Viser Technology Pte. Ltd.
Research and Application of Materials Science
DOI: 10.33142/rams.v4i2.8465

Research Article **Open Access**

The effect of binder phase content on WC-$AlCoCrFeNiTi_{0.2}$ high entropy cemented carbides microstructure and mechanical properties

Yuxin WEN[1], Mingchen ZHANG[2], Yong ZHANG[1*]

1 State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China
2 Inspection and Certification Co., Ltd., MCC, Beijing 100088, China

***Corresponding Author:** drzhangy@ustb.edu.cn*

Abstract:
This work aims to explore WC-G201 high entropy cemented carbides properties fabricated by spark plasma sintering with $AlCoCrFeNiTi_{0.2}$ and WC as binder phase and hard phase respectively. $AlCoCrFeNiTi_{0.2}$ powder and WC powder were mixed at the mass ratio of 5: 95, 10: 90 and 15: 85 respectively, and then via SPS at 1300℃ for 5min. The results show that the binder phase has good wettability to WC, and with the increase of binder phase content, the hardness of the alloy decreases gradually, fracture toughness increases first and then decreases, the maximum value is 7.88 MPa $m^{1/2}$. It is estimated that the comprehensive mechanical property of cemented carbides is the best when the binder content is between 5wt% and 10wt%.

Keywords: *High entropy alloys; cemented carbides; binder phase*

1 Introduction

Cemented carbides is an alloy material synthesized by powder metallurgy technology with hard refractory carbides powder and Co, Ni or other adhesive powders as the binder phase [1]. Owing to its excellent hardness, wear resistance, corrosion resistance and oxidation resistance, it is widely used in tools, molds and other fields [2]. At present, WC is mostly used as the hard phase and Co as the adhesive phase, but this cemented carbide has some shortcomings such as poor oxidation resistance at high temperature, Co is unhealthy due to toxic, and it is very scarce in our country, there are some disadvantages such as the difficulty of extracting and the high price of Co [3]. Therefore, it is particularly important to find a new binder phase that can replace Co binder.

High entropy alloy is a kind of solid solution structure composed of multiple components. High entropy alloy has become a research hotspot, due to the crystal structure of high entropy alloy brings some excellent performances, such as high strength, high wear resistance and thermal stability [4-8], generally the softening resistance temperature of traditional tool steel is less than 550℃ [9]. Some scholars [10] found that the hardness of FeCoNiCuAl high-entropy alloy can still keep 532HV above after annealing at 1000℃ for 5h, showing excellent high temperature hardness. The good wettability of the binder phase to the hard phase is the premise that the alloy can be applied to the binder phase of the cemented carbides. It has been found that the high entropy alloy has good wettability and can inhibit the ceramic grain growth. If the equilibrium contact angle is between 0 and 30°, it is considered to have good wettability. Luo et al.[11] studied the wettability of $Al_xCoCrCuFeNi$ (x=0, 0.5, 1, 1.5) on WC, and measured the size of the equilibrium contact angle as 0.5°, 0.9°, 2.0° and 4.6° respectively, which research has enabled scholars to discover the potential of high entropy alloys as cemented carbide. Zhou Panlong et al. [12] used $Al_xCrFeCoNi$ high entropy alloy as the binder phase to produce high entropy cemented carbides with tungsten carbide as matrix. The mechanical property test found that cemented carbides had higher hardness than traditional WC-10Co cemented carbides, and also had good fracture toughness. In summary, it can be seen that it is feasible to select the high entropy alloy as the binder phase. High entropy alloys with the right elements as binder phases can improve the mechanical properties of cemented carbides. Studies have found that Al, Co, Fe, Ni and their intermetallic compounds have good wettability to WC. Zhou Yunjun et al. [13] studied the effect of Ti content on $AlCoCrFeNiTi_x$ (x=0, 0.5, 1, 1.5), after the Ti was added, the lattice distortion of the alloy was aggravated, it caused solution strengthening and nanophase diffusion strengthening, thereby improving the strength and hardness of the alloy. The yield strength

Received on November 18, 2022; Accepted on December 20, 2022

of the alloy system is higher than 1.5 GPa, the breaking strength is higher than 2.5 GPa, and the plastic deformation is as high as 23.22%. Later Zhang Yong research group found that when x = 0.2 in $AlCoCrFeNiTi_x$, the strength and plasticity of the alloy have been improved, it shows excellent mechanical properties. Therefore, $AlCoCrFeNiTi_{0.2}$ was selected as the binder phase.

The three most commonly used methods for preparing high entropy cemented carbide are vacuum sintering, vacuum hot pressing sintering and spark plasma sintering (SPS). Yang Mei et al. used SPS to prepare high entropy cemented carbides, which overcame the problem of mechanical properties deteriorated due to the excessively growth of WC grains [14]. Dai Pinqiang et al. sintered WC-FeCoCrNiAl high entropy cemented carbides by using these three methods respectively, and found that the hardness of cemented carbides by SPS was the highest, reaching 1900 HV [15]. SPS has the characteristics of short sintering time to inhibition of grain growth, so that it can reduce the formation of other harmful phases, resulting in excellent mechanical properties of the high entropy cemented carbides.

In this study, The $AlCoCrFeNiTi_{0.2}$ (noted as GS201) [16] was used as the binder phase and WC was used as the hard phase to fabricate high entropy cemented carbides by SPS. The influence of the binder phase content of GS201 on the microstructure and mechanical properties of high entropy cemented carbides was studied.

2 Materials and methods

GS201 high-entropy alloy powder prepared by WLL-100 vacuum atomization equipment was used in the experiment. Figure1 shows the morphology of GS201 powder. Tungsten carbide-powder was purchased from Hebei Jiuyue New Material Technology Co., Ltd.

High entropy alloy powder and tungsten carbides powder were mixed for 6h with 200rpm in the SFM-2 vertical planetary mixer at the ratio of 5: 95, 10: 90 and 15: 85 respectively. After the mixed progress, the powder was dried at 80℃ in a vacuum drying oven for 24h. Then 40g of dried powder was sintered in SPS-20T-10-III spark furnace. The sintering process is as follows: when the vacuum degree is maintained below 10^{-3}Pa, the temperature is raised to 650℃ at 100℃/min, the heat is kept for 5min, and then the pressure is increased to 30MPa. Then the temperature is raised to 1200℃ at 100℃/min, and the temperature is increased to 1300℃ at 50℃/min, and the sintering is performed for 5min. Figure2 is the prepared high entropy cemented carbides, from left to right it is WC-5wt%GS201, WC-10wt%GS201 and WC-15wt%GS201.

The melting point of high entropy alloys was tested using equipment of the German company Netzsch model DSC404F1. The contact angle measurement instrument of OCA25-HTV1800 of Data physics was used to measure the contact angle between GS201 and WC at high temperature. The phase analysis was carried out by Rigaku Smart Lab diffractometer. The surface and cross section morphologies of high entropy cemented carbides samples were observed by using ZEISS SUPRA55 field emission scanning electron microscope and Olympus 3D laser measuring microscope model LEXT OLS4100. 430SVD Walport (Shanghai) digital hardness tester was used for hardness test. The fracture toughness of cemented carbides was calculated by indentation method according to Vickers indentation. According to GB/T2997-2000, the Archimedes principle is used to measure the actual density of the sample, and then the relative density of the high entropy cemented carbides is calculated.

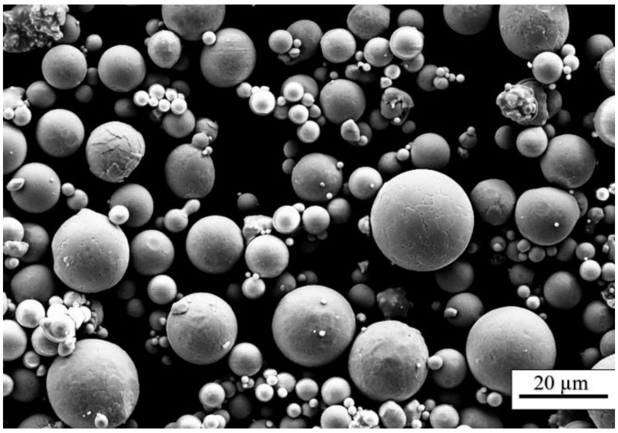


Figure 1 Morphology of GS201 powder

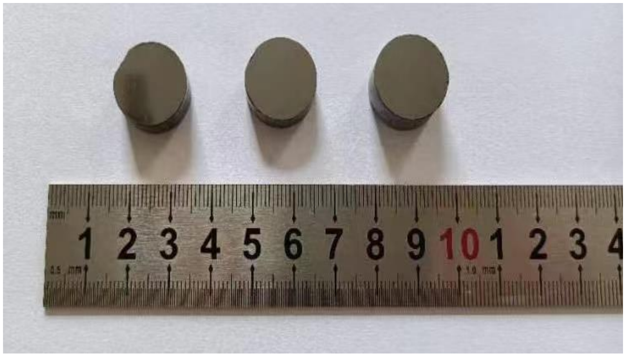


Figure 2 High entropy cemented carbides blocks

3 Results

3.1 Analysis of the wetting ability of GS201 to WC

Figure 3 shows the DTA curve of GS201. It can be seen from the figure that the melting point of GS201 is 1312.79°C, there are two endothermic peaks at 650°C and 1000°C, which should be due to phase transition. GS201 completely melted at 1368°C, therefore, when studying the wettability of GS201 to WC, the sintering temperature should be increased to more than 1358°C. It provides a reference for the temperature setting of our wetting experiment.

Figure 4 shows the contact angle between GS201 and WC at high temperature. Before the temperature rises to 1368°C, the high entropy alloy block does not melt, and the contact angle between the high entropy alloy and tungsten carbides remains 90 ° as shown by (a) in Figure 5 When the temperature rises to 1368℃, both sides of the block gradually bend outward with a curved profile. The contact angle increases and reaches a maximum of 130 ° at 1376℃. With the temperature rise continuously, the alloy block began to melt and spread, and the spreading speed accelerated at 1378℃. When the temperature rose to 1380℃ within 1 min, the contact angle rapidly decreased to 33 °. Subsequently, the melting rate of the high entropy alloy block slows down, and the change rate of the wetting Angle decreases correspondingly. After 7 min, the temperature rises to 1400℃, and the contact Angle decreases to 16.5 °, as shown in Figure5 (c). After the temperature rises to 1408℃ within 9 min, the contact angle decreases to 3.8 °. As the temperature further rises to 1420℃, the contact angle is basically unchanged, decreasing from 3.8 ° to 3.4 °. When the temperature is kept at 1420℃ for 20 min, the contact angle is almost unchanged, as shown in Figure4, which is between 3.3 °and 3.4 °, as shown in Figure5 (d). The results analysis shows that GS201 has excellent wettability to WC and meets the requirements of cemented carbides with binder phase.

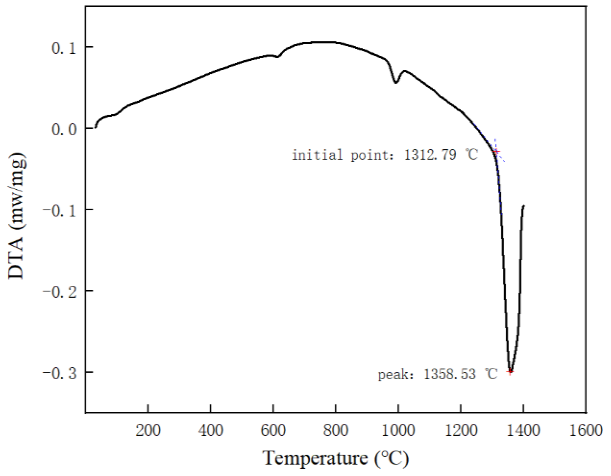


Figure 3 The DTA data graph of GS201

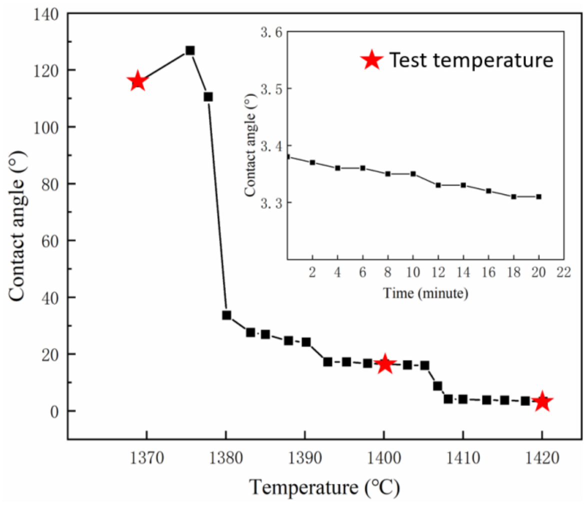


Figure 4 Changes of antennae of GS201 on WC with temperature and time

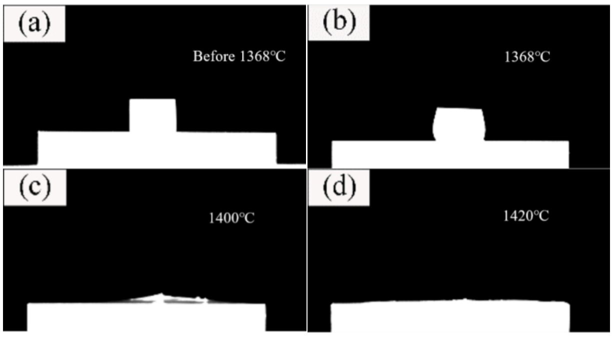


Figure 5 Profile of WC wetting process of GS201

3.2 Phase analysis and microstructure morphology analysis of WC-AlCoCrFeNiTi0.2 high entropy cemented carbides

Figure6 shows the XRD pattern of high entropy cemented carbides with different contents of GS201 at the sintering temperature of 1300℃. There are only diffraction peaks of WC and GS201 in WC-5wt%GS201. With the increase of GS201 content, diffraction peaks of unknown phases (denoted as γ phase) appear at about 41°. γ phase is the most obvious in WC-15wt%GS201. It could be that when the content of GS201 is higher than a certain value, WC will react with some elements of GS201 to form intermetallic compounds. Under this specific value, GS201 can exist stable after SPS sintering.

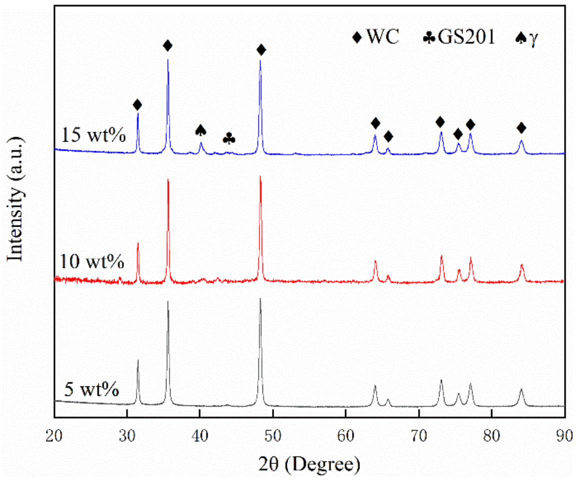


Figure 6 XRD pattern of WC-GS201 after sintering at 1300℃

Figure 7 shows the microstructure of WC-5wt%GS201, WC-10wt%GS201 and WC-15wt%GS201 high entropy cemented carbides sintered at 1300℃. In the figure, gray is tungsten carbides grains, with smooth grain profiles and wide grain size distribution range. The black material is GS201 binder phase. In WC-5wt%GS201, GS201 binder phase is not fully filled in the grain gap of WC, and there are still pores. With the increase of the binder phase content, the WC grain gap was gradually fully filled. When the binder phase content increased to 15%, a new dark gray substance was found in the WC grain gap, which should be the new phase generated by the reaction of WC and GS201, which was consistent with the results of the unknown phase at about 41 ° in the XRD analysis above.

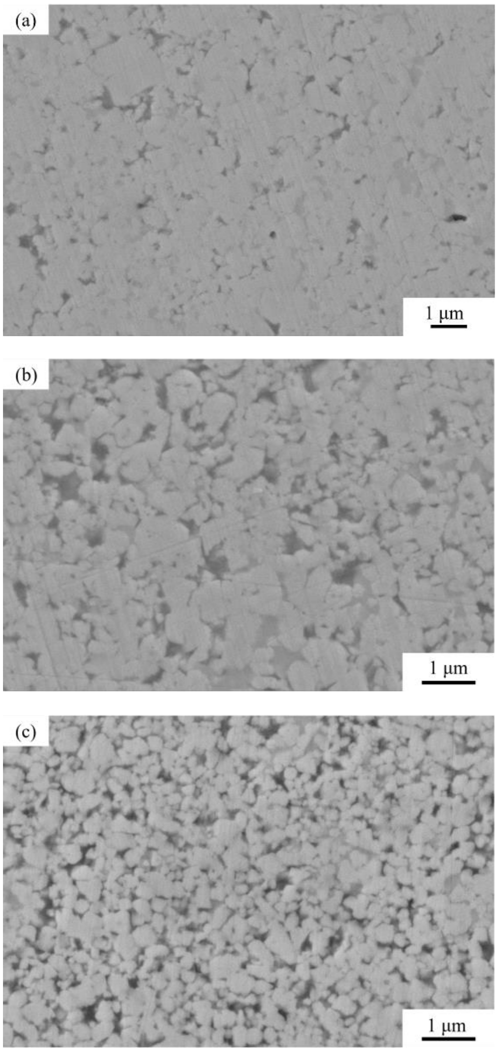


Figure 7 Microstructure of WC-GS201 high entropy cemented carbides

(a), (b) and (c) are cemented carbides with binder phase content of 5wt%, 10wt% and 15wt% sintered at 1300℃, respectively.

3.3 Grain size analysis of WC-GS201 high entropy cemented carbides

The growth of WC grains follows Ostwald theory [17], which progress can be divided into three stages: (1) dissolution of WC grains at high temperature, (2) precipitation of dissolved WC grains with the decrease of temperature, and (3) WC grains grow up. The process of WC grain growth combines with the continuous dissolution and precipitation of W and C elements. According to the BSE image of WC-GS201 high entropy cemented carbides, the average grain size of tungsten carbides is calculated with Image software, and the calculation results are shown in Figure8 WC-5wt% GS201 has the largest grain size of 0.61μm. The grain size of WC-15wt% GS201 is the smallest, which is 0.33μm, indicating that the binder phase of GS201 inhibits the growth of WC grains, but this inhibition is not linearly related to the binder phase content. With the increase of binder phase content, the inhibition effect on grain growth is gradually enhanced, and the grain size of WC decreases gradually.

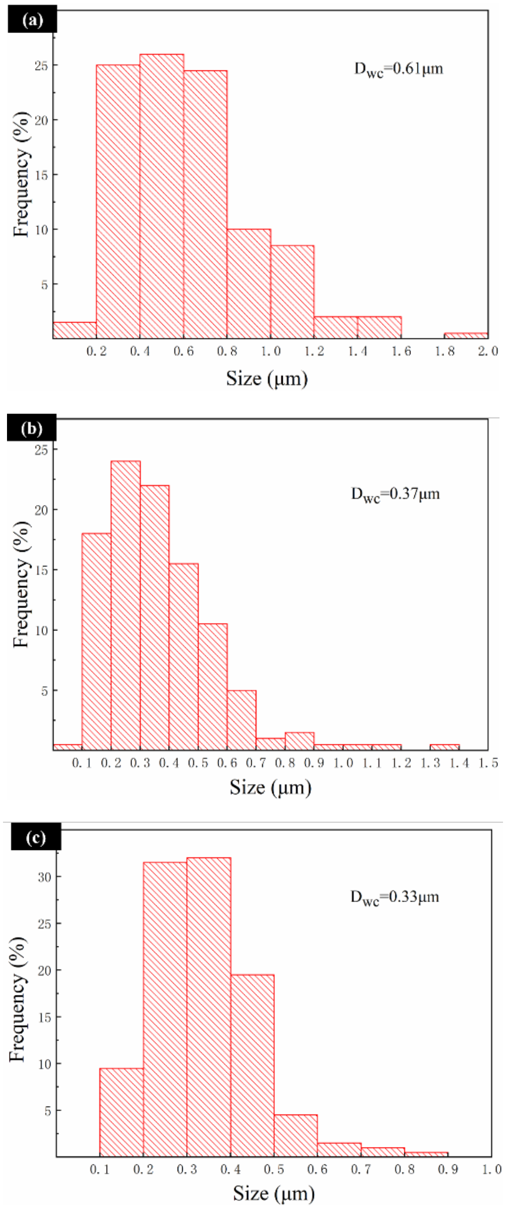


Figure 8 Grain size distribution of WC-GS201 high entropy cemented carbides

(a), (b) and (c) are cemented carbides with binder phase content of 5wt%, 10wt% and 15wt% sintered at 1300℃

3.4 Analysis of relative density and mechanical properties of WC-GS201 high entropy cemented carbides

Figure 9 shows the density and relative density of WC-GS201 at the sintering temperature of 1300℃. With the increase of GS201 binder phase content, the relative density of high entropy cemented carbides gradually increases. Through the microstructure analysis, 5wt% GS201 binder phase did not completely fill the gap between WC grains, resulting in direct contact or gaps between WC grains, so the relative density is relatively low. Under the effect of high temperature and pressure, the liquid binder with sufficient content flows quickly to the grain space and then solidifies, and the internal defects (such as voids) of the material are reduced and the relative density is increased. When the content of adhesive phase is 10wt% and 15wt %, the relative density is both greater than 99%, indicating that the gap of WC grains at this time has been fully filled, which is consistent with the microscopic morphology observed under scanning electron microscopy. GS201 and WC grains have good wettability, meeting the requirements for adhesive phase. The relative density value reflects the internal defects of the material. The higher the relative density of the alloy, resulting from the fewer defects such as pores inside the alloy, facilitate the mechanical properties of the alloy promotion.

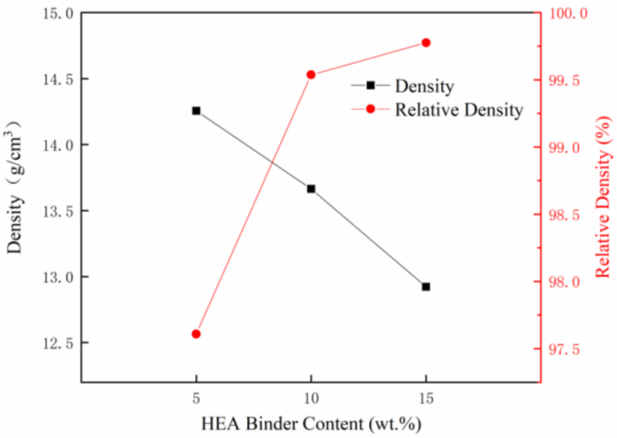


Figure 9 Relationship between the relative density of WC-GS201 after sintering at 1300℃ and the content of bond phase

Figure 10 shows the relationship between the hardness and fracture toughness of WC-GS201 high entropy cemented carbides sintered at 1300℃ and the content of bond phase. With the increase of binder content, Vickers hardness decreases gradually. When the binder content increases from 5wt% to 10wt%, the hardness of alloy decreases from 1568 HV_{30} to 1368 HV_{30}. According to the above grain size analysis, the grain size decreases and the hardness of the alloy increases with the increase of the cohesive phase content. The high hardness of hard phase is also the reason for the high hardness of high entropy cemented carbides. The results show that with the decrease of hard phase content, the overall hardness of the alloy decreases accordingly. In summary, it can be seen that the effect of the decrease of hard phase content on the decrease of alloy hardness is greater than the effect of fine crystal strengthening on the increase of hardness, so the overall hardness of the alloy shows a decreasing trend. The fracture toughness of the alloy increases first and then decreases, and the maximum value is 7.88MPa $m^{1/2}$.

Figure 11 shows the SEM image of the indentation crack of WC-GS201. The red arrow marks the crack deflection, the yellow circle marks the crack bridging, the blue arrow marks the grain pulling out, and the white arrow marks the transcrystal fracture, all of which will enhance the fracture toughness of the alloy [18][19]. The reason is that the fracture toughness is related to the resistance encountered during crack propagation. The greater the resistance it is, the higher the fracture toughness will be. When the binder phase content is 5wt%, the crack is relatively gentle; when the binder phase content is increased to 10wt%, the relative density of the alloy increases, and the transgranular fracture and crack deflection increase, which consumes a lot of energy during fracture and improves the fracture toughness of the alloy [20]. When the binder phase content increased to 15wt%, the relative density slightly increased, but the fracture toughness decreased. Combined with the XRD analysis above, the unknown corresponding brittle phase was generated, thus reducing the fracture toughness of the alloy. The alloy has the best comprehensive mechanical property when the binder phase content is between 5wt% and 10wt%. Combined with XRD and relative density analysis, with the increase of binder phase content, when the relative density reaches 99%, it can be regarded as the binder phase has been fully filled in the WC grain gap, and no other intermetallic compounds are formed at this time, namely no new phase appears in XRD. At this time the comprehensive mechanical properties of the alloy should be the best.

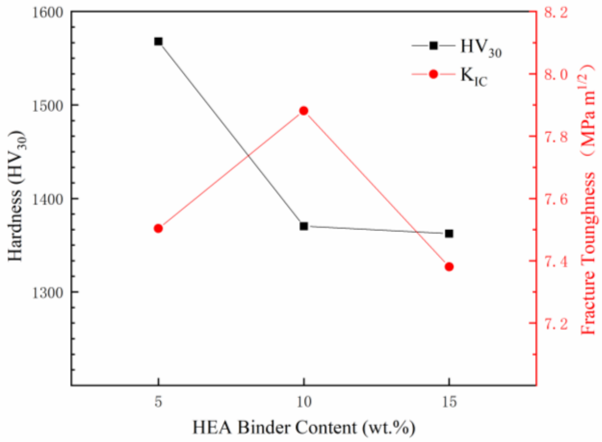
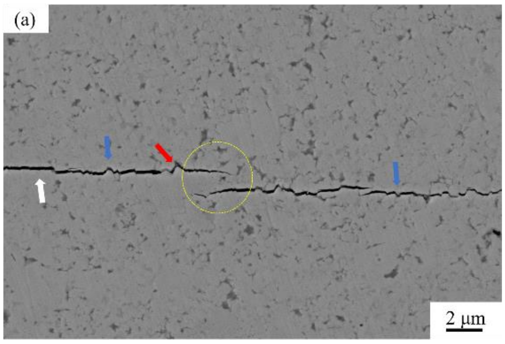


Figure 10 Relationship between hardness and fracture toughness of WC-GS201 sintered at 1300℃ and bond phase content



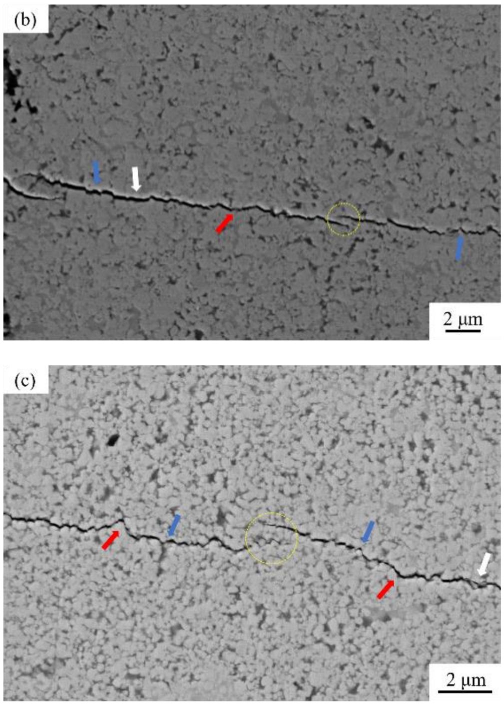


Figure 11 SEM image of the indentation crack of WC-GS201

4 Conclusions

(1) GS201 has excellent wettability to WC. The high temperature contact angle between GS201 and WC is between 3.3° and 3.4° at 1420°C respectively, meeting the requirements of cemented carbides for adhesive phase.

(2) With the increase of the binder content, the Vickers hardness of the alloy decreases gradually, and the influence of the hardness of the cemented carbides is greater than that of the fine hardening. The fracture toughness increases first and then decreases, and the maximum value is 7.88MPa $m^{1/2}$. The optimal comprehensive mechanical property should be a value of binder phase content between 5wt% and 10wt%.

References

[1] Yang J G, Dai Y. Development trend of cemented carbides and preparation technology of special powder [J]. Rare metals and hard metals, 2011(1): 48-51.

[2] Chu K Y. Development status and prospect of Chinese cemented carbides industry [J]. Rare metals and hard metals, 2011, 39(1): 52-56.

[3] Kim H C, Shon I J, Garay J E, et al.. Consolidation and properties of binderless sub-micron tungsten carbide by field-activated sintering [J]. International Journal of Refractory Metals and Hard Materials, 2004, 22(6): 257-264.

[4] Ji W, Wang W, Wang H, et al.. Alloying Behavior and Novel Properties of CoCrFeNiMn High-Entropy Alloy Fabricated by Mechanical Alloying and Spark Plasma Sintering [J]. Intermetallics, 2015(56): 24-27.

[5] Tong C J, Chen M R, Yeh J W, et al. Mechanical Performance of The Al$_x$CoCrCuFeNi High-Entropy Alloy System with Multiprincipal Elements [J]. Metallurgical and Materials Transactions A, 2005, 36(5): 1263-1271.

[6] Varalakshmi S, Rao G A, Kamaraj M, et al.. Hot Consolidation and Mechanical Properties of Nanocrystalline Equiatomic AlFeTiCrZnCu High Entropy Alloy after Mechanical Alloying [J]. Journal of materials science, 2010, 45(19): 5158-5163.

[7] Song X F, Zhang Y. Research progress of high entropy alloys [J]. Powder Metallurgy Technology, 2022, 40(5): 451-457.

[8] Zhang Y. Discovery and development of high entropy alloys [J]. Journal of Sichuan Normal University, 2022, 45(6): 711-722.

[9] Kwak B W, Song J H, Kim B S, et al.. International Journal of Refractory Metals and Hard Materials, 2016(54): 244-250.

[10] Zhuang Y X, Xue H D, Chen Z Y, et al.. Effect of Annealing Treatment on Microstructures And Mechanical Properties of FeCoNiCuAl High Entropy Alloys[J]. Materials Science and Engineering: A, 2013(572): 30-35.

[11] Luo W Y, Liu Y Z, Tu C. Wetting behaviors and interfacial characteristics of molten Al$_x$CoCrCuFeNi high-entropy alloys on a WC substrate [J]. Journal of Materials Science & Technology, 2021(78): 192-201.

[12] Zhou P L, Xiao D H, Zhou P F, et al.. Microstructure and properties of ultrafine crystal WC-Al$_x$CrFeCoNi composites prepared by hot pressing[J]. Powder metallurgy materials Science and Engineering, 201, 11(30): 95-103.

[13] Zhou Y J, Zhang Y, Wang Y L, et al.. Mechanical properties and strengthening mechanism of Ti$_x$CrFeCoNiAl multicomponent solid solution alloy system [J]. Chinese Journal of Materials Research, 2008 (5):461-466.

[14] Yang M, Luo X, Long J P. Chengdu University of Technology. The invention relates to a preparation method of high entropy alloy binder phase cemented carbides. 109161773A[P]. 2019-01-08.

[15] Dai P Q, Liu X Q, Guo K K, et al.. The invention relates to a preparation method of WC - based cemented carbides with high entropy alloy powder as binder: CN201811445236.0[P]. 2019-02-22.

[16] Wu Y Q, Liaw P K, Zhang Y. Preparation of bulk TiZrNbMoV and NbTiAlTaV high-entropy alloys by powder sintering [J]. Metals, 2021, 11(11): 1748.

[17] García J, Collado Ciprés V, Blomqvist A, et al.. Cemented carbide microstructures: a review [J]. International Journal of Refractory Metals and Hard Materials, 2019(80): 40-68.

[18] Zhou P F, Xiao D H, Yuan T C. Comparison between ultrafine-grained WC-Co and WC-HEA-cemented carbides [J]. Powder Metallurgy, 2017, 60(1): 1-6.

[19] Fu Z, Koc R. TiNiFeCrCoAl high-entropy alloys as novel metallic binders for TiB2-TiC based composites [J]. Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 2018(735): 302-309.

[20] Ji W, Zhang J Y, Wang W M, et al.. Fabrication and properties of TiB$_2$-based cerments by spark plasma sintering with CoCrFeNiTiAl high-entropy alloy as sintering aid [J]. Journal of the European Ceramic Society, 2015, 35(3): 879-86.