio. Figure 7(b)

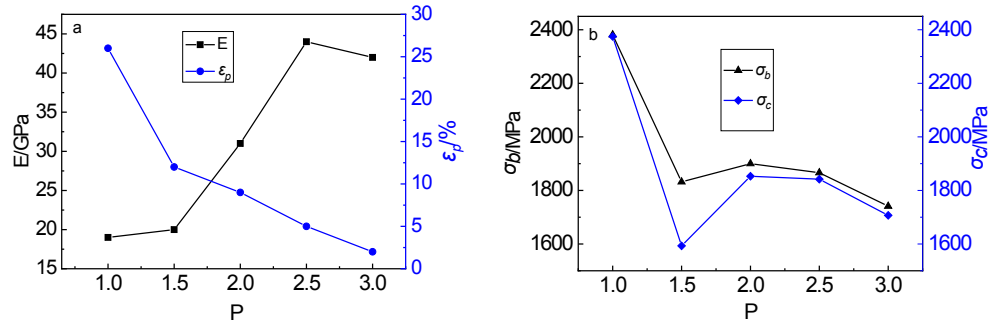


Figure 7 The relationship between elastic modulus, strength, plastic strain and aspect ratio of specimen.

3.4.2 Analysis of fracture morphology

It can be found from figure 8 that the fracture morphology of the specimens after compression fracture is composed of typical vein patterns. Figure 8(a, b, c, d) in turn represents the fracture morphology with an aspect ratio of 1.5:1, 2:1, 2.5:1 and 3:1. The specimen with the aspect ratio of 1:1 didn't break after compression, therefore, the fracture morphology of specimens was not observed. From figure 8(a), the fracture morphology of specimens is composed of fine vein patterns, and the size is relatively small, which conforms to the rule that the finer vein patterns of metallic glass correspond to the higher strength and plasticity^[25]. In

addition, the size of the specimen vein patterns increases with the increase of aspect ratio, and indicates the characteristics of uneven distribution of the grain. When the aspect ratio is 3:1, the fracture morphology of the specimen appears with the vein patterns of large size and discontinuity distribution, which may be one of the causes for the poor plasticity at room temperature. Compared with figure 8(a-d) and figure 4(a-e), we can find that there is a negative correlation between the size of vein patterns in the fracture morphology of specimens and the plastic strain of specimens. As a result, the size of vein patterns is also one of the gist for explaining the plastic strain of metallic glasses^[25].

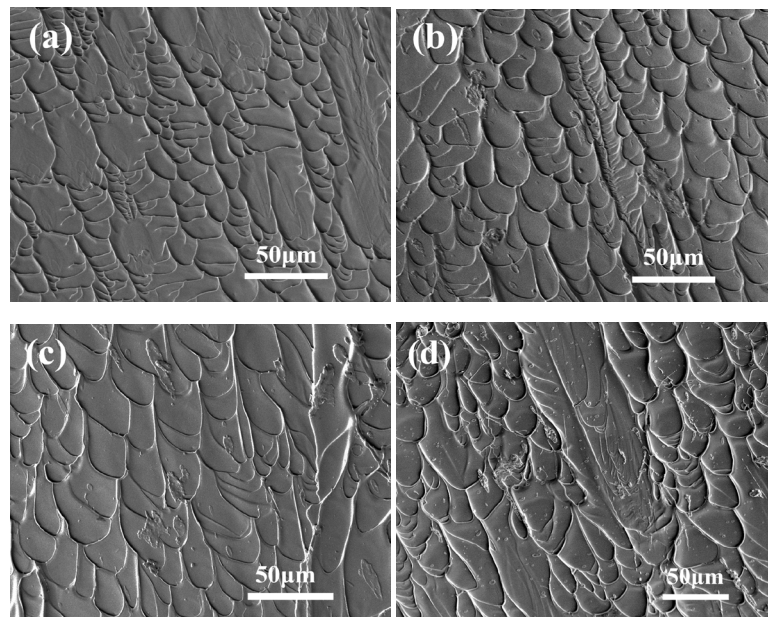


Figure 8 The compression fracture morphology of specimen with different aspect ratio at room temperature.

(a)1.5:1; (b)2:1; (c)2.5:1; (d)3:1

4. Conclusions

(1) The plastic deformation at room temperature of the specimen is sensitive to the strain rate. When the strain rate is $1 \times 10^{-5} \text{ s}^{-1}$, the specimen holds excellent mechanical properties, due to the shear bands with large number and dense distribution produced at lower strain rate can be uniformly extended and diffused. An increase in strain rate decreases the fracture strength, plastic strain and compressive strength of specimen.

(2) The compression plasticity of specimens at room temperature is closely related to the aspect ratio of compression specimens, which is mainly manifested by the deterioration of the compressive mechanical properties at room temperature with the increase of aspect ratio. Furthermore, specimen containing the aspect ratio of 1:1 possesses well excellent mechanical properties, among which the plastic strain is 25.42%, the compressive strength is 2381 MPa, and the fracture strength is 2375 MPa.

Conflict of Interest: The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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References

- [1] Li N, Xu X, Zheng Z, et al. Enhanced formability of a Zr-based bulk metallic glass in a supercooled liquid state by vibrational loading[J]. *Acta Materialia*, 2014, 65:400-411.
- [2] Deng L, Yao D, Zhou P, et al. Influence of size-dependent free volume variation and distribution on the thermoplastic flow behavior of Zr-based bulk metallic glass[J]. *Journal of Alloys and Compounds*, 2019, 783:272-278.
- [3] Ping Z, Zhong M, Long Z, et al. Universal percolation threshold for ductile-brittle transition of amorphous alloys[J]. *Journal of Non-Crystalline Solids*, 2018, 488:14-18.
- [4] Jafary-Zadeh M, Tavakoli R, Koh J J, et al. Effect of chemical composition and affinity on the short- and medium-range order structures and mechanical properties of Zr-Ni-Al metallic glass[J]. *Journal of Non-Crystalline Solids*, 2017,456:68-75.
- [5] Bibhu P.S., Amlan D, Rahul M. Mechanism of negative strain rate sensitivity in metallic glass film[J]. *Journal of Alloys and Compounds*,2019,784:488-499.
- [6] Hasani S, Rezaei-Shahreza P, Seifoddini A, et al. Enhanced glass forming ability, mechanical, and magnetic properties of $\text{Fe}_{41}\text{Co}_7\text{Cr}_{15}\text{Mo}_{14}\text{Y}_2\text{C}_{15}\text{B}_6$ bulk metallic glass with minor addition of Cu[J]. *Journal of Non-Crystalline Solids*, 2018,497:40-47.
- [7] Bordeenithikasem P, Shen Y, Tsai H L, et al. Enhanced mechanical properties of additively manufactured bulk metallic glasses produced through laser foil printing from continuous sheet metal feedstock[J]. *Additive Manufacturing*, 2018, 19:95-103.
- [8] Meduri C, Hasan M, Adam S, et al. Effect of temperature on shear bands and bending plasticity of metallic glasses[J]. *Journal of Alloys and Compounds*, 2018, 732:922-927.
- [9] Zhang H Y, Zheng G P. Simulation of shear banding in bulk metallic glass composites containing dendrite phases[J]. *Journal of Alloys and Compounds*, 2014, 586:262-266.
- [10] Zhang S G, Hu J, Zhu X X et al. High strain rate compression deformation behavior of Zr-based amorphous alloy in the supercooled liquid region[J]. *Chinese Journal of Nonferrous Metals*, 2005, 15(8):1219-1224
- [11] Chen D M, Wang G, Sun J G et al. Deformation behavior of tungsten wire reinforced zirconium-based bulk amorphous alloy composites at high strain rate[J]. *Journal of metals*,2006, 42(9):1003-1008
- [12] Lewandowski J J, Lowhaphandu P. Effects of hydrostatic pressure on the flow and fracture of bulk amorphous metal [J]. *Philos Mag A*, 2002, 82(17 - 18) :3427 - 3441.
- [13] Yuan B. The study of the serrated flow behavior in Zr-based bulk metallic glasses at room temperature[D]. *Taiyuan University of Technology*, 2018.
- [14] Wei R, Chang Y, Yang S, et al. Strain Rate Sensitivity Variation in Cu-Zr-based Bulk Metallic Glass Composites Containing B2-CuZr Phase[J]. *Rare Metal Materials and Engineering*, 2016, 45(3):542-547.
- [15] Tomasz K, Krzysztof P, Grzegorz C, et al. Effect of strain rate and crystalline inclusions on mechanical properties of bulk glassy and partially crystallized $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ alloy [J]. *Transactions of Nonferrous Metals Society of China*, 2019, 1036-1045.
- [16] Huang J S, Liu Y, Chen S Q, et al. Progress and application of Zr-based amorphous alloys[J]. *The Chinese Journal of Nonferrous Metals*. 2019,29:1036-1045.
- [17] Tariq N H, Akhter J I, Khalid A, et al. Effect of prior compression treatment on the deformation behavior of Zr based bulk metallic glass[J]. *Materials Chemistry and Physics*, 2014, 143(3):1384-1390.
- [18] Mihailov L, Spassov T, Bojinov M. Effect of microstructure on the electrocatalytic activity for hydrogen evolution of amorphous and nanocrystalline Zr-Ni alloys[J]. *International Journal of Hydrogen Energy*, 2012, 37(14).
- [19] Zhou M, Huang X, Hagos K, et al. Nanoporous copper fabricated from $\text{Zr}_{65}\text{Cu}_{17.5}\text{Fe}_{10}\text{Al}_{7.5}$ amorphous alloy and its electrocatalytic oxidation performance[J]. *Intermetallics*, 2017, 90:23-29.
- [20] Khan M. M, Deen K. M, Haider W. Combinatorial development and assessment of a Zr-based metallic

- glass for prospective biomedical applications[J]. *Journal of Non-Crystalline Solids*, 2019, 523: 119544.
- [21] Hong X, Tan Y, Zhou C, et al. Microstructure and tribological properties of Zr-based amorphous-nanocrystalline coatings deposited on the surface of titanium alloys by Electrospark Deposition[J]. *Applied Surface Science*, 2015, 356:1244-1251.
- [22] Jiang W H, Fan G J, Choo H, et al. Ductility of a Zr-based bulk-metallic glass with different specimen geometries[J]. *Materials Letters*, 2006, 60(29-30):3537-3540.
- [23] Christopher A S, Alan C L, Nieh T G. New regime of homogeneous flow in the deformation map of metallic glasses: elevated temperature nanoindentation experiments and mechanistic modeling[J]. *Acta Materialia*, 2004, 52(20):5879-5891.
- [24] Qu B. The Study of the Serrated Flow Behavior in Zr-based Bulk Metallic Glasses at Room Temperature [D]. Taiyuan University of Technology, 2018.
- [25] Sun M, Liu L, Wang J F, et al. Effect of Nb addition on thermal stability, glass forming ability and mechanical properties of Zr-based bulk amorphous alloys (in Chinese). *Acta Metall Sin*, 2005, 41(5):534 -538
- [26] Farnaz A, Davani S H, Harald R, David G, Annett G, Gerhard W. On the shear-affected zone of shear bands in bulk metallic glasses[J]. *Journal of Alloys and Compounds*, 2020, 837.
- [27] Han Z H, Feng Y Y, Li F. Minor Nb Addition Induced Microstructure Evolution and Multiplication of Shear Bands in Cu-Zr-Ti Based Bulk Metallic Glasses[J]. *Hot Working Technology*, 2019, 048(008):84-87.
- [28] Yedla N, Ghosh S. Nature of atomic trajectories and convective flow during plastic deformation of amorphous Cu₅₀Zr₅₀ alloy at room temperature-classical molecular dynamics studies[J]. *Intermetallics*, 2017, 80:40-47.
- [29] Inoue A, Zhang W, Tsurui T, et al. Unusual room-temperature compressive plasticity in nanocrystal-toughened bulk copper-zirconium glass[J]. *Philosophical Magazine Letters*, 2005, 85(5):221-237.
- [30] Wang X D, Qu R T, Wu S J, et al. Improving fatigue property of metallic glass by tailoring the microstructure to suppress shear band formation[J]. 2019, 7(100407).
- [31] Hufnagel T.C, El-Deiry P, Vinci R P. Development of shear band structure during deformation of a Zr₅₇Ti₅Cu₂₀Ni₈Al₁₀ bulk metallic glass[J]. *Scripta Materialia*, 2000, 43(12):1071–1075.
- [32] Han Z H, Wu W F, Li Y, et al. An instability index of shear band for plasticity in metallic glasses [J]. *Acta Mater*, 2009, 57(5): 1367-1372

Synthesis and Thermotropic of PAMEs Based on 1-Phenethyl-4-Piperidone Moiety

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Abstract:

New poly(azomethine-ether)s PAMEs containing 1-phenethyl-4-piperidone moiety have been synthesized through a solution polymerization of various diformyl-a,w-diphenoxyalkanes, I-IV with 3,5-bis(p-aminobenzylidene)-1-Phenethyl-4-piperidone VI. The structures of these polymers were confirmed using spectroscopic techniques. The inherent viscosities of the resulting polymers were found to range from 0.65 to 0.95 dl/g. The solubility of the PAMEs was estimated, showing good solubility in aprotic solvents. The thermal properties of the PAMEs were also evaluated by DSC technique. Liquid crystalline state of the polymers was observed on polarizing microscope exhibiting nematic phase for most of the synthesized polymers.

Keywords: PAMEs; Piperidone; Thermotropic; Texture observation

1 Introduction

Recently, liquid crystal polymers had become a well-known technology due to their wide range of applications such as electronic devices and super-strong materials [1-3]. There has been a great interest in liquid crystalline polymers that consist of a solid linear mesogenic group and flexible methylene groups. In general, the mesogenic groups and elastic modules were bound by the ether, ketone, ester or amide group [4-8]. There has been a significant progress in the development of thermotropic liquid crystalline polymers which have flexible units with linked azomethine-ether in order to lead to lower melting temperatures, more flexibility, improved solubility and enhanced specific properties such as mesomorphism [9-13]. As mentioned in many scientific papers, transitional temperatures decrease with the presence of methylene groups where the elasticity of polymer depends on the number of methylene groups, but the solubility is still not satisfactory. An improvement in the solubility of the urinary PAMEs containing substituted groups such as alkyl and alkoxy groups has been reported [14-16]. The presence of a heterogeneous atom in the hydrocarbon rings of the polymer main chain such as a nitrogen and sulfur atom has a direct effect on the physical properties of polymer. Moreover it increases thermal stability and improves the solubility of the polymer as a mesogenic group [17-19]. The introduction of piperidone

moiety as heterocyclic ring in the polymer back bone has an effect on the properties of the polymer. However, there are few reports related to the preparation of PAMEs containing heterocyclic rings [20-22]. The aim of this paper is to report on the preparation of a new PAMEs containing a heterocyclic ring of piperidone moiety and study of some properties such as solubility, thermal stability and thermotropic liquid crystal.

2 Materials and Methods

2.1 Reagents and solvents

4-Hydroxy-3-methoxybenzaldehyde, 1-phenethyl-4-piperidone and dihaloalkanes were purchased from (Aldrich) whereas 4-nitrobenzaldehyde was purchased from (Fluka) they were used without purification. Ethanol (95%), and all other solvents were of a high purity however they were purified by standard methods [23].

2.2 Measurements

Melting points of the synthesized samples were determined on an Electro thermal IA9100 melting point apparatus and are reported as such. The elemental composition was determined by Elementary Vario EL III instrument. The infrared spectra in the range 4000-650 cm⁻¹ of solid samples of the synthesized monomers and polymers were obtained using a Cary 630 FTIR spectrophotometer. The ¹H-NMR

spectra were recorded on Varian a Gemini 200 MHz NMR spectrophotometer at room temperature in DMSO solvent using TMS as the internal reference. Mass spectra were recorded on a Shimadzu Qp-2010 mass spectrometer. The inherent viscosities were measured using an Ubbelohde viscometer using a suspension in DMF at 25°C (0.5dIg-1). The thermal properties of the samples were investigated using Differential Scanning Calorimetry (DSC). The DSC recordings were carried out in inert nitrogen using a Shimadzu DSC-50 thermal analyzer. Liquid crystalline behavior was investigated by POM using an Optika B-1000 Polarizing Optical Microscope (POM) attached to a hot stage.

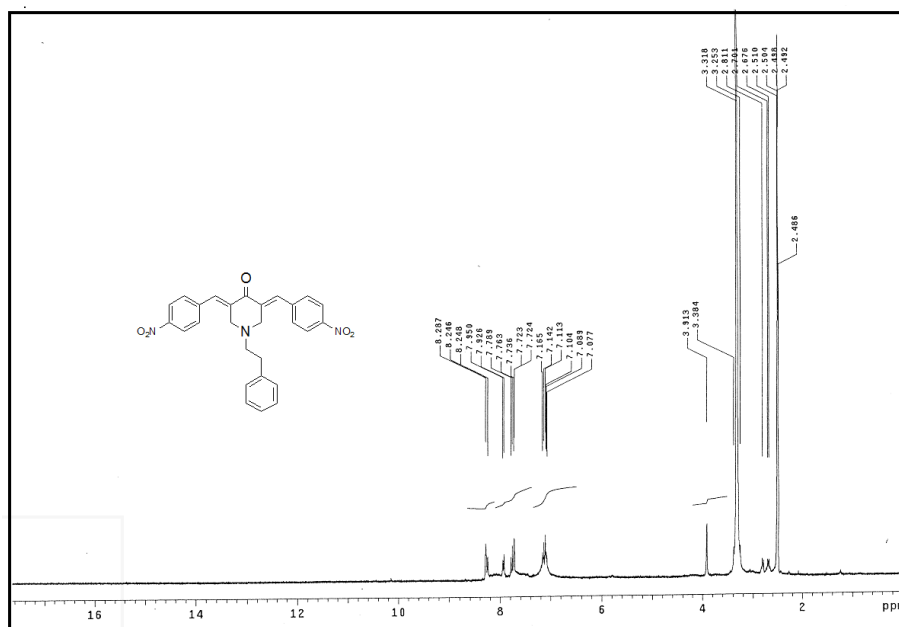
2.3 Monomer synthesis

4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes I-IV were synthesized by reported method [15].

2.1.1 3,5-Bis(p-nitrobenzylidene)-1-phenethyl-4-piperidone (V)

In a 150 ml round-bottomed flask was dissolved a

mixture of 4-nitrobenzaldehyde 6.04g(40mmol) and of 1-phenethyl-4-piperidone 4.06g(20mmol) in 25 ml ethanol while stirring at 50 °C. A few drops of alcoholic potassium hydroxide were then added to the reaction mixture with a continuous stirring for a period of two hours where the yellow precipitate was formed. The desired product V was collected by filtration and recrystallized from ethanol, yield 80%, mp 163 °C . Anal Calcd for $C_{27}H_{23}N_3O_5$: C, 69.01; H, 4.93; N,8,95%. Found: C, 69.35; H, 4.61; N,8,34%. IR (cm^{-1}); 2990 (C-H aliphatic stretching); 1660 (C=O); 1600 (C=C); 1340, 1530 (NO_2) and 1435 (piperidone C-H deformation). The mass spectrum showed molecular ion peak at $m/z = 469$ (13.4%) in agreement with its molecular formula ($C_{27}H_{23}N_3O_5$), and other peaks appeared at , $m/z = 423$ ($M^+ - NO_2$, 7.3%) and $m/z = 364$ ($M^+ - CH_2CH_2C_6H_5$, 9.8%). 1H -NMR (DMSO- d_6 ppm): 8.2 (s, 2H of $2CH=C$), 7.9-7.7 (m, 8H of benzylidene), 7.1-7.0 (m, 5H of Ar-H), 3.9 (s, 4H of methylene group of piperidone), 2.8(t 2H of CH_2 attached with phenyl group) and 2.6(t 2H of CH_2 attached with -N= of piperidone) (figure 1).



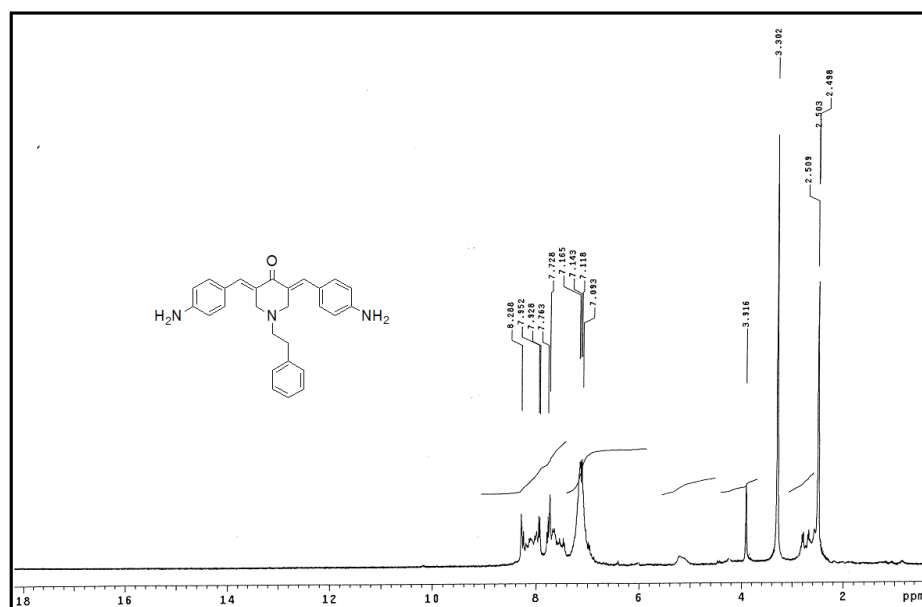


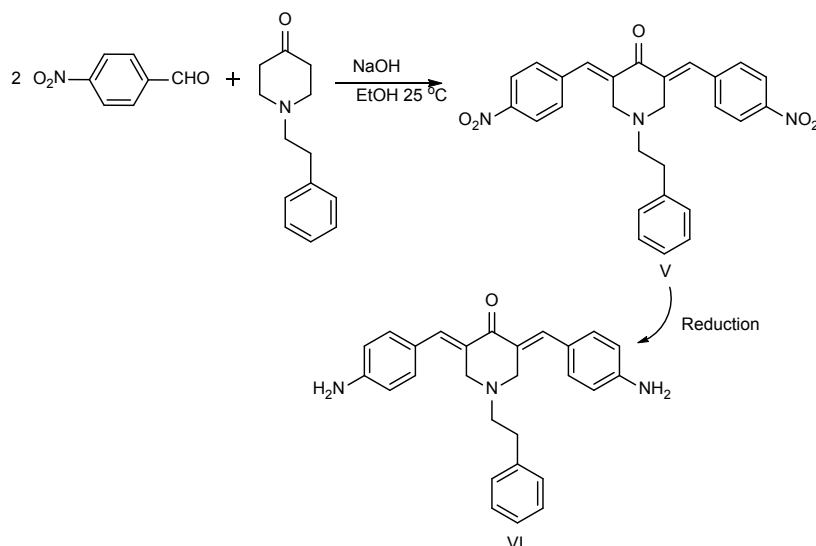
Figure 2 ¹H-NMR spectrum of monomer VI

2.4 Polymerization

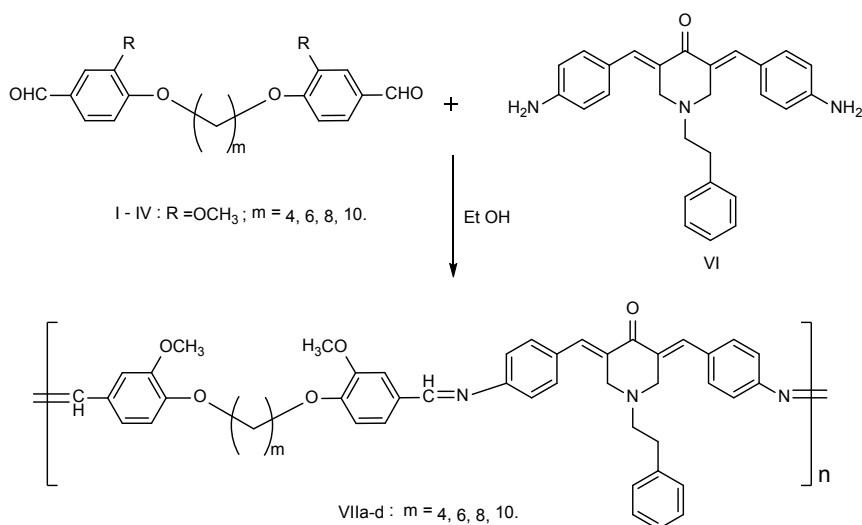
One polymer was used as a model for solution polymerization. The polymerization steps were carried out as follows: Bis-(p-aminobenzylidene)-1-phenethyl-4-piperidone **VI** (0.409 g, 1 mmol) was dissolved in absolute ethanol (20 ml) and to this solution, the diformyl **I** was added (0.358g, 1 mmol) at 25°C. The mixture was stirred at the same temperature for 20 minutes under nitrogen gas, then the stirring continued at 80 °C for 3 hours. During this time, the viscosity of the polymer solution increased rapidly and samples were taken from the polymer solution during different time periods to confirm the polymerization by analyzing the infrared spectrum. The polymer began to appear as precipitate, the polymer was separated by filtration, washed with various organic solvents and then dried. The yield was 90%.

3 Results and Discussion

The aim of this work is the preparation of new PAMEs **VII_{a-d}** through solution polymerization of the 3,5-Bis(p-aminobenzylidene)-1-phenethyl-4-piperidone with various diformyl-*a,w*-diphenoxyalkanes **I-IV**. (**Scheme1**) formulates the methods used for the preparation of the dibenzylidene-1-phenethyl-4-piperidone. As shown, this compound was prepared by the base-catalyzed condensation of two moles of p-nitrobenzaldehyde with one mole of 1-phenethyl-4-piperidone followed by hydrogenation using palladium on activated carbon in ethanol at 50°C. This method was used for the synthesis of PAMEs [14,16]. The expected structures of the resulting PAMEs **VII_{a-d}** were confirmed by elemental analyses and IR spectroscopy. The monomers used and the polymers are depicted in (**Schemes 1 and 2**).



Scheme 1. Synthesis of Monomers V, VI.



Scheme 2 Synthesis of PAMes VII_{a-d}.

In this work, the polymerization reaction between a diamine monomer and a formyl monomer is usually done in ethanol to form relatively medium molecular weight. The reason for choosing ethanol is that the monomers dissolve

easily and have a low boiling point. The polymers obtained have an inherent viscosity from 0.65 to 0.90 dl / g and can be easily obtained in high yields after a few minutes. The physical properties of these polymers are listed in (Table 1).

Table 1 Elemental analysis, yields and inherent viscosities of PAMes VII_{a-d}.

Polymer number	Yield (%)	η_{inh}^a dl g ⁻¹	Molecular formula (mol. wt)	Percentage of		
				C	H	N
VII _a	90	0.83	C ₄₇ H ₄₅ N ₃ O ₅ (731)	Calc.	77.15	6.15
				Found	77.65	5.98
VII _b	85	0.95	C ₄₉ H ₄₉ N ₃ O ₅ (759)	Calc.	77.47	6.45
				Found	77.87	6.10
VII _c	85	0.76	C ₅₁ H ₅₃ N ₃ O ₅ (787)	Calc.	77.76	6.73
				Found	77.12	6.11
VII _d	84	0.65	C ₅₃ H ₅₇ N ₃ O ₅ (815)	Calc.	78.03	6.99
				Found	77.89	6.50

^a Measured for solutions in DMF, with C= 0.5 dl g⁻¹ at 25°C

The infrared spectrum was used to confirm the structure of these polymers which containing the azomethine-ether unit. The infrared spectra of all prepared polymers indicate the disappearance of the absorption band of the amino group at 3300 cm⁻¹, new absorption bands have also appeared at 1660 cm⁻¹ for the azomethine

groups in addition to the appearance of the distinctive absorption band due to CH stretching of methylene groups at 2940-2860 cm⁻¹. The absorption band of carbonyl group of piperidone ring occurred at 1670-1685 cm⁻¹; C=C at 1620-1625 cm⁻¹ and C-O-C bonds (ether linkages), at 1230-1275 cm⁻¹(figure 3).

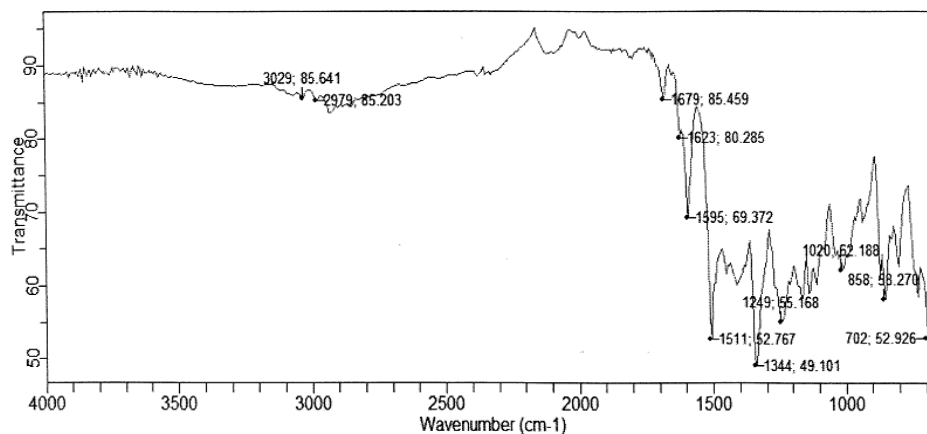


Figure 3 IR spectrum of polymer VII_a

3.1 Polymer characterization

The solubility properties of the prepared PAMEs in various solvents at room temperature are shown in (Table 2). It was noted that all PAMEs dissolve easily in concentrated sulfuric acid that can be attributed to the decomposition of the polymer core. These polymers were completely dissolved in aprotic solvents such as dimethylsulfoxide and *N*-dimethylformamide. The good solubility of these PAMEs may be due to the loose packing of the polymer construction with the 1-phenethyl-4-piperidone ring as a pendent group [18]. Among halogenated solvents such as methylene chloride and chloroform, all PAMEs were found to be partially soluble in methylene chloride and insoluble with the rest of the halogenated solvents. Moreover, as

for the common organic solvents such as methanol and benzene, these PAMEs were insoluble. Comparing the solubility of PAMEs containing cycloalkanone moiety^[16] with those containing piperidone ring, it was found that the former possessed less solubility than the latter. This may be due to the effect of the phenethyl moiety as a pendent group in which the polymer chains are far from each other, allowing the solvent to penetrate between the polymer chains. Therefore, the presence of the piperidone ring with the phenethyl group increases the solubility of the polymer compared to the previously prepared polymers.^[18,19] Furthermore, the introducing 1-phenethyl-4-piperidone ring as a polar group into the polymers chain gives rise to a slightly increased in the solubility process.

Table 2 Solubility characteristics of PAMEs VII_{a-d}

Polymer Number	DMF	DMSO	NMP	THF	CH ₃ Cl	CH ₂ Cl ₂	C ₆ H ₆	CH ₃ OH	H ₂ SO ₄
VII _a	++	++	+	+	-	+	-	-	++
VII _b	++	++	+	+	-	+	-	-	++
VII _c	++	++	++	++	+	++	+	+	++
VII _d	++	++	++	++	+	++	+	+	++

(++) Soluble at room temperature (RT); (+) Partially soluble at (RT); (-) Insoluble at (RT).

3.1.1 Thermotropic behavior of PAMEs

The thermotropic behavior of PAMEs VII_{a-d} was determined using the DSC and OPM devices at the heating period. Having the DSC device several thermal transformations were applied, some of which were endothermic peaks and some exothermic peaks. The polymers VII_{a-d} display melt birefringence and stirred glimmering through OPM. Table 3 shows the phase transfer temperatures for the PAMEs and the isotropic phase of these polymers was observed in

a temperature range of 233-357°C for the PAMEs VII_{a-d}. In DSC studies, most of the polymers revealed multiple endothermic peaks by the heating traces of the PAMEs and that gave a glass-transition (*T_g*) that was weak in the case of the polymer VII_d. The DSC profiles of the melting process of polymer VII_b which revealed multiple endotherms at 123.00 (*T_g*), 204.91 melting point (*T_m*), 252.07 isotropic temperature (*T_i*) and 399°C, also probably with decomposition.

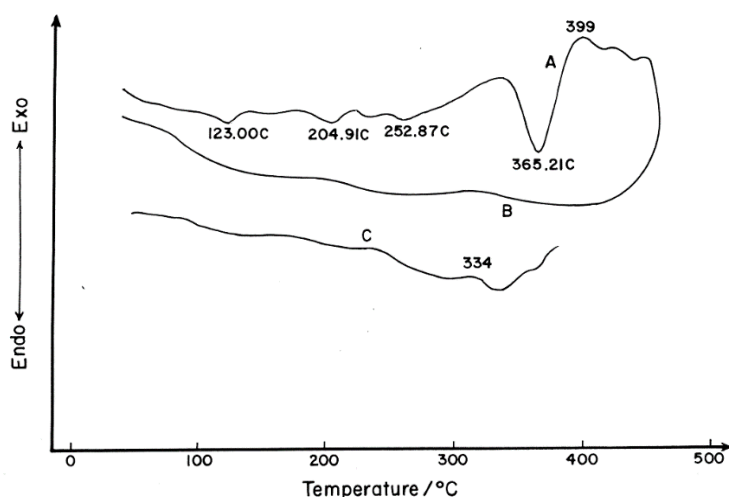


Figure 4 The DSC thermo gram of polymer VII_b.

When the polymer sample was cooled after preheating up to 450°C, there were no exothermic or endothermic peaks. On a second heating cycle there was an endothermic at 334°C. This phenomenon could be due to the presence of

different transition temperatures^[18,20]. The effect of spacer length on the thermal properties of the PAMEs VII_{a-d} is shown in Table 3. It can also be clarified from (Table 3) that the Phase transition temperatures decrease when the

methoxy groups are inserted with the elastic aliphatic spacer in the polymer core chain. [13,18].

Table 3 Phase transition temperatures of PAMEs VII_{a-d}*

Polymer number	N*	Gave brightness	T _m and T _i by (POM)			T _m and T _i by (DSC)		
			T _m	T _i	ΔT	T _m	T _i	ΔT
VII _a	4	Non	213	-	-	215	-	-
VII _b	6	Yes	202	248	46	204	252	48
VII _c	8	Yes	208	241	33	210	245	35
VII _d	10	Yes	190	233	43	190	230	40

* Number of methylene units.

Thus, the unsubstituted para-linked PAMEs are infusible below its decomposition temperature. However it was found that the inclusion of the methoxy substituent in the solid aromatic ring as a mesogenic group reduces the glass transition temperature (*T_g*), melting point (*T_m*), and isotropic temperature (*T_i*). Moreover, the methoxy group controls the direction of the reactions that occur in the polymer structure during thermal transformations^[24]. In the DSC measurements, the peaks are broad and sometimes sharp, due to the nature of the polymer construction, which creates interference in the various transformation

temperatures.

3.1.2 Texture observation

The behavior of polymer tissue at a certain temperature has been studied by quenching it in liquid nitrogen. It appears that all PAMEs have a highly melt viscosity (with the exception of Polymer VII_a) indicating that the appearance of the nematic stage. Observation of the polymer VII_b in the anisotropic melt displays nematic thread-like texture as shown in (figure 5) at 202°C (A) and (figure 5) at 248°C (Ti) (B). Similar nematic textures were observed for polymers VII_{c,d}.

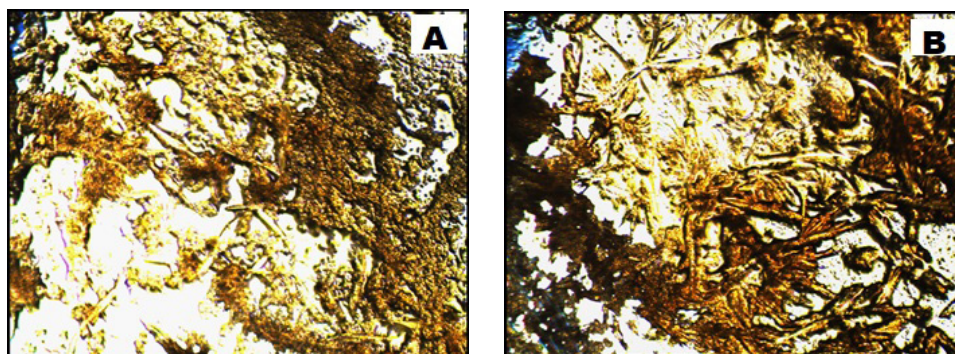


Figure 5 Photomicrographs of polymer VII_b, (A) at 202°C (before *T_m*); (B) 248°C (*T_i*).

4 Conclusions

New chains of PAMEs which contain the piperidone moiety were prepared using the solution polymerization. Most of the polymers are found to be soluble in aprotic solvents and exhibit birefringence and glittering under polarized microscope. The *T_m* and *T_i* values increase as the length of the flexible methylene spacers are decreased and decrease with the introduction of the methoxy group as a substituent in the polymer core.

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References

- [1] Grigoras M, Catanescu CO. Imine oligomers and polymers.

J Macromol Sci Part C. Polym Rev. 2004; 44:131–73.

- [2] Tanaka H, Shibahara Y, Sato T, Ota T. Preparation and thermal behavior of spin polymers and their precursors based on azomethine mesogens. Eur Polym J. 1993;2:1525–30.
- [3] Dutta PK, Jain P, Sen P, Trivedi R, Sen PK, Dutta J. Synthesis and characterization of a novel polyazomethine ether for NLO application. Eur Polym J. 2003;39:1007-1011.
- [4] Rahman MM, Hussein M A, Aly KI, Asiri AM. Thermally stable hybrid polyarylidene(azomethine-ether)s polymers (PAAP): an ultrasensitive arsenic(III) sensor approach Des Monomers Polym. 2018; 21(1): 82–98.
- [5] Sana B, Koyilapu R, Dineshkumar S. High temperature PEMs developed from the blends of Polybenzimidazole and poly(azomethine-ether) Journal of Polymer Research. 2019; 26(2): 55.
- [6] Yen H-J, Liou G-S. Novel blue and red electrochromic poly(azomethine ether)s based on electroactive

- triphenylamine moieties. *Organic Electronics*. 2010;11: 299–310.
- [7] Shukla U, Rao KV, Rakshit AK. Thermotropic liquid-crystalline polymers: synthesis, characterization, and properties of poly(azomethine esters). *J Appl Polym Sci*. 2003;88:153–60.
- [8] Sun S-J, Chang TC, Li CH. Synthesis and properties of thermotropic liquid crystalline poly(azomethine-carbonate)s. *Eur Polym J*. 1993;29:951–955.
- [9] Li CH, Chang TC. Synthesis and properties of poly(amide-azomethine-ester). *J Polym Sci Chem*. 1991;29:361–367.
- [10] Tanaka H, Shibahara Y, Sato T, Ota T. Preparation and thermal behavior of spin polymers and their precursors based on azomethine mesogens. *Eur Polym J*. 1993;2:1525–1530.
- [11] Cozan V, Butuc E, Stoleriu A, Rusa M, Rusu M, Ni Y, Ding M. Poly(azomethine sulfones) with thermotropic liquid crystal-line behavior. *J. Macromol. Sci., Pure Appl. Chem*. 1995;A32:1243–1262.
- [12] Parks SB, Kim H, Zin WC, Jung, JC. Synthesis and properties of polyazomethines having flexible (n-alkyloxy)methyl side chains. *Macromolecules*. 1993;26:1627–1632.
- [13] Hussein MA, Abdel-Rahman MA, Asiri AM, Alamry KA, Aly KI. Review on: liquid crystalline polyazomethines polymers. Basics, syntheses and characterization. *Des Monomers Polym*. 2012;15:431–463.
- [14] Marin L, Cozan V, Bruma M, Grigoras V C. Synthesis and thermal behaviour of new poly(azomethine-ether). *Eur Polym J*. 2006;42: 1173–1182.
- [15] Aly KI, Ahmed R A. Thermotropic liquid crystalline PAMEs containing cycloalkanone moiety in the polymer backbone. *Liquid Crystals*. 2000; 27: 451–458.
- [16] Aly KI, Khalaf AA, Alkaskas IA. Thermotropic liquid crystalline PAMEs containing dibenzylidene derivatives in the main chain. *Eur Polym J*. 2003;39:1035–1044.
- [17] Kannan P, Raja S, Sakthivel P. Synthesis and characterization of thermotropic liquid crystalline poly(azomethine ether)s. *Polymer*. 2004;45: 7895–7902
- [18] Alkaskas IA, El-Gnidi B. Thermotropic Liquid Crystalline Poly(Azomethine-Ether)s Containing Dibenzylidene Derivatives in the Main Chain. *J. Macromol. Sci. – Pure Appl. Chem* 2006; 43:1435–1443.
- [19] Aldred MP, Vlachos P, Dong D, Kitney SP, Tsoi WC, Neill MO. Heterocyclic reactive mesogens: synthesis, characterisation and mesomorphic behaviour. *Liq Cryst*. 2005;32:951–965.
- [20] Ha, ST, Koh TM, Yeap GY, Lin HC, Lee SL, Win YF, Ong ST. Synthesis and mesomorphic properties of 6-methoxy- and 6-ethoxy-2-(2-hydroxy-4-alkanoyloxybenzylidenamino) benzothiazoles. *Mol. Cryst. Liq. Cryst*. 2010; 528: 10-22.
- [21] Aly KI, Abbady MA, Mahgoub SA, Hussein MA. Liquid crystalline polymers. IX. Main chain thermotropic poly(azomethine-ether)s containing thiazole moiety linked with polymethylenespacers. *Journal of Express Polymer Letters*. 2007;1:197–207.
- [22] Kaya İ, Avcı A, Kolcu F, Çulhaoğlu S. Synthesis, characterization, optical, and electrochemical properties of thermal stable novel PAMEs Designed Monomers & Polymers. 2014;17(5): 481-490.
- [23] Perrin DD, Armario WLF. Purification of laboratory chemicals. 3rd ed. New York: Pergamon Press; 1988.
- [24] Demus D, Goodby J, Gray GW, Spiess H-W, Vill V. Low molecular weight liquid crystals. In: Demus D, editor. *Handbook of Liquid Crystals*. 1st ed. 2B. Wiley-VCH; Weinheim, Germany: 1998. pp. 10–40.

Neutron Diffraction Study on the Magnetic Structure of $^{153}\text{EuMnO}_{3-\delta}$: One Way to Assess the Magnetic Structure of $\text{EuMnO}_{3-\delta}$

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Abstract:

Owing to the strong neutron absorption of ^{151}Eu , ^{151}Eu free $^{153}\text{EuMnO}_{3-\delta}$ has been synthesized to collect the neutron diffraction data for analyzing the magnetic structure of $\text{EuMnO}_{3-\delta}$. The obtained neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ indicates that the magnetic diffraction peaks corresponding to cAAFM (canted A-type antiferromagnetic) phase can be observed, but the magnetic diffraction peaks corresponding to expected ICAFM (incommensurate antiferromagnetic) phase may be too weak to be observed.

Keywords: Magnetic structure; Neutron diffraction; $^{153}\text{EuMnO}_3$; Perovskite

1 Introduction

The multiferroicity in $\text{LnMnO}_{3-\delta}$ ($\text{Ln}=\text{Y}, \text{Tb}, \text{Ho}$)^[1-3] and the colossal magnetoresistance or charge-ordering in $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A}=\text{alkaline earth}$)^[4,5], have induced a lots of studies on the series $\text{LnMnO}_{3-\delta}$ ($\text{Ln}=\text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}$). During a systematical study of the magnetic and orbital structures in the series of $\text{LnMnO}_{3-\delta}$ as a function of Mn-O-Mn bond angle φ , T. Kimura et al.^[6] established a magnetic phase diagram for orthorhombic $\text{LnMnO}_{3-\delta}$ ($\text{Ln}=\text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$) using the neutron diffraction data of $\text{LnMnO}_{3-\delta}$ ($\text{Ln}=\text{La}, \text{Pr}, \text{Nd}, \text{Tb}, \text{Dy}, \text{Ho}$)^[7-11] and X-ray diffraction data of $\text{LnMnO}_{3-\delta}$ ($\text{Ln}=\text{Sm}, \text{Eu}, \text{Gd}$, the corresponding neutron diffraction data contain less information given the high neutron absorption cross section of the corresponding rare earths) to obtain the value of Mn-O-Mn bond angle φ for each compound by Rietveld refinement.^[12] This magnetic phase diagram^[6] indicates that $\text{EuMnO}_{3-\delta}$ is paramagnetic (PM) above 51K, incommensurate antiferromagnetic (ICAFM) between 51K and 46K, and canted A-type antiferromagnetic (cAAFM) below 46K. The phase transition temperatures are different from the values of 47K and 35K reported by Y. M. Mukovskii et al.^[13] This difference may be due to the composition of the so-called

$\text{EuMnO}_{3-\delta}$ sample obtained in different research group is different as indicated by I.O. Troyanchuk et al.^[14] and J. M. Deng et al.^[15]. Similar phenomena can also be found in other $\text{LnMnO}_{3-\delta}$ system.^[16-23] As well known, magnetic phase transitions usually relate to the changes of magnetic structure, which may induce the change of magnetic reflections in the neutron diffraction data collected around the phase transition temperature.^[21,22] However, the neutron diffraction data of $\text{EuMnO}_{3-\delta}$ is not easy to be analyzed because ^{151}Eu (50% of natural Eu is ^{151}Eu , the other ~50% is ^{153}Eu) can strongly absorb neutrons to let the obtained data showing very weak useful information. This is why there is no data found in literature. Until 2005, B. Dabrowski et al. presented the room temperature neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ in their published work^[24] to obtain a precise value of Mn-O-Mn bond angle by Rietveld refinement. Soon after, the neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ at 3 K have been obtained,^[15] which shows the magnetic reflections related to the cAAFM phase of $\text{EuMnO}_{3-\delta}$. The corresponding magnetic space group for the cAAFM phase of $\text{EuMnO}_{3-\delta}$ is $Pnma1$, with $a = 5.8183(2)$, $b = 7.2082(3)$, $c = 5.3269(2)$ Å at 3 K. However, the expected ICAFM phase of $\text{EuMnO}_{3-\delta}$ around 50 K is still waiting for confirmation. Therefore, it is very important to obtain the neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ around

50 K. The corresponding neutron diffraction data obtained by us could not confirm the existence of the expected ICAFM phase of $\text{EuMnO}_{3-\delta}$.

2 Experimental

$^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ are synthesized using a traditional solid-state reaction from stoichiometric $^{153}\text{Eu}_2\text{O}_3$ (99.995%), Eu_2O_3 (99.995%) and MnCO_3 (A.R.) for the comparing studies. The oven-dried reagents were homogenized for about 30 min of grinding with an agate mortar and a pestle. The mixture was subjected to 6 h of calcination at 800 °C. They were then pressed into pellets to undergo four 12 h heat treatments at 1200 °C, followed by a furnace cooling every time with intermediate grinding. All the treatments were carried out under air. The weights of the samples were monitored before and after heat treatment. The maximum difference was about 4 mg for the 6 g samples. Therefore, the final compositions of the samples were considered the same as the initial ones. Powder X-ray diffraction (PXRD) data were collected on a PANalytical X'Pert3 Powder diffractometer with $\text{Cu K}\alpha$ ($\lambda_1=1.5405$ Å and $\lambda_2=1.5443$ Å) radiation (2θ range: 5–120°; step size: 0.0131; scan speed: 1°/min) at 40 kV and 40 mA at room temperature. Neutron powder diffraction (NPD) data for $^{153}\text{EuMnO}_{3-\delta}$ were collected on the instrument Echidna at the OPAL reactor (Lucas Heights, Australia) at the Australian Nuclear Science and Technology Organization (ANSTO) at $\lambda=2.43950$ Å. The X-ray diffraction data and the neutron diffraction data were analyzed using GSAS software.^[12, 25] The magnetic properties were investigated using a Cryogenic physical property measurement system (PPMS, supplied by East Changing, China) from

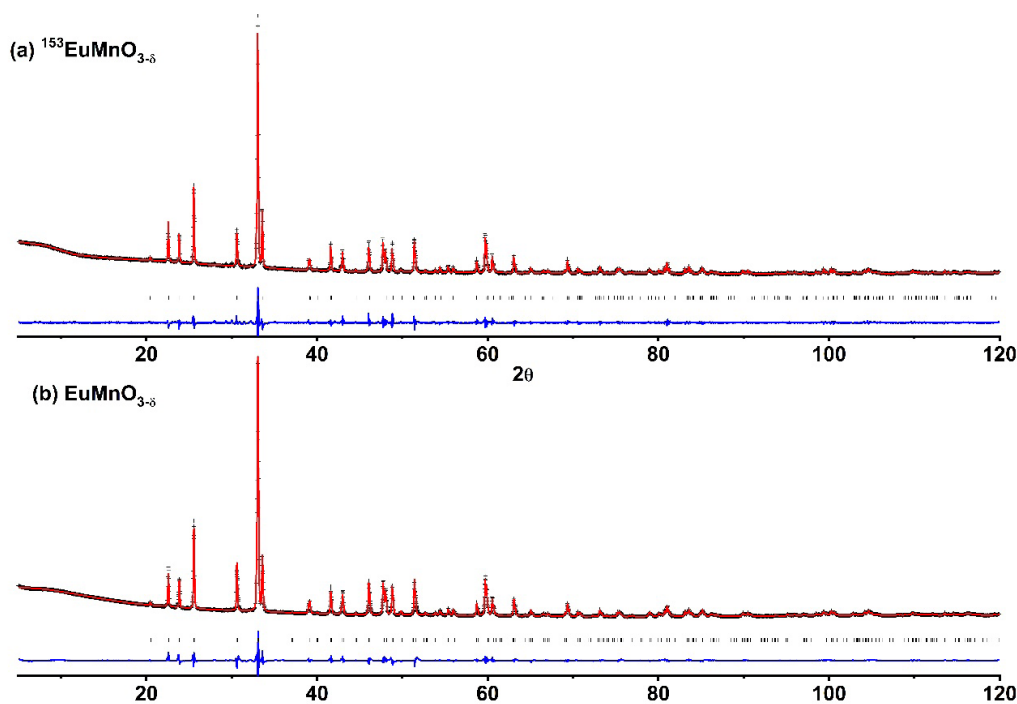
2 to 300 K.

3 Results and discussions

Usually, one may believe that the structure and magnetic properties of $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ are almost the same. However, it is still better to have a careful check if one keeps in mind the isotope effect in superconductor.^[26-28] Therefore, $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ have been synthesized under the same condition as described above. Their X-ray diffraction data and magnetic properties have been compared carefully. No significant differences are found between $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$. Therefore, the magnetic structure obtained from the neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ should be applicable to EuMnO_3 . The details are presented below.

3.1 X-ray diffraction data

The X-ray diffraction data of the synthesized $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ can be refined well using the same crystallographic parameters. The corresponding Reitveld plots are shown in figure 1. The space group *Pnma* is used in the refinement with ^{153}Eu or Eu at (0.0781(3), 0.2500, 0.9831(2)), Mn at (0.0000, 0.0000, 0.5000), and O1 at (0.4800(2), 0.2500, 0.1009(3)), O2 at (0.3126(3), 0.0441(2), 0.7131(3)). The obtained lattice parameters are $a=5.8401(3)$, $b=7.4601(3)$, and $c=5.3347(3)$ Å. These data agree well with the reported ones,^[13-15] which indicates the samples studied in this work are similar to that reported by other researchers and the replacement of Eu (a natural mixture of 50% ^{153}Eu and 50% ^{151}Eu) by pure ^{153}Eu isotope does not change the structure significantly.



3.2 Magnetic properties

The temperature dependence of magnetization of the sample $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ in ZFC (Zero Field Cooling) and FC (Field Cooling) modes is shown in figure 2. As mentioned in the previous studies, [29-32] it is not easy to perform a zero-field cooling. The so called zero-field is usually a very small field, which is randomly positive or negative. Therefore, the “ZFC” is used instead of simple ZFC in figure 2. The “ZFC” curves for $\text{EuMnO}_{3-\delta}$ and $^{153}\text{EuMnO}_{3-\delta}$ are similar. They seem to be obtained by first cooling the sample under a very small negative field because a negative magnetization is found at low temperature. This can be understood from the field dependent magnetization (M-H) curves obtained at selected temperature shown in figure 3 for $\text{EuMnO}_{3-\delta}$ and figure 4 for $^{153}\text{EuMnO}_{3-\delta}$. The details are described below.

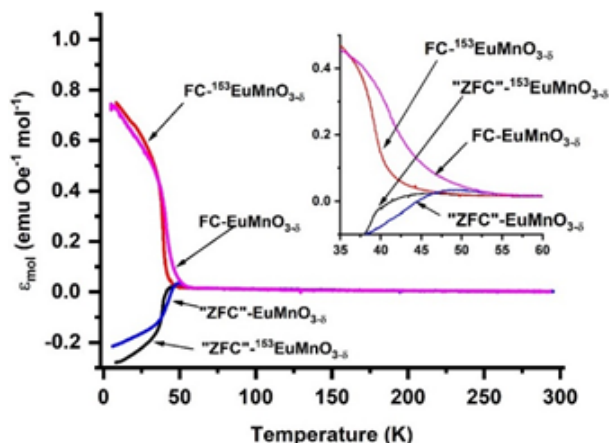


Figure 2 Temperature dependent magnetization of $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ measured at 500 Oe.

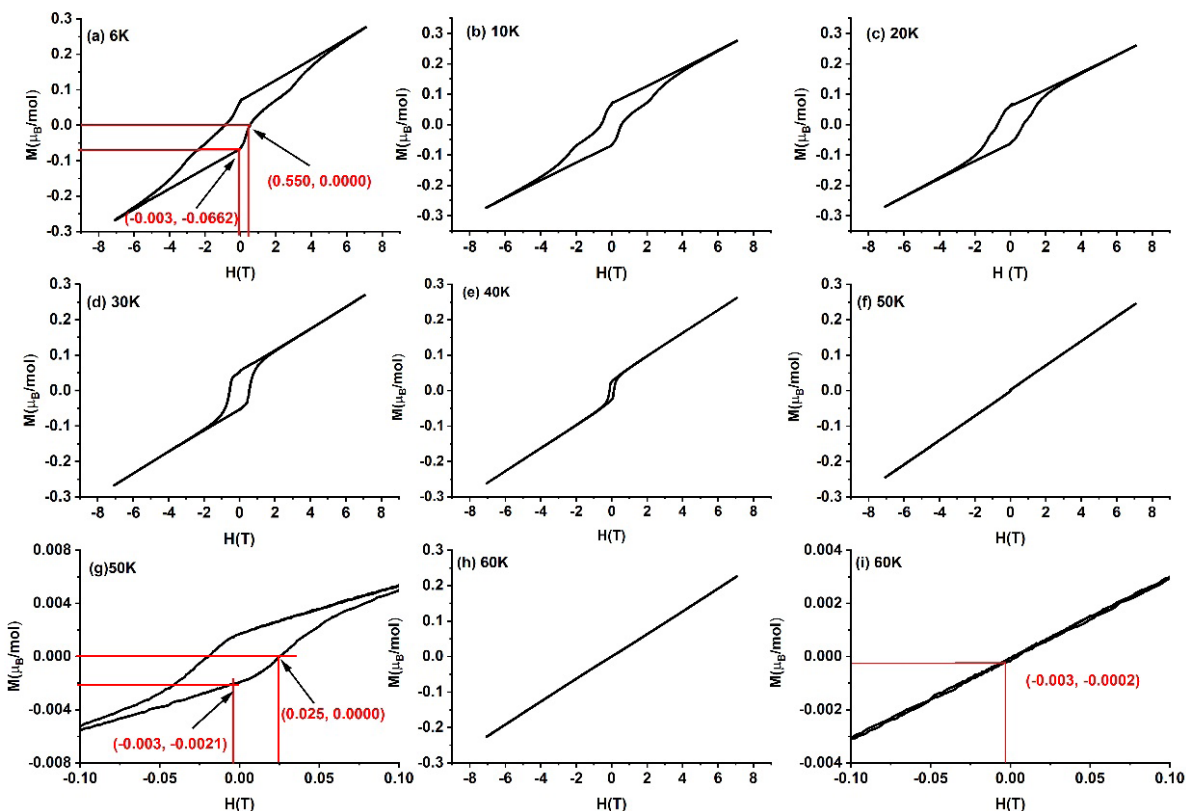


Figure 3 Field dependent magnetization of EuMnO_3 at 6 K(a), 10 K(b), 20 K(c), 30 K(d), 40 K(e), 50 K(f), and 60 K (h), enlargement of the data at 50 K (g) and 60 K(i).

Above 60 K, the M-H curve is a straight line for $\text{EuMnO}_{3-\delta}$ with a positive slope. The magnetization is positive when the field is positive, or is negative when the field is negative. This is a typical case for a paramagnetic compound. For simplicity, only the data at 60 K is shown in figure 3h and figure 3i. The data shown in figure 3i is the enlarged part of the data shown in figure 3h at the weak magnetic field between -0.10 and 0.10 T to show a clear linear relationship. Let's set the random “zero field” to be a small negative field about -0.003 T, the magnetization for

the present sample $\text{EuMnO}_{3-\delta}$ at 60 K may be $-0.0002 \mu_B/\text{mol}$ as indicated in figure 3i. If a positive magnetic field is applied at this temperature, positive magnetization should be obtained immediately. When the temperature decreases to about 50 K, the relationship between magnetization and magnetic field becomes complex. A loop is found when the magnetic field is between -0.10 and 0.10 T as shown in figure 3g. This means a magnetic phase transition occurs above 50K. As shown in figure 3g, if the magnetic field is still about -0.003 T, the corresponding magnetization at 50

K may be $-0.0021 \mu_B/\text{mol}$. At this case, if a positive magnetic field less than 0.025 T is applied, a negative magnetization can be obtained as shown also in figure 3g. The magnetic loop became larger and larger when the temperature decreases. As indicated at figure 3a, the observed magnetization of $\text{EuMnO}_{3-\delta}$ at 6 K may be $-0.0662 \mu_B/\text{mol}$ for the small negative field of -0.003 T. If a positive field about 0.05 T is applied at 6 K for measurement, the observed magnetization should be negative. This is an explanation for the observation of “ZFC” curve of $\text{EuMnO}_{3-\delta}$ shown in

figure 2. If one wants to obtain a positive magnetization, the applied field should be larger than 0.55 T as indicated in figure 3a. This agrees well with the previous studies.^[29]

The “ZFC” curve for $^{153}\text{EuMnO}_{3-\delta}$ presented in figure 2 also shows negative magnetization, which indicates the data is obtained by first cooling the sample under a very small negative field. The understanding of this observation for $^{153}\text{EuMnO}_{3-\delta}$ is similar to that for the sample $\text{EuMnO}_{3-\delta}$, which is shown in figure 4.

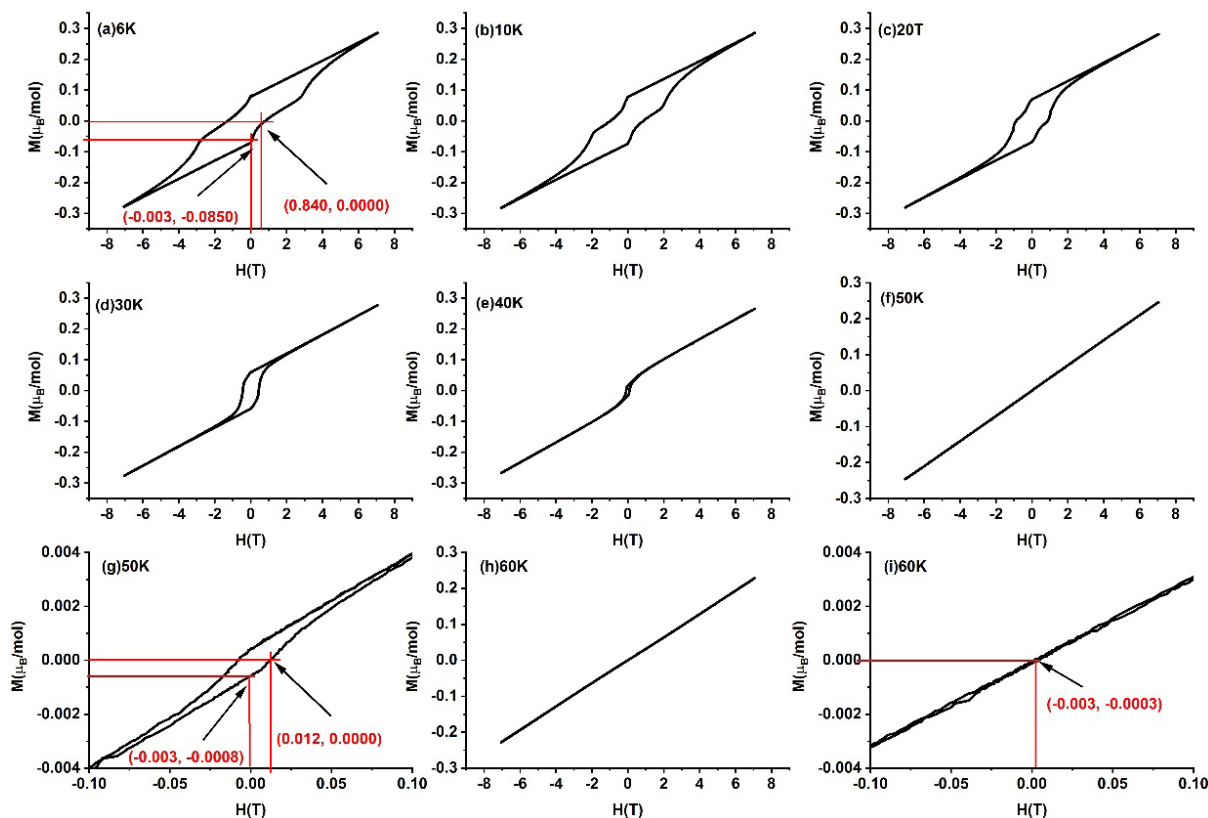


Figure 4 Field dependent magnetization of $^{153}\text{EuMnO}_3$ at 6 K(a), 10 K(b), 20 K(c), 30 K(d), 40 K(e), 50 K(f), and 60 K (h), enlargement of the data at 50 K (g) and 60 K(i).

The FC curves of $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ are very similar but not the same (see figure 2). This may mean that the difference between the value of δ of $^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ is very small because I. O. Troyanchuk et al.^[4] reported that the magnetic properties of $\text{EuMnO}_{3-\delta}$ may be different when the value of δ is different. The second possibility may be that the obtained sample is $^{153}\text{Eu}_{1-x_1}\text{Mn}_{1+x_1}\text{O}_{3-\delta}$ or $\text{Eu}_{1-x_2}\text{Mn}_{1+x_2}\text{O}_{3-\delta}$ with $x_1 \sim x_2$ because the magnetic properties of $\text{Eu}_{1-x}\text{Mn}_{1+x}\text{O}_{3-\delta}$ are different when x is different.^[15, 23]

The departure of the FC and “ZFC” curves of $\text{EuMnO}_{3-\delta}$ is around 52 K, which can be clearly found from the inset of figure 2. This value agrees well with the reported data.^[6, 33] The departure of the FC curve and “ZFC” curve of $^{153}\text{EuMnO}_{3-\delta}$ seems to be around 51 K. An M-H loop can be observed at 50 K for $^{153}\text{EuMnO}_{3-\delta}$ as shown in figure 4. The M-H curves for $\text{EuMnO}_{3-\delta}$ (figure 3) and $^{153}\text{EuMnO}_{3-\delta}$ (figure 4) are very similar, which also agree well with the

data for EuMnO_3 reported previously.^[29] Therefore, the present data indicates that the replace of Eu by ^{153}Eu does not change the magnetic properties significantly.

3.3 Neutron diffraction data for $^{153}\text{EuMnO}_{3-\delta}$

As mentioned in section 3.2, negative magnetization can be observed for EuMnO_3 if it cooled down to low temperature under a negative field. In order to know what happens in this negative magnetization, neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ between 10 K and 60 K at a magnetic field of 1 T after field cooling under a magnetic field of -0.05 T are obtained. For comparison, neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ between 10 K and 60 K at a magnetic field of 1 T after zero field cooling, and between 42 and 48 K at a zero field, are also obtained. The corresponding data are shown in figure 5.

The neutron diffraction data after negative field cooling and zero field cooling are very similar to each other, which

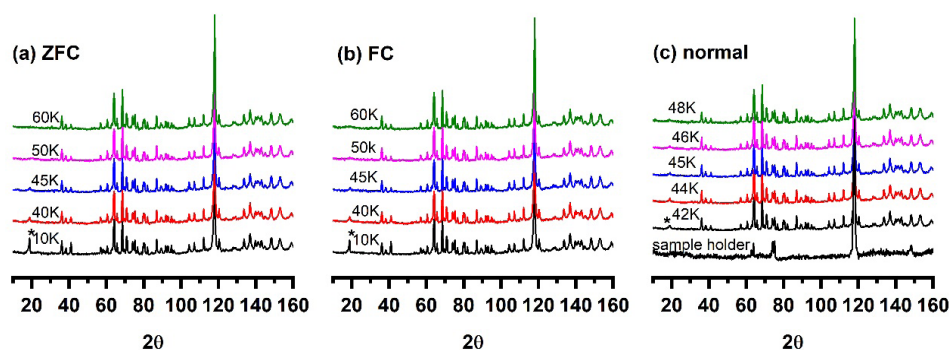


Figure 5 Neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ at selected temperature under a magnetic field of 1 T after zero field cooling (a), field cooling (the magnetic field is about -0.05 T) (b), and under a zero magnetic field (c).

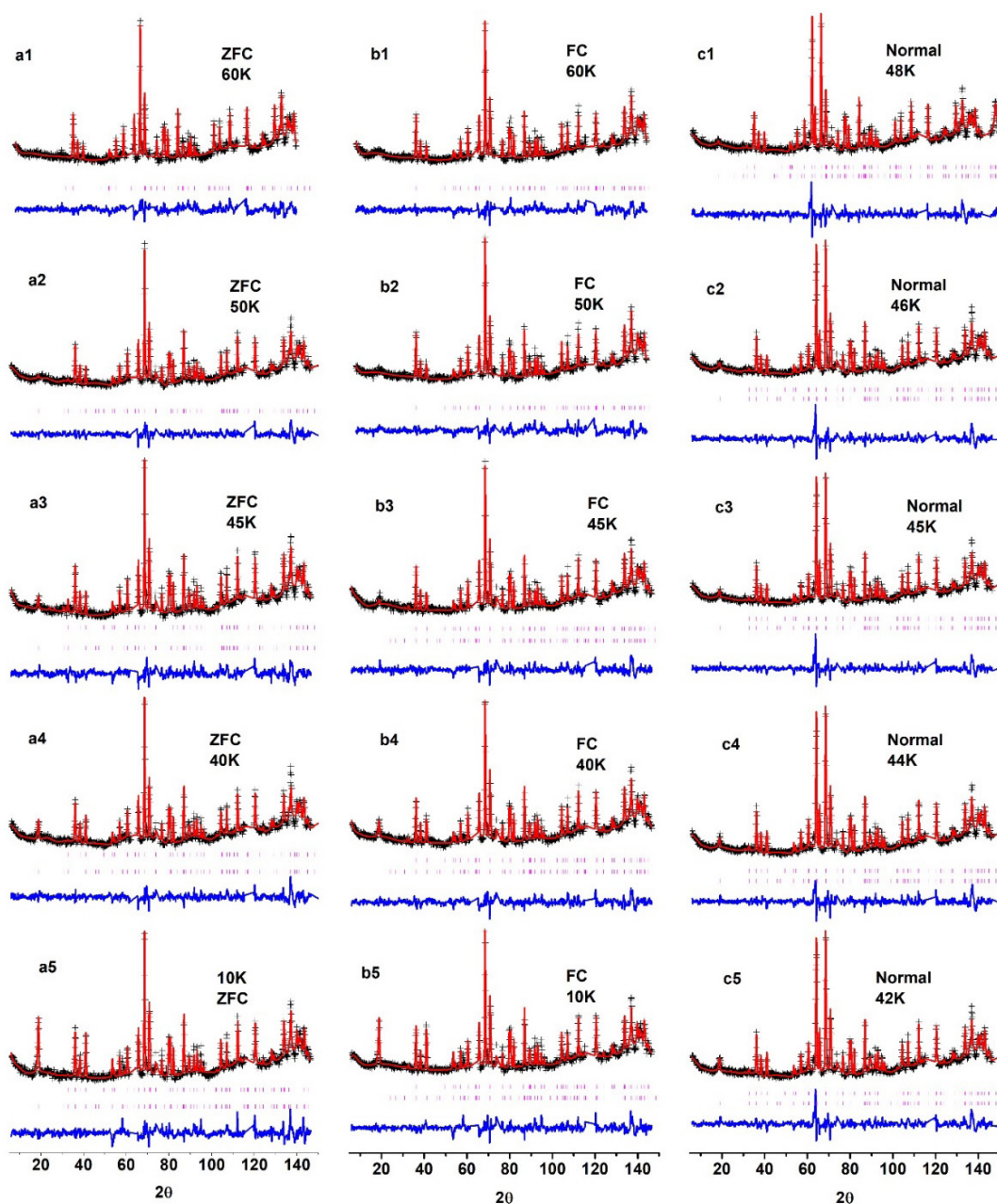


Figure 6 Rietveld plots of the neutron diffraction data of $^{153}\text{EuMnO}_3$ at selected temperature under a magnetic field of 1 T after zero field cooling (a), field cooling (the magnetic field is about -0.05 T) (b), and under a zero magnetic field (c).

means that the structure of $^{153}\text{EuMnO}_{3-\delta}$ (both nuclear structure and magnetic structure) are almost the same at two different situations. The diffraction peak marked by star in figure 5 is a magnetic diffraction peak from the cAAFM phase of $\text{EuMnO}_{3-\delta}$, which had been described in a previous paper.^[15] This magnetic diffraction peak can be observed at the temperature of 50K or lower and disappear at the temperature of 60K.

The temperature dependent magnetization of $^{153}\text{EuMnO}_{3-\delta}$ (see figure 2) indicates a magnetic phase transition around 51K. Therefore, it is easy to accept that the magnetic diffraction peak can be observed in the neutron diffraction data at 50K and disappears in the neutron diffraction data at 60K. The field dependent magnetization of $^{153}\text{EuMnO}_3$ (see figure 4) also indicates that a loop can be observed around 50K and no loop is found at 60K. It is very surprising that only one set of magnetic peaks for the cAAFM phase of $\text{EuMnO}_{3-\delta}$ are found in the obtained data (see figure 5a and 5b). This may mean the ICAFM phase of $\text{EuMnO}_{3-\delta}$ does not exist. One may argue that the ICAFM phase of EuMnO_3 is restrained by a magnetic field of 1T. Therefore, the neutron diffraction data of

$^{153}\text{EuMnO}_{3-\delta}$ was obtained between 42K and 48K without an applied magnetic field (called as the normal state). The corresponding data are shown in figure 5c. It is found that the diffraction data are similar to that shown in figure 5a and 5b. The magnetic diffraction peaks shown in the data belong to the cAAFM phase of $\text{EuMnO}_{3-\delta}$. The ICAFM phase of $\text{EuMnO}_{3-\delta}$ expected around this temperature was not be observed. Really some diffraction peaks are not belonging to the nuclear phase of $\text{EuMnO}_{3-\delta}$ and the ICAFM phase of $\text{EuMnO}_{3-\delta}$. These diffraction peaks come from the sample holder as shown in figure 5c.

The data at 60 K are refined with only the nuclear phase in the space group $Pnma$. The data at 10 to 50K are refined with both the nuclear phase in the space group $Pnma$ and the magnetic phase in magnetic space group $Pnma1'$. The corresponding Rietveld plots of the obtained neutron diffraction data are shown in figure 6. All the data can be refined well. The obtained lattice parameters are shown in figure 7. Lattice parameters a , b , and volume of unit cell of $^{153}\text{EuMnO}_3$ increases with the increase of temperature, while lattice parameters c decreases with the increase of temperature.

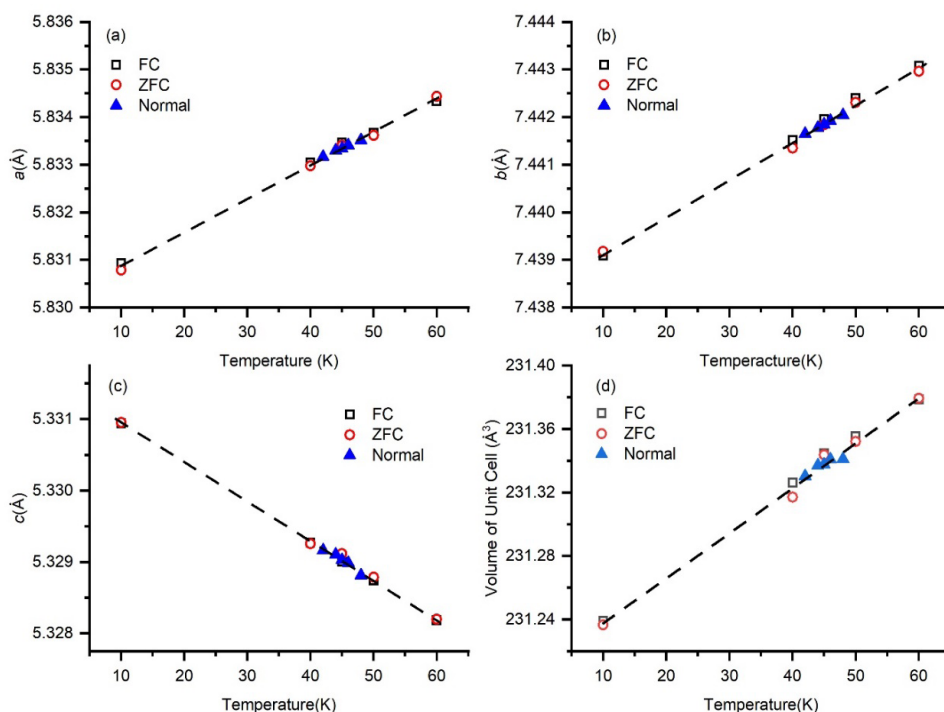


Figure 7 Lattice parameters a (a), b (b), c (c) and volume of unit cell (d) of $^{153}\text{EuMnO}_3$ at selected temperature under a magnetic field of 1 T after zero field cooling (ZFC), field cooling (the magnetic field is about -0.05 T) (FC), and under a zero magnetic field (Normal). The dash line in the figure is for the guide of eye.

4 Conclusion

$^{153}\text{EuMnO}_{3-\delta}$ and $\text{EuMnO}_{3-\delta}$ have similar structural and magnetic properties. Neutron diffraction data of $^{153}\text{EuMnO}_{3-\delta}$ between 10 K and 60 K has been analyzed carefully. The magnetic diffraction peak can be observed at the temperature of 50K or lower and disappear at the temperature of 60K. It is very surprising that only one set

of magnetic peaks for the cAAFM phase of $^{153}\text{EuMnO}_{3-\delta}$ are found in the obtained data. No other magnetic peaks are found even after applying ZFC, FC (the magnetic field is about -0.05 T) and under normal condition (a zero magnetic field). The present results indicate that the ICAFM phase of EuMnO_3 could not be confirmed by neutron diffraction data.

Conflict of Interest: No conflict of interest was reported

by the authors.

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References

- [1] Fiebig M, Lottermoser T, Frohlich D, et al. Observation of coupled magnetic and electric domains. *Nature* 2002; 419(6909): 818-820.
- [2] Kimura T, Goto T, Shintani H, et al. Magnetic control of ferroelectric polarization. *Nature* 2003; 426(6962): 55-58.
- [3] Lottermoser T, Lonkai T, Amann U, et al. Magnetic phase control by an electric field. *Nature* 2004; 430(6999): 541-544.
- [4] Ramirez AP. Colossal magnetoresistance. *J. Phys: Condens. Matter* 1997; 9: 8171-8199.
- [5] Rao CNR, Arulraj A, Santosh PN, et al. Charge-ordering in manganates. *Chemistry of Materials* 1998; 10(10): 2714-2722.
- [6] Kimura T, Ishihara S, Shintani H, et al. Distorted perovskite with e_g^1 configuration as a frustrated spin system. *Physical Review B* 2003; 68(6): 060403.
- [7] Alonso JA, Martínez-Lope MJ, Casais MT, et al. Evolution of the Jahn-Teller Distortion of MnO_6 Octahedra in $RMnO_3$ Perovskites (R = Pr, Nd, Dy, Tb, Ho, Er, Y): A Neutron Diffraction Study. *Inorg. Chem.* 2000; 39(5): 917-923.
- [8] Quezel S, Tcheou F, Rossat-mignod J, et al. Magnetic Structure of the Perovskite-like Compound $TbMnO_3$. *Physica* 1977; 86-88: 916-918.
- [9] Wu SY, Kuo CM, Wang HY, et al. Magnetic structure and spin reorientation of the Mn ions in $NdMnO_3$. *J. Appl. Phys.* 2000; 87: 5822-5824.
- [10] Jiráček Z, Krupička S, Šimša Z, et al. Neutron Diffraction Study of $Pr_{1-x}Ca_xMnO_3$ Perovskites. *Journal of Magnetism and Magnetic Materials* 1985; 53:153-166.
- [11] Munoz A, M. T. Casais, A. Alonso JA, et al. Complex Magnetism and Magnetic Structures of the Metastable $HoMnO_3$ Perovskite. *Inorg. Chem.* 2001; 40: 1020-1028.
- [12] Rietveld H. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* 1969; 2(2): 65-71.
- [13] Mukovskii YM, Hilscher G, Michor H, et al. Magnetic properties, resistivity, and heat capacity of $EuMnO_3$ and $Eu_{0.7}A_{0.3}MnO_3$ (A=Ca, Sr) compounds. *Journal of Applied Physics* 1998; 83(11): 7163-7165.
- [14] Troyanchuk IO, Samsonenko NV, Kasper NV, et al. Magnetic and Transport Properties of $EuMnO_{3+x}$ Substituted by Ca, Sr and Cr Ions. *Physica Status Solidi (a)* 1997; 160(1): 195-203.
- [15] Deng JM, Yang AM, Farid MA, et al. Synthesis, structure and magnetic properties of $(Eu_{1-x}Mn_x)MnO_{3-\delta}$. *RSC Advances* 2017; 7(4): 2019-2024.
- [16] Pollert E, Jirak Z. Study of $Pr_{1-x}Mn_{1+x}O_3$ Perovskites. *J. Solid State Chem.* 1980; 35(2): 262-266.
- [17] Lescano G, Figueiredo FM, Marques FMB, et al. Synthesis and electrical conductivity of $Y_{1-x}Mn_{1-y}O_{3-\delta}$. *J. Eur. Ceram. Soc.* 2001; 21(10-11): 2037-2040.
- [18] Gélard I, Jehanathan N, Roussel H, et al. Off-Stoichiometry Effects on the Crystalline and Defect Structure of Hexagonal Manganite $REMnO_3$ Films (RE = V, Er, Dy). *Chem. Mater.* 2011; 23(5): 1232-1238.
- [19] Ulyanov AN, Pismenova NE, Yang DS, et al. Local structure, magnetization and Griffiths phase of self-doped $La_{1-x}MnO_{3+\delta}$ manganites. *J. Alloys Compd.* 2013; 550: 124-128.
- [20] Wang R, Yang CX, Fan M, et al. Phase relationship of the $TbO_{1.81}-Mn_3O_4-Fe_2O_3$ system synthesized at 1200°C. *J. Alloys Compd.* 2013; 554: 385-394.
- [21] Zhang H, Flacau R, Sun JL, et al. Synthesis, Structure, and Magnetic Properties of $(Tb_{1-x}Mn_y)MnO_{3-\delta}$. *Inorg. Chem.* 2014; 53(9): 4535-4540.
- [22] Zhang H, Flacau R, Du X, et al. Multiferroicity Broken by Commensurate Magnetic Ordering in Terbium Orthomanganite. *ChemPhysChem*, 2016; 17(8): 1098-1103.
- [23] Fedorova OM, Balakirev VF, Golikov YV. Stability region of $Eu_{2-x}Mn_xO_{3+\delta}$ solid solutions in air. *Inorg. Mater.* 2007; 43(9), 994-999.
- [24] Dabrowski B, Kolesnik S, Baszczuk A, et al. Structural, transport, and magnetic properties of $RMnO_3$ perovskites (R=La, Pr, Nd, Sm, ^{153}Eu , Dy). *Journal of Solid State Chemistry* 2005; 178(3): 629-637.
- [25] Larson AC, von Dreele RB. Report LAUR, Los Alamos National Laboratory, Los Alamos, NM 1985; 86-748
- [26] Hoshi K, Goto Y, Mizuguchi Y, et al. Selenium Isotope Effect in the Layered Bismuth Chalcogenide Superconductor $LaO_{0.6}F_{0.4}BiSe_2$. *Physical Review B* 2018; 97(9): 094509.
- [27] Bud'ko SL, Lapertot G, Petrovic C, et al. Boron Isotope Effect in Superconducting MgB_2 . *Physical Review Letters*, 2001; 86(9): 1877-1880.
- [28] Batlogg B, Cava RJ, Jayaraman A, et al. Isotope Effect in the High-Tc Superconductors $Ba_2YCu_3O_7$ and $Ba_2EuCu_3O_7$. *Physical Review Letters* 1987; 58(22): 2333-2336.
- [29] Yang AM, Sheng YH, Farid MA, et al. Copper doped $EuMnO_3$: synthesis, structure and magnetic properties. *RSC Advances* 2016; 6(17): 13928-13933.
- [30] Kumar N, Sundaresan A. On the observation of negative magnetization under zero-field-cooled process. *Solid State Communications* 2010; 150(25): 1162-1164.
- [31] Katari V, Achary SN, Deshpande SK, et al. Effect of Annealing Environment on Low-Temperature Magnetic and Dielectric Properties of $EuCo_{0.5}Mn_{0.5}O_3$. *The Journal of Physical Chemistry C* 2014; 118(31): 17900-17913.
- [32] Kumar A, Yusuf SM, The phenomenon of negative magnetization and its implications. *Physics Reports* 2015; 556(0): 1-34.
- [33] Das R, Poddar P. Observation of exchange bias below incommensurate antiferromagnetic (ICAFM) to canted A-type antiferromagnetic (cAAFM) transition in nanocrystalline orthorhombic $EuMnO_3$. *RSC Advances* 2014; 4(21): 10614-10618.

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