ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Influence of ZrC addition on the microstructure, mechanical properties and oxidation resistance of Ti(C,N)-based cermets

Xiyue Kang[a], Nan Lin[b], Yuehui He[a,*], Meimei Zhang[a]

[a] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, PR China
[b] College of Materials Science and Engineering, Hunan University, Changsha 410082, PR China

ARTICLE INFO

Keywords:
Ti(C,N)-based cermets
ZrC
Mechanical properties
Wear resistance
Oxidation resistance

ABSTRACT

In this study, Ti(C,N)-WC-NbC-ZrC-Co-Ni cermets were prepared by sintering-hip at 1450 °C. The effect of ZrC addition on the microstructure, mechanical properties, oxidation resistance and wear resistance of Ti(C,N)-WC-NbC-Co-Ni cermets were explored in detail. The results show that ZrC addition plays the role of inhibitor in the dissolution–reprecipitation process, which can increase the wear-resistant carbide phases and inhibit the precipitation of brittle (Ti,W,Nb)(C,N) rim phase. Therefore, the core-rim structures are refined and the Nb content in binder increases, which enhance mechanical properties and oxidation resistance of cermets. With the increasing ZrC content, the oxidation resistance of cermets can be improved constantly, while the transverse rupture strength, fracture toughness and wear resistance of these cermets increase first and then decrease. The cermet with 1 wt% ZrC exhibits the transverse rupture strength of 2549 MPa and highest fracture toughness of 13.0 MPa $m^{1/2}$. The oxidation weight gain of cermets containing 5 wt% ZrC after holding 100 h at 750 °C in air is 2.8×10^{-6} g mm^{-2}, which is only 22% of that in the cermets without ZrC addition.

1. Introduction

With the development of the modern industrial technology, the traditional hard materials can't meet the ever-growing demands. As a representative of traditional hard materials, WC-Co cemented carbides are the most widely-used materials as cutting tools or wear resistant parts owing to their outstanding strength and toughness [1–3]. However, it is due to the insufficient hardness and oxide-resistance at an elevated temperature that limit their applications in high speed machining [4,5]. Nowadays, Ti(C,N)-based cermets are extensively utilized in plenty fields related to their excellent hardness, high strength, low density, great wear-resistance, low friction coefficient, good-quality surface processing and outstanding high-temperature oxidation resistance. The Ti(C,N)-based cermets attract increasingly closer attentions and become competitive enough in high-speed cutting process, milling operations and heat-proof parts and so on [6].

The Ti(C,N)-based cermets are mainly made up of both ceramic phase and metal phase, in which the higher hardness and excellent wear resistance of the cermets are given by more hard ceramic phase, and the plasticity and tenacity are provided by the metal phase as binder. Furthermore, the microstructure of the cermets is usually designed to be built as a special core-rim structure. As the core of the structure the Ti(C,N) ceramic particle is encircled by the solid solution rim phase which is generated through the dissolving-precipitating process during the liquid phase sintering [7]. In the case of Ti(C,N) based cermet products, the addition of other carbides such as tungsten carbide, molybdenum carbide, niobium carbide, tantalum carbide is essential for cermets to meet the various requirements of cutting [8,9]. For improving the poor wettability between Ti(C,N) and Co/Ni, WC and Mo_2C are added in Ti(C,N) based cermets to bring about the new rim phase of (Ti,W,Mo)(C,N) wrapping Ti(C,N) particles that can be wetted by the metallic binder phase of Co/Ni, which enhances the interfacial binding force of ceramic phase and metal phase and then results in improved mechanical properties [10–12]. As common carbide additives with high hardness at elevated temperature, the existence of niobium carbide and tantalum carbide can cause cermets to achieve the better mechanical properties and higher hardness [13]. Meanwhile, the TaC and NbC have positive effects on the oxidation resistance of materials [14]. Compared with TaC, NbC is more widely used in the production of Ti(C,N) based cermets due to its better thermo-hardness, lower density and the ability of lowering the sintering temperature [15]. Moreover, the microstructure and mechanical properties of the Ti(C,N)-based cermets can be changed significantly with the addition of NbC powder, in which the proportion of Ti(C,N) black phase becomes smaller result from the generation of complex carbonitride (Ti,W,Nb)(C,N) rim phase, which can promote the wettability between ceramic phase and metal

* Corresponding author.
E-mail address: yuehui@csu.edu.cn (Y. He).

https://doi.org/10.1016/j.ceramint.2018.03.131
Received 18 January 2018; Received in revised form 11 March 2018; Accepted 14 March 2018

Please cite this article as: Kang, X., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.03.131

binder phase. The high-temperature performance of cermets can be reinforced by the addition of NbC, but meanwhile a thicker rim phase is obtained in cermets. It should be pointed out that the thick brittle rim has negative effects on mechanical properties of cermets [15–17]. There is thereby an urgent need but it is still a significant challenge to develop the cermets that both have satisfactory mechanical properties and excellent high-temperature behavior in the case of adding NbC.

It is well known that zirconium carbide is a typical high-temperature refractory material possessing high hardness, which is considered as a common carbide additive in a variety of advanced materials. The grain boundary precipitation and abnormal growth of grains can be inhibited by adding an appropriate amount of ZrC, which can make the materials achieve a homogeneous microstructure, great strength, fracture toughness and outstanding high-temperature behavior [18–20]. Moreover it was found that the cutting performance and the fracture toughness of cermets could be improved by the addition of Zr [8,9,21,22]. However, the effect of a small amount of ZrC addition on various performances of Ti(C,N)-based cermets is hardly ever investigated, especially the behaviors of oxidation resistance and wear resistance of cermets. Particularly, the recently researches mainly focused on the influence of adding ZrC individually, but haven't investigated the synergistic effect between ZrC and other carbides. Thus, the main purpose of the work is improving the mechanical properties, wear resistance and oxidation resistance of Ti(C,N)-based cermets. The effects of ZrC on the microstructure, mechanical properties, oxidation resistance and wear resistance of Ti(C,N)-WC-NbC-Co-Ni cermets are investigated.

2. Experimental procedure

The chemical compositions of the cermets prepared in this work are given in Table 1. Commercially-obtained powders of Ti($C_{0.5}$,$N_{0.5}$) (the average particle size of 2 μm), WC (5 μm), NbC (4 μm), ZrC (4 μm), Ni (6 μm), Co (5 μm) were used as raw powders. The particle sizes were measured by the laser particle size analyzer. These Ti(C,N)-WC-NbC-Co-Ni cermets samples are respectively added 0 wt%, 1 wt%, 3 wt%, and 5 wt% ZrC, and the sample ZrCx represents the Ti(C,N)-WC-NbC-Co-Ni cermets with X wt% ZrC. A traditional powder metallurgy method was used to prepare the experimental samples. First, the carbides and metal powders were mixed according to the design compositions listed in Table 1 and wet-milled with WC-Co balls (ball-to-powder weight ratio: 8:1) by a planetary ball miller for 72 h. Then the double action pressing method was used to provide a green compact with the uniform densities at 150 MPa. After degreased at 750 °C in a hydrogen atmosphere, all green compacts were sintered by pressure sintering at 1450 °C for an hour in the argon atmosphere of 3 MPa and the experimental bar samples with dimensions of 5 mm × 5 mm × 35 mm were obtained. Finally, specimens were polished to achieve the experimental results more accurate.

The microstructure morphology was observed by scanning electron microscope (SEM) (QUANTA FEG-250, FEI, USA) in backscattered electron (BSE) mode and secondary electron mode equipped with an energy-dispersive spectrometer (EDS). The Nb content in binder is determined by the EDS(energy dispersive spectrum). The measurement of each sample was repeated in three randomly selected regions of cermets. Meanwhile, the proportions of different phases are determined by analyzing the micrographs of cermets with the statistical software Image J. The measurement of each sample was repeated in five randomly selected regions. In order to identify phases, X-ray diffraction (XRD) analysis was conducted by X-ray diffractometer (Rigaku, D/max 2550). The hardness (HRA) of specimens was determined by Rockwell hardness tester. Universal material testing machine was used to carry out transverse rupture strength tested by a three-point bending method and fracture toughness tested by the single edge notched beam (SENB) method, respectively. The value of fracture toughness is calculated by the following formula [23]:

$$K_{IC} = Y\frac{3PL}{2bh^2}\sqrt{a}\left(Y = 1.93 - 3.07\left(\frac{a}{h}\right)+14.53\left(\frac{a}{h}\right)^2-25.11\left(\frac{a}{h}\right)^3 +25.8\left(\frac{a}{h}\right)^4\right)$$

In this formula Y is the geometrical factor, P is the critical rupture load and α is the size of the pre-crack.

Specimen strips with same dimension of 5 mm × 5 mm × 30 mm were cut from the central part of sintered cermets and polished in the oxidation study. The isothermal oxidation was carried out at 750 °C for 100 h in muffle furnace, and samples were tied to platinum wire to keep dangling, which could maximize the surfaces reacted with the surrounding atmosphere. The weight gain of oxidized samples was measured periodically by the electronic balance.

Friction and wear experiments were conducted with a ball-on-reciprocating-flat tribometer at room temperature. The ball with the diameter of 6 mm in tribometer was made of YG6 WC–Co cemented carbide ball with a hardness of HRA91, which was polished and cleaned in acetone before the experiment. In this experiment, the normal load was 50 N, and the sliding speed was 1500 mm/min. After having been conducted for 20 min, the experiment was halted and each test was repeated 3 times. Then the worn surfaces were observed by a profilometer and SEM.

3. Results and discussion

3.1. Microstructure and mechanical properties

Fig. 1(a)–(d) displays the microstructures of Ti(C,N)-based cermets with different ZrC contents. Different phases are distinguished by the contrast level in the BSE mode. Overall, three contrasts are observed in the microstructure of cermets: black, grey and white. The black phases are Ti(C,N) particles, the grey phase is (Ti,W,Nb,Zr,Mo)(C,N) solid solution and the white phases are other carbides particles(WC, NbC, ZrC) or the Co/Ni binder phase. And the microstructures of Ti(C,N)-based cermets consist of two dominant typical structures: black core-grey rim and white core-grey rim that have different carbide core phases(WC, NbC, ZrC). Meanwhile, the proportion of different phases can be determined by measuring the proportion of corresponding color present in BSE mode. Fig. 1(e) displays the variation of proportion of Ti(C,N) particles and (Ti,W,Nb,Zr,Mo)(C,N) solid solution in cermets with different ZrC content.

As we all know, the black core-grey rim structure is the conventional structure of cermets. Among the black core-grey rim traditional structure, the black core phase is undissolved Ti(C,N) particle, which is hard, antioxidative but brittle. It is well established that the hardness is positively related to the wear property of materials. Therefore, the black Ti(C,N) particles endow cermets splendid wearing resistance due to the highly hardness of Ti(C,N). The rim phase is generated in the dissolving-precipitating process during the liquid-phase sintering. Ostwald ripening happens in the dissolving-precipitating process, which is driven by the interfacial energy. This mechanism means that the small carbide particles dissolve in the binder, meanwhile (Ti,W,Nb,Mo)(C,N) solid solution rim precipitates surrounding the undissolved big Ti(C,N) particles, which causes the formation and grain

Table 1
Chemical compositions of the experimental cermets (wt%).

Cermets	Ti(C,N)	WC	NbC	ZrC	Ni	Co
ZrC0	53	20	12	0	7.5	7.5
ZrC1	52	20	12	1	7.5	7.5
ZrC3	50	20	12	3	7.5	7.5
ZrC5	48	20	12	5	7.5	7.5