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Structure evolution in undercooled CoCrNi medium entropy alloys by glass fluxing method

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Abstract:
Undercooling of ternary CoCrNi medium entropy alloy (MEA) was achieved by molten glass fluxing method. The influence of undercooling on microstructure and mechanical properties of was investigated. The microstructure changes during the undercooling process identified by transmission electron microscope and scanning electron microscope shows that the grain size and intergranular phase all change after the undercooling treatment. The yield strength of the ternary MEA increased significantly after undercooling treatment, which attribute to the refined grain size and the formation of the new phase. Undercooling method can be used as a potential method to modify the microstructure and improve the mechanical properties of MEAs.
Keywords: *Medium-entropy alloy; undercooling; microstructure; mechanical properties*

1 Introduction

Traditional alloys include one or two principal elements, but high entropy alloys (HEAs) have broken the traditional concept defined by Yeh et al. [1-4], which brings many challenges and opportunities for the traditional material industry. Different from traditional alloys, although HEAs are composed of multiple elements, these alloys tend to form simple structures rather than complex intermetallic compound such as face-centered-cubic (FCC), body-centered-cubic (BCC), hexagonal-close-packed (HCP) or a mixture of FCC and BCC [3]. Since the mixing entropy of the HEA is very high, when the component increases, the high entropy effect enhances the mutual solubility of alloying elements, which inhibits the formation of intermetallic compounds and complex phases, and promotes the appearance of simple solid solutions [5-7]. Compared with conventional alloys, HEAs have lots of outstanding properties such as high hardness, good high temperature strength, potential to be thermoelectric materials, great resistance to friction, oxidation, corrosion, evaluation wear and fatigue [3, 8-19]. Recently, equiatomic ternary and quaternary high-entropy alloys have also attracted the attention of researchers with the development of the research on high-entropy alloys [21-22] for being model alloys because of the less elements.

Rapid solidification is one of the most active fields in metal materials research and have attracted great interest in recent years [22-24]. Compared with conventional solidification, rapid solidification is a typical non-equilibrium process, and its main characteristics are as follows: with the increasing of the solidification rates, the distribution of solutes will deviate from equilibrium and the microstructure of the alloy will be greatly refined. Under the condition of rapid solidification, the precipitation of the equilibrium phase is inhibited and the metastable phase is precipitated. In the rapid solidification processes, the cooling rate can reach 10^5 K/s [25], such a high cooling rate can lead to considerable undercooling. Undercooling technique [26-27] enables a bulk alloy rapidly solidification. In 1951, Turnbull achieved an undercooling of 80 K in mercury [28]. There are several ways to achieve undercooling, including glass fluxing method [29], electromagnetic levitation [30] and drop tube technique [31-32]. Li et al. research on CoCrFeNi high entropy alloy has been solidified with a high undercooling up to 300 K adopting glass fluxing method. It is known that CoCrFeNi HEA possesses a single-phase FCC structure. Different from the as-cast sample with solely FCC structure, the sample solidified with a large undercooling of 300 K shows a mixture of FCC and BCC phase [33]. The undercooling method is an effective way to obtain metastable phase and refine grain structure in the solidification treatment [34-35]. The purpose of this paper is to invest the evolution of the microstructure and mechanical properties of CoCrNi ternary medium entropy alloy (MEA) after glass fluxing treatment.

2 Experimental

The alloy was prepared by the arc-melting method in a vacuum-titanium-gettered high purity argon (99.999

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volume percent, vol %) which using high purity (99.95 wt %) raw elements of cobalt, chromium, and nickel and cooled by the water in a copper crucible. To ensure the homogeneity of the sample, these materials were flipped and remelted at least five times. The glass fluxing method was used in the undercooling experiment. The high-entropy alloy was melted in the high-frequency furnace under an argon gas together with B_2O_3 glass. It is generally believed that the purification process of molten glass plays a role in two aspects, on the one hand, the molten glass covers the surface of the metal melt to isolate air and liquid metal, and inhibits the nucleation caused by oxides. On the other hand, the melt is separated from metal oxides and impurities by the viscous adsorption and chemical reaction of the molten glass to achieve physical or chemical purification. It has been proved that the molten B_2O_3 glass does not react with the sample. Before the experiment, the B_2O_3 was dehydrated in the muffle furnace at 873 K for 2 h. The alloy and the B_2O_3 glass were put in the quartz tube and adjust the relative position between the alloy and the induction coil so that the sample is in the middle of the coil. When heated, the B_2O_3 glass will melt and wrap the metal sample in it. In this way, it can effectively prevent the metal from oxidizing during the melting process and contact with the wall. In addition, deep undercooling can achieve the ideal degree of undercooling, so as to realize rapid solidification of metal at relatively slow cooling rate. In our study, natural cooling can be used for rapid solidification process without fast cooling rate [36-37].

Crystal structure was identified by X-ray diffraction (XRD), which is a D/MAX-2500/PC X-ray diffractometer instrument equipped with Cu-Kα radiation (λ= 1.54056 Å), and scanning was performed over the range of two theta (2θ) from 20° to 100° with a speed of 4 °/min. Microstructure was characterized by optical microscope (Axiovert 200MAT), scanning electron microscopy (SEM, Hitachi S-4800 microscope). The device is equipped with energy-dispersing X-rays Diffraction spectra (EDS). The components of precipitated phase in CoCrNi alloy were analyzed by EDS patterns. Before SEM observation, proceed first cutting, mosaic, mechanical grinding, polishing, cleaning, blow drying, corrosion, cleaning, blow drying and other steps to prepare the sample.

Transmission electron microscopy (TEM) were conducted on a Talos F200X instrument facility operating at 200 kV. The microstructure of the samples was also characterized by TEM. The TEM image of the sample and the corresponding selected area electron diffraction (SAED) of the image are obtained. TEM slices were mechanically grounded to 50 μm, and then twin-jet polished in a solution of 10 vol % perchloric acid and 90 vol % carbinol at 20 V.

A universal compression machine (INSTRON-5982) was employed at room temperature with an engineering strain of 5×10^{-4} s^{-1}. The cylindrical samples for compression have a size of Φ 3×6 mm. More than 3 times measurements were repeated for each alloy to obtain the accurate data. The Vickers hardness was determined on HVS-1000 under a load of 500 g for 10 s. The mean value from ten measurements was taken for each sample.

3 Results and discussion

3.1 Microstructure Characterization

Figure 1 presents the XRD patterns of CoCrNi MEA solidified at as-cast and undercooled conditions. The as-cast CoCrNi MEA alloy has a typical single-phase FCC structure, and after the undercooling treatment, new phases are precipitated, but the FCC phase is still the main phase of the sample. The diffraction peak of the precipitated new phase coincides with the CoCr hexagonal-close-packed phase (HCP) diffraction peak. The XRD results show that the undercooling treatment can lead to the change of the internal structure of the ternary high-entropy alloy [38].

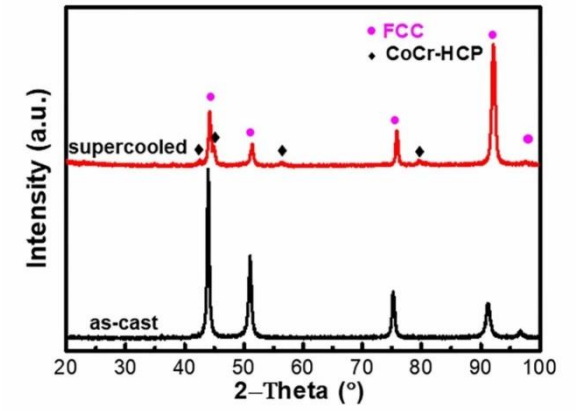

Figure 1 XRD patterns of CoCrNi MEA at as-cast and undercooled conditions

Identifying the microstructure changes of the CoCrNi MEA during the undercooling process by SEM and TEM is crucial for elucidating the machinal propertied promotion after the undercooling treatment. Figure 2(a) shows SEM images of the as-cast CoCrNi MEA. The solidified structure of CoCrNi MEA after undercooling treatment were shown in Figure 2(b). The as-cast CoCrNi alloy has a single-phase FCC structure with a large grain size of approximately 500 μm. After the undercooling treatment, the grain size of the sample significantly refined [35, 38-39]. A dendrite structure of the precipitated phase can be found in CoCrNi alloy. The precipitated phase is a Co-, Cr-rich phase which was identified by EDS patterns shown in Figure 2(c).

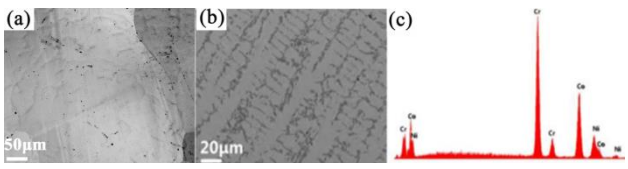

Figure 2 (a) SEM images of the as-cast CoCrNi MEA(b) SEM images of CoCrNi MEA after undercooling treatment, (c) EDS of precipitation phase in the CoCrNi MEA

In order to further reveal the effect of undercooling on the medium entropy alloys, TEM analyze were carried out. Figure 3 is the TEM images of CoCrNi MEA, Figure 3(a) is the microstructure of the matrix. We can see that there is nanophase precipitation on the FCC matrix. The darker areas are precipitated phases, and the size of the precipitated phase is about 20 nm. The spots with higher brightness shown in Figure 3(b) are SAED patterns of FCC matrix phase. Due to the thickness of the sample or the high energy of the incident electron, secondary diffraction is caused, resulting in the formation of secondary diffraction spots. Figure 3(c) is the microstructure of the interdendrite phase, and Figure 3(d) is the diffraction spots. Combined with the diffraction spots, we can see that the interdendrite phase is hexagonal phase. The stacking fault energy of CoCrNi is relatively low. Due to rapid solidification after deep undercooling, the HCP phase was precipitated by martensitic transformation at FCC. This is like the quenching of martensite in steel [40-41].

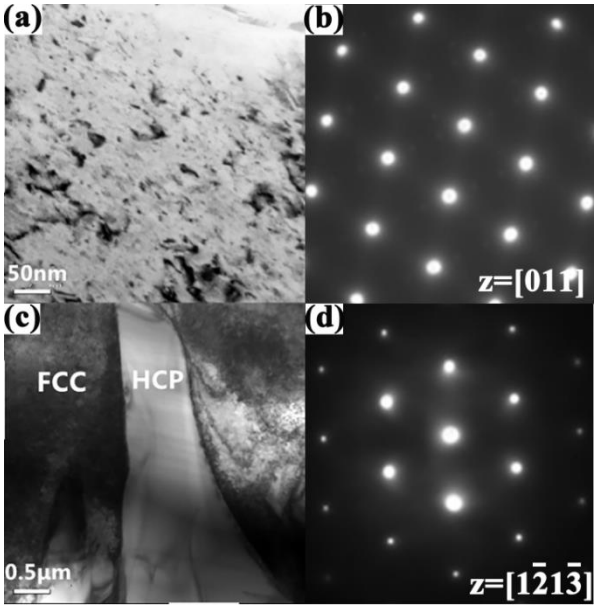

Figure 3 (a) TEM images of CoCrNi matrix, (b) SAED patterns of matrix, (c) TEM images of CoCrNi precipitation phase, (d) SAED patterns of precipitation phase

In the undercooling melt, there is a great driving force for crystal growth [31-35]. If nucleation occurs, the crystal will start to grow at a very fast rate, and then a large amount of crystal will be quickly released during the rapid growth of the crystal. The latent heat of crystallization leads to the re-glow phenomenon, which causes the temperature to rise rapidly until it is near the liquidus line, therefore the newly formed dendrites are under severe overheating, which leads to the occurrence of remelting [34-35]. The remelting of dendrites will lead to the apparent refinement of grains.

3.2 Mechanical Properties

The mechanical properties of the CoCrNi MEA were investigated and shown in Figure 4. From the strain-stress curves (Figure 4a) and hardness of CoCrNi MEA (Figure4 b), we can see that the plasticity and Vickers hardness of the ternary alloys after undercooling have been significantly improved. It shows that the room temperature compressibility of CoCrNi alloy has been greatly improved, and the yield strength has been increased from 180 MPa to 900 MPa. Hardness is a measure of the ability of the object to resist deformation, and it is a means of characterizing the mechanical properties of the material. The Vickers hardness of the CoCrNi alloy has been increased from 183 HV to 328 HV. The reason of the room temperature compression performance and Vickers hardness improved after undercooling treatment is that the grain size of the sample is significantly refined and the precipitation of the hard and brittle phase [35, 38]. The phase interface of FCC and HCP will hinder the dislocation movement, and dislocation plug will be formed at the phase boundary. Due to the toughness of FCC, the stress concentration caused by dislocation plugging can be relieved by the deformation of FCC in the deformation process to a certain extent, and the stress of micro-crack formation can be increased, thus improving the tensile strength and hardness [42-43]. The precipitation of the nano-precipitated phase in the matrix plays a key role in precipitation strengthening, resulting in a significant increase in the strength of the alloy and compressibility at room temperature [44-46].

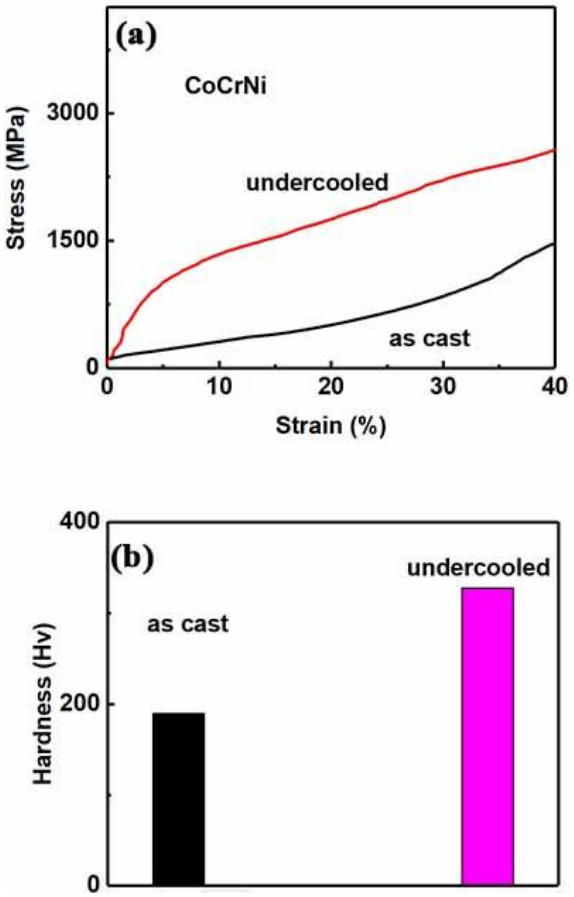

Figure 4 Mechanical properties curves of CoCrNi MEA. (a) The compression curves of CoCrNi MEAs at as-cast and undercooled conditions, (b) Vickers hardness

of CoCrNi MEAs at as-cast and undercooled conditions

4 Conclusions

In summary, the as-cast ternary CoCrNi medium entropy alloy is a single FCC structure, which has evolved into the dendrite structure with hexagonal precipitates in the matrix after undercooling treatment, and the grain size is obviously refined. The Vickers hardness of CoCrNi alloy increased from 183 to 328 HV, and the yield strength increased from 180 to 900 MPa. The grain refinement together with nanometer phase precipitation is the main reason for the increase of mechanical strength of those ternary medium entropy alloy.

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References

[1] J.W. Yeh. Recent progress in high-entropy alloys. European Journal of Control [J]. 2006(31): 633-648.

[2] J.W. Yeh, S.K. Chen, S.J. Lin, et al. Nanostructured high-Entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. Advanced Engineering Materials [J]. 2004(6): 299-303.

[3] Y. Zhang, T.T. Zuo, Z. Tang, et al.. Microstructures and properties of high-entropy alloys. Progress in Materials Science [J]. 2014(61): 1-93.

[4] B. Cantor, I.T.H. Chang, P. Knight. Microstructural development in equiatomic multicomponent alloys. Materials Science and EngineeringA [J]. 2004(213): 375-377.

[5] J.W. Yeh, S.J. Lin, T.S. Chin. Formation of simple crystal structures in Cu-Co-Ni-Cr-Al-Fe-Ti-V alloys with multiprincipal metallic elements. Metallurgical and Materials Transactions A [J]. 2004(35): 2533-2536.

[6] C.J. Tong, Y.L. Chen, J.W. Yeh, et al.. Microstructure characterization of Al_xCoCrCuFeNi high-entropy alloy system with multiprincipal elements. Metallurgical & Materials Transactions A [J]. 2005(36): 881-893.

[7] B.S. Murty, J.W.; Yeh, et al.. Chapter 1–A Brief History of Alloys and the Birth of High-Entropy Alloys.M.Boston：Butterworth-Heinemann Press [D], 2014.

[8] M.R. Chen, S.J. Lin, J.W. Yeh, et al.. Effect of vanadium addition on the microstructure, hardness, and wear resistance of Al0.5CoCrCuFeNi high-entropy alloy. Metallurgical and Materials Transactions A [J]. 2006(37): 1363-1369.

[9] P.K. Huang, J.W. Yeh, T.T. Shun, et al.. Multi-principal-element alloys with improved oxidation and wear resistance for thermal spray coating. Advanced Engineering Materials [J]. 2004(6): 74-78.

[10] A. Poulia, E. Georgatis, A.E. Lekatou, et al.. Microstructure and wear behavior of a refractory high entropy alloy. International Journal of Refractory Metals and Hard Materials [J]. 2016(57): 50-63.

[11] M.D. Zhang, L.J. Zhang, J.T. Fan, et al.. Novel Co-free CrFeNiNb0.1Tix high-entropy alloys with ultra high hardness and strength, Materials Science & Engineering A [J], 2019,764(9): 138212-138221.

[12] W.Q. Dong, Z. Zhou, M.D. Zhang, et al.. Applications of high-pressure technology for high-entropy alloys: A review, Metals, 2019(9): 867.

[13] X. M. Liu, J. T. Fan, X. S. Liu, et al.. Nonlinear vibration of Al-Al based high entropy alloy circular sandwich panel, AIP Advances, 2019, 9(3): 035351.

[14] J. T. Fan, L. J. Zhang, G. Li, et al.. A novel high-entropy alloy with dendrite-composite microstructure and remarkable compression performance, Scripta Materialia, 2019(159): 18–23.

[15] Y. Shi, B. Yang, P.K. Liaw, Corrosion-Resistant High-Entropy Alloys: A Review.J. Metals - Open Access Metallurgy Journal.2017(7): 43.

[16] X. S. Liu, R. Li, X.F. Fan, et al.. Excellent strength-ductility combination in Co36Cr15Fe18Ni18Al8Ti4Mo1 multi-principal element alloys by dual-morphology B2 precipitates strengthening，Journal of Materials Science & Technology [J]. 2023(134): 60–66.

[17] A.X. Li, P.F. Yu, Y.P. Gao, et al.. Ultra-high strength and excellent ductility high entropy alloy induced by nano-lamellar precipitates and ultrafine grain structure, Materials Science & Engineering A [J]. 2023(862): 14428.

[18] D.B. Miracle, O.N. Senkov. A critical review of high entropy alloys and related concepts. Acta Materialia [J].2017(122): 448-511.

[19] M.H. Jiang, Y.P. Gao, Y.Y. Wang, et al.. Study on structure evolution of CoCrFeNi high entropy alloy in containerless processing using neutron differaction, Nuclear Analysis [J]. 2022(3): 100034.

[20] Z. Wu, H. Bei, G.M. Pharr, et al.. Temperature dependence of the mechanical properties of equiatomic solid solution alloys with face-centered cubic crystal structures. Acta Materialia [J]. 2014(81): 428-441.

[21] C. Niu, A.J. Zaddach, A.A. Oni, et al.. Spin-driven ordering of Cr in the equiatomic high entropy alloy NiFeCrCo. Applied. Physics. Letter [J].2015(106): 161906.

[22] D.M. Herlach, Non-equilibrium solidification of undercooled metallic melts. Advances in Space Research [J].1991(12): 177.

[23] C. Suryanarayana, Phase formation under non-equilibrium processing conditions: rapid solidification processing and mechanical alloying. Journal of Materials Science [J]. 2018(53): 13364-13379.

[24] X. Bai, Y. Wang, C. Cao, Metastable phase separation and rapid solidification of undercooled $Co_{40}Fe_{40}Cu_{20}$ alloy. Chinese Physics B [J]. 2018(27): 305-309.

[25] A. Munitz, A. Venkert, P. Landau, et al.. Microstructure and phase selection in supercooled copper alloys exhibiting metastable liquid miscibility gaps. Journal of Materials Science [J]. 2012(47) 7955-7970.

[26] J.H. Perepezko. Solidification of highly supercooled liquid metals and alloys. Journal of Non-Crystalline Solids [J]. 1993(2): 463-472.

[27] J.H. Perepezko, G. Wilde. Amorphization and alloy metastability in undercooled systems. Journal of Non-Crystalline Solids [J]. 2000(274): 0-281.

[28] T. David. Kinetics of Solidification of Supercooled Liquid Mercury Droplets. Journal of Chemical Physics [J]. 1952(20): 411-424.

[29] J.S. Li, W.J. Jia, J. Wang, et al.. Enhanced mechanical properties of a CoCrFeNi high entropy alloy by supercooling method. Materials and Design [J].2016(95): 183–187.

[30] R. Li, X.S Liu, P.F. Yu, et al.. Unveiling the phase evolution and mechanical properties of Ni1.5Co1.5CrTix alloy composites with ultrafine/nano structure, Materials and Design [J]. 2022(223): 111165

[31] L.L. Lacy, M.B. Robinson, T.J. Rathz. Containerless undercooling and solidification in drop tubes. Journal of Crystal Growth [J]. 1981(51): 47-60.

[32] W.H. Hofmeister, M.B. Robinson, R.J. Bayuzick. Undercooling of pure metals in a containerless, microgravity environment. J. Applied Physics Letters [J]. 1986(49): 1342-1344.

[33] J.S. Li, W.J. Jia, J. Wang, et al.. Enhanced mechanical properties of a CoCrFeNi high entropy alloy by supercooling method. Materials & Design [J]. 2016(95): 183-187.

[34] A.M. AMullis, P.C. Bollada, P.K. Jimack, Phase-Field Modelling of Intermetallic Solidification. M. TMS 2018 147th Annual Meeting & Exhibition Supplemental Proceedings [D], 2018.

[35] Y.L. Liu, L. Luo, Z.S. Ming, et al.. Microstructure and mechanical properties of Al-5.5Fe-1.1V-0.6Si alloy solidified under near-rapid cooling and with Ce addition. Rare Metals [J]. 2018(12): 1070-1075.

[36] J. Wang, T. Guo, J. Li, et al.. Microstructure and mechanical properties of non-equilibrium solidified CoCrFeNi high entropy alloy. Materials Chemistry and Physics [J]. 2018(210): 192-196.

[37] X. Hao, Y.G. Li, Y. Hu, et al.. Effect of the Third Element Ni on the Solidification Microstructure of Undercooled Cu-40 wt.% Pb Monotectic Alloy Melt. Advances in Materials Science and Engineering [J]. 2019(2): 1-7.

[38] J. Wang, G. Tong, J. Li, et al.. Microstructure and mechanical properties of non-equilibrium solidified CoCrFeNi high entropy alloy. Materials Chemistry and Physics [D], 2017.

[39] R.D. Li, P.D. Niu, T.C. Yuan, et al.. Selective laser melting of an equiatomic CoCrFeMnNi high-entropy alloy: Processability, non-equilibrium microstructure and mechanical property. Journal of Alloys and Compounds: An Interdisciplinary Journal of Materials Science and Solid-state Chemistry and Physics [D], 2018.

[40] Q. Gao, X.S. Jiang, H.L. Sun, et al.. Effect mechanism of cryogenic treatment on ferroalloy and nonferrous alloy and their weldments: a review. Materials Today Communications [J]. 2022(1): 104830.

[41] X.W. Hong, C.H. Hsueh. Effects of yttrium addition on microstructures and mechanical properties of CoCrNi medium entropy alloy. Intermetallics [J]. 2022(140): 107405.

[42] H.W. Deng, Z.M. Xie, B.L. Zhao, et al.. Tailoring mechanical properties of a CoCrNi medium-entropy alloy by controlling nanotwin-HCP lamellae and annealing twins. Materials Science and Engineering [J]. 2019(744): 241-246.

[43] J.P. Liu, J.X. Chen, T.W. Liu, et al.. Superior strength-ductility CoCrNi medium-entropy alloy wire. Scripta Materialia [J].2020(181): 19-24.

[44] B. Gwalani, T. Torgerson, S. Dasari, et al.. Influence of fine-scale B2 precipitation on dynamic compression and wear properties in hypo-eutectic Al0.5CoCrFeNi high-entropy alloy. Journal of Alloys and Compounds: An Interdisciplinary Journal of Materials Science and Solid-state Chemistry and Physics [J]. 2021, 853(1): 5.

[45] Z.Y. Jia, S.Z. Zhang, J.T. Huo, et al.. Heterogeneous precipitation strengthened non-equiatomic NiCoFeAlTi medium entropy alloy with excellent mechanical properties. Materials Science and Engineering [J]. 2022(834):142617.

[46] L. Zhang, X. Du, L. Zhang, et al.. Achieving ultra-high strength in a precipitation-hardened CoCrNi-based medium-entropy alloy with partially recrystallized microstructure and heterogeneous grains [J]. Vacuum, 2021, 188(28):110169.