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Preparation of TiC based Cermet with Different Ratio of Cu and Al

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Abstract. TiC based cermet belongs to superhard tool material, which has high melting point, high hardness and excellent chemical stability. It is the preferred material for cutting tools and wear-resistant components. At the same time, it has excellent conductivity and is also the preferred material for electrode. In this experiment, TiC based cermet was prepared by atmosphere protection sintering method with TiC, Cu and Al as raw materials. The phase analysis was carried out by X-ray diffractometer(XRD), the microstructure was observed by scanning electron microscope (SEM), the element analysis was carried out by energy spectrometer, and the bending strength was tested by universal material tester. The different sintering temperature and the ratio of additive Cu and Al were systematically studied under the premise of controlling the total mass of TiC based cermet, which effect on microstructure and mechanical properties of TiC based cermet. The experimental results show that the bending strength of cermet increases obviously with the increase of copper content in a certain range, and the best mechanical properties of cermet are obtained when the ratio of Cu and Al is 6:4. With the increase of sintering temperature, the mechanical properties of TiC based cermet are significantly strengthened. When the sintering temperature reaches 1100 °C, the grain size is fine and uniform, and the comprehensive properties of the material are the best.

1. Introduction

Cermet is an heterogeneous composite composed of metal or alloy and ceramic phase, in which ceramic phase accounts for about 15% and 85%. It not only maintains the high strength, high hardness, wear resistance, high temperature resistance, chemical stability and oxidation resistance of ceramics, but also has good metal toughness and plasticity. It is a very important and excellent tool material and structural material in modern industrial production [1]. It is widely used, involving all sectors of national economic production and various fields of modern social application, and has promoted the development of industry and the improvement of productivity.

However, the fatal weakness of cermet is brittleness, which seriously restricts the application of cermet. In the 1950s, based on the shortcomings of TiC-Ni based cermet, such as high brittleness and low strength, the addition of Mo to TiC-based cermet can form an annular phase metal around it to enhance the wettability of TiC and N, and greatly improve the strength of the alloy [2]. This important technological breakthrough makes TiC based cermet become the most valuable and promising cermet material at present.

The microstructure of TiC based cermet is composed of carbide hard phase and metal bonded phase. A coating layer is formed at the edge of hard phase. It is formed by the solid solution of Mo, W, Ta, Nb and other elements in TiC. The ring structure is exactly the same as that of TiC lattice, and the lattice parameters are very close. Therefore, dislocations can pass through the ring and hard phase continuously. In fact, the ring is a structure covering the surface of TiC particles, which is formed by

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the diffusion of Mo, Ni and other atoms to the surface of TiC. The coating greatly improves the wettability between hard ceramic phase and metal bonded phase and holds back the aggregation and growth of hard phase. However, since the coating itself is still in the brittleness stage, its thickness must be appropriate. It is reported that the average thickness of annular phase can not exceed 0.5 μm, otherwise the bending strength of the material will decrease significantly [3]. TiC based cermet is the most widely developed material in titanium, zirconium and chromium transition metal carbides. TiC can be made into all kinds of multiphase ceramic materials with TiN, WC, Al2O3 and other raw materials. TiC based cermet has been used in the cutting of high speed wire rod and carbon steel because it does not have crescent depression wear and good oxidation resistance with steel. Multiphase ceramic tools containing titanium carbide have been widely used [4].

2. Experimental Process

In the experiment, a series of TiC based cermet samples were prepared by traditional powder metallurgy method and different ratio of Cu and Al according to the optimum technological conditions. The total mass was 25g, the addition of TiC accounted for 60%, and the total addition of additive Cu and Al accounted for 40% of the total mass. The ratio of Cu and Al components was set to 5 groups: 0:10, 2:8, 4:6, 6:4, 8:2, respectively. So as to ensure that the microstructure and properties of each group were comparable, the composition ratio was shown in Table 1.

The mixture was put into nylon grinding tank and cemented carbide ball was used as grinding ball. Under the condition of rotating speed 175r/min, the continuous ball milling was carried out in the star ball mill for 24 hours. Then the ground powder and the grinding ball were poured into the powder plate, dried at 80 °C for 12 hours, the dried powder was sieved, the cemented carbide ball was taken out, and then the mixed powder was ground until there was no greater agglomeration. Polyvinyl alcohol solution was used as forming agent, and two drops of polyvinyl alcohol solution were added to the mortar for granulation every 25g dried powder for about 20 minutes, until the powder was fully mixed with the molding agent. The granulated mixture was molded by four-column hydraulic press in steel die. The samples with different ratios of Cu and Al were sintered at 900 °C, 1000 °C and 1100 °C, respectively.

Table 1. Composition design (wt.%)

Sample number	TiC	Cu	Al	Cu:Al
1	60	0	40	0:10
2	60	8	32	2:8
3	60	16	24	4:6
4	60	24	16	6:4
5	60	32	8	8:2

Then the properties of the samples were tested according to the requirements of the experiment, including porosity and bending strength. Then the phase analysis was carried out by X-ray diffractometer(XRD), the microstructure was observed by scanning electron microscope (SEM), the element analysis was carried out by energy spectrometer.

3. Analysis and Discussion

3.1. Porosity Analysis

In the process of sintering, densification and grain growth are two simultaneous processes. With the increase of sintering time and temperature, the density of TiC based cermet increases and the porosity decreases, which will improve the hardness of cermet. The porosity of cermet at different temperatures is shown in Fig. 1. Through the analysis and processing of the experimental data, sample 2 is much lower than sample 1 with the increase of Cu content at 900 °C. Through the SEM analysis of the sample, it is found that the microstructure of TiC based cermet shows a typical core-shell structure, and the addition of Cu greatly promotes the wettability of Al and makes the TiC powder reunite closely. At the same time, the electron valence compounds formed by Cu and Al are also fully filled with gaps, so the porosity of the samples decreases to a great extent. At 1000 °C and 1100 °C, with the increase of Cu content, the porosity increases to a certain extent, the Cu content is too much, the sintering temperature is not high, so the porosity of the sample continues to increase.

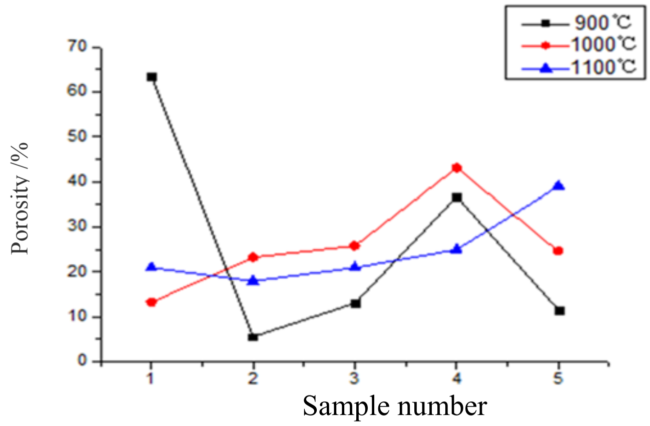


Figure 1. Porosity change at different temperatures

3.2. Analysis of Bending Strength

Bending strength refers to the ability of materials to resist bending and non-fracture, which is mainly used to reflect the strength of brittle materials such as ceramics. In order to improve the bending strength of cermet materials, it is necessary to have a good core / shell and interface bonding between bonded phase and shell. It can be found from the experimental results that the bending strength of TiC based cermet samples increases with the increase of Cu content, and the increasing trend is very obvious, the variation of bending strength is shown in figure 2.. This is because on the one hand, Cu, as a metal phase itself, has a certain strength, and the increase of Cu content is beneficial to improve the bending strength of cermet materials.On the other hand, with the increase of Cu content, the microstructure of cermet began to refine, according to the classical Hall-Petch formula, the bending strength of cermet was enhanced by fine grain strengthening, and the metal and ceramic phase dissolved in bonding phase increased with the increase of Al-Ti alloy content in TiC expansion ceramics, which resulted in solid solution strengthening.

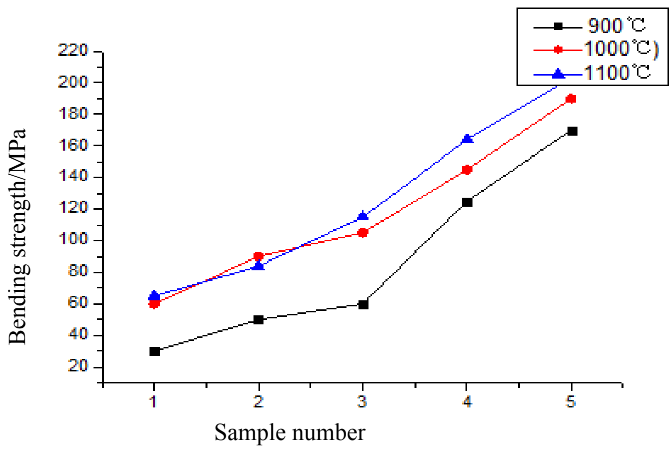


Figure 2. Variation curve of bending strength at different temperatures

3.3. Observation of Morphology of SEM and EDS Analysis

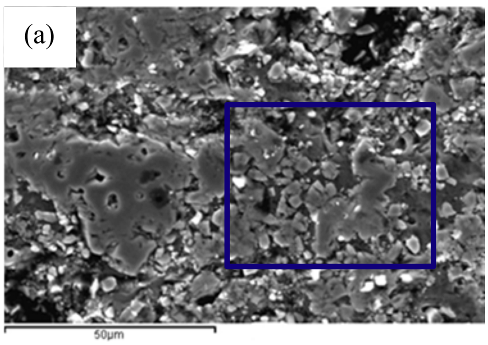
Before the addition of Cu, the cermet phase is mostly spherical. With the addition of Cu, some ceramic phase particles changed from circular to polygons (most of them were quadrilateral), and the interface between ceramic phase and bonded phase is a flat straight line. The orientation relationship of the ceramic phase / bonded phase interface is straight and straight, which indicates that after liquid phase sintering, the liquid phase of cermet is solidified and grown by heterogeneous nucleation with ceramic phase as substrate interface. At this time, the curvature size and direction (concave and convex) of the substrate interface (ceramic phase) will affect the difficulty of crystal nucleus growth, the concave crystal nucleus growth is the easiest, the plane is in the middle, and the convex crystal nucleus growth is the most difficult. There is no concave surface in ceramic phase, so the relatively straight surface part is easy to become the non-uniform nucleation part of liquid phase. Because the relationship between bonded phase nucleation and ceramic phase is beneficial to reduce the interface energy needed for nucleation, there is a certain relationship between the two. However, due to the difficulty of nucleation, there is no orientation relationship in the protruding part of ceramic phase.

The results of EDS identification of TiC based cermet elements containing 16%Cu at 900 °C, 1000 °C and 1100 °C are shown in table 2. It indicates that the burning rate of Al increases gradually, and the atomic percentage of Cu does not change obviously with the increase of sintering temperature. The melting point of Al element is about 660C, and the boiling point is about 2 500 °C, which indicates that with the increase of sintering temperature, the Al element changes from solid phase to liquid phase, the physicochemical phenomenon of dissolution and precipitation occurs in tic-based cermet. Finally, the Al vapor escapes with the protective argon gas, and the weight percentage of Al decreases.

The distribution of elements at 1000 °C for TiC-based cermet containing 16% Cu is showed in fig. 3. It can be seen from the diagram that there is no obvious boundary between the distribution of Cu and Al elements, and the distribution is very similar. The reason may be that Cu and Al mix very evenly on the one hand, and on the other hand, Cu and Al form electronic valence compounds. Copper as wetting agent wet TiC and Al,. Al is used as bonding phase to promote the agglomeration of TiC particles. At the same time, Cu and Al miscibility fills the gap between TiC particles and reduces porosity.

Table 2. The weight percent of TiC-based cermet elements containing 16% Cu at different sintering temperatures. (wt.%)

Temperature/°C	Element type					
	C	O	Al	Ti	V	Cu
900	57.33	6.67	10.02	18.21	1.22	6.77
1000	58.41	7.04	7.85	18.69	1.10	6.52
1100	59.60	7.37	6.09	19.71	1.04	6.23



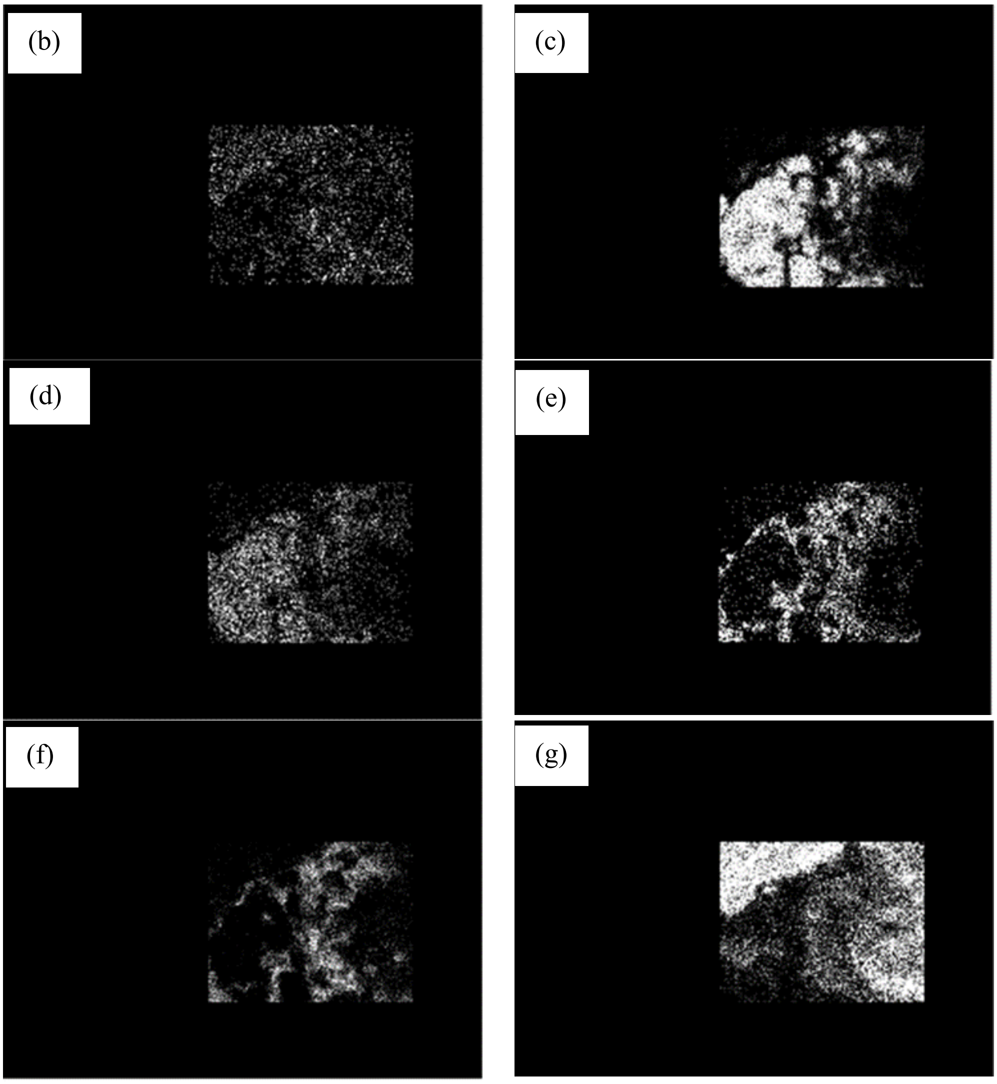


Figure 3. Distribution of Elements of the TiC-based cermet with 16% Cu at 1000 °C

(a)Selection analysis of EDS; (b) Distribution of O elements; (c) Distribution of Ti elements; (d) Distribution of V elements; (e) Distribution of Cu elements; (f) Distribution of Al elements; (g) Distribution of C elements

3.4. Phase Analysis of XRD

The XRD diffraction pattern of five different Cu and Al ratios at 1100 °C is shown in fig. 4. Through the comparative analysis of five groups of diffraction patterns, it can be seen that the diffraction peak of hard phase TiC remains unchanged, and the peak value matches well with the standard sample in PDF card with the increase of the amount of Cu metal powder. In addition to the line emission peak of TiC, there is a diffraction peak of solid solution with Cu3Al4. With the increase of copper content , the diffraction peak intensity of bonded phase Cu3Al4 is increasing. Through PDF card inspection, it is found that the diffraction peak is basically the same as that of Al. It can be considered that the continuous enhancement of the diffraction peak is the result of the superposition of the two diffraction peaks. In addition, the existence of C was found in XRD diffraction pattern. It is considered that the heating temperature of TiC based cermet sample is too high, or the residence time at high temperature is too long, decarbonization reaction occurs, which makes the C in TiC free on the surface of the sample.

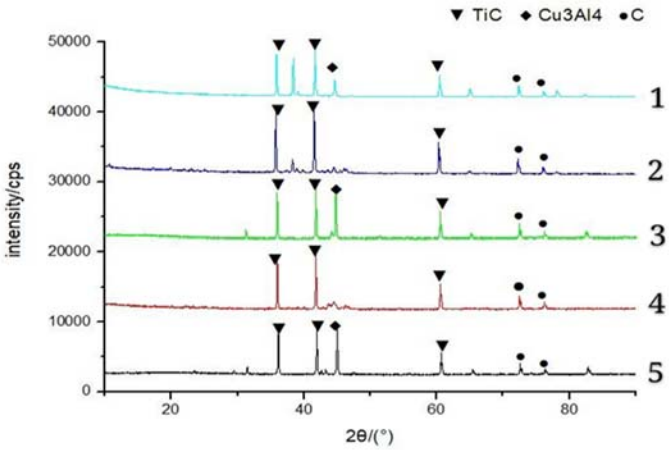


Figure 4. XRD diffraction Analysis of cermet samples

(1)32%Cu; (2)24%Cu; (3)16%Cu; (4)8%Cu; (5)0%Cu

4. Conclusions

In this study, TiC based cermet materials with different Cu and Al ratios were successfully prepared by traditional powder metallurgy method. The materials were characterized and analyzed by XRD, SEM, EDS. The main results are as follows:

(1) In a certain range, with the increase of Cu content, the microstructure of TiC-based cermet is gradually refined, and the microstructure of TiC-based cermet is the classical black-core gray shell structure.

(2) The microstructure elements of TiC based cermet containing 16%Cu were identified by EDS at 900 °C, 1000 °C and 1100 °C. The results showed that with the increase of sintering temperature, the burning rate of Al increased gradually, and the atomic percentage of Cu did not change obviously. The physicochemical phenomenon of dissolution and precipitation occurred in TiC based cermet, and finally Al exudated again to its surface, so the weight percentage of Al showed a downward trend.

(3) Cu and Al, were added to the sample, but in addition to the incident peak of TiC, the diffraction peak of the solid solution with the main composition of Cu3Al4 appeared, and with the increase of the amount of Cu alloy, the intensity of the diffraction peak of the bonded phase Cu3Al4 increased more and more.

5. Reference

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