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Effect of W content in solid solution on properties and microstructure of (Ti,W)C-Ni_3Al cermets

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ABSTRACT

$(Ti_{1-x}W_x)C$ solid solutions (x = 0.05, 0.15, 0.25, 0.35) were synthesized by carbothermal reduction and then were used as hard phases to prepare (Ti,W)C-Ni_3Al cermets by vacuum sintering. (Ti,W)C-Ni_3Al cermets showed weak core-rim structure carbide particles embedded in Ni_3Al binder. As W content in (Ti,W)C increased, core-rim structure of carbide particles got weaker and the contrast of particles lowered down in SEM-BSE morphologies. Furthermore, the densification of cermets was promoted with W content in solid solution increasing, meanwhile TRS and toughness of cermets were improved obviously. In this paper, the wettability of molten metal on different group transition metal carbides was discussed in detail based on valence-electron configurations (VECs) of carbides.

1. Introduction

Ti(C,N)-based cermets bonded with Ni or/and Co, are promising candidates for cutting tools, forming tools and wear-resistant parts, due to their exceptional wear resistance, excellent plastic deformation resistance and superior oxidation resistance at high temperature as well as high thermal conductivity [1–4]. However, applications of cermets at elevated temperature are restricted for the high temperature softening of metal binder like Ni and Co. Therefore, much attention has been paid on replacing Ni or/and Co with Ni_3Al intermetallic compound as binder of cermets, which was attributed to its exceptional high temperature strengthening effect, good oxidation resistance and resistance to aqueous acidic corrosion environments [5–9]. In decades, much effort [5–11] has been done on TiC-Ni_3Al cermets, while somewhat lower mechanical properties have been achieved compared with conventional Ni/Co bonded cermets [3,4], which should be owing to the relatively insufficient wettability of Ni_3Al on TiC compared with that of Ni on TiC.

It has been reported that TiC can be wetted completely by Ni with a small amount of Mo addition [12], whereas the contact angle of Ni_3Al on TiC cannot be close to zero even with 5 wt.% Mo addition [13]. Therefore, it is essential to improve the wettability of Ni_3Al on TiC. Plucknett et al. [8] studied Ti(C,N)-Ni_3Al cermets with Mo_2C addition and found that Mo_2C can improve upon the wettability during sintering, thus enhancing the densification, especially for cermets with low binder contents (20 vol.%). Previous research showed that the equilibrium contact angle of Ni_3Al on (Ti,W)C solid solution decrease steadily with W content increasing in solid solution [14].

In recent years, solid solution based cermets have attracted much attention owing to their higher toughness compared with conventional cermets. It has been reported that fracture toughness and transverse rupture strength (TRS) of (Ti,W)C complete solid solution cermets were improved with W content increasing, while the hardness is much lower than that of commercial cermets [15–17]. Liu et al. [18] reported that the (Ti,W,Mo,V) (C,N) complete solid solution based cermet shows high fracture toughness but low TRS and hardness, meanwhile its densification is only 93.5% yet. Furthermore, research [19] has also showed that TRS and hardness of $(Ti_{0.68},W_{0.32})C$-Ni cermets can be improved apparently with Mo addition, while the toughness declined with Mo content increasing. However, all these researches are focused on Ni/Co binder and few reported intermetallic compound bonded solid solution cermets. In this paper, microstructure and mechanical properties of (Ti,W)C-Ni_3Al cermets with different W content in solid solution would be

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studied. In addition, wetting behavior of Ni_3Al on (Ti,W)C with different W content would be discussed.

2. Experimental details

The starting materials used in this research were anatase-TiO_2 (>99 wt.%, <40 μm), WO_3 (>99 wt.%, <50 μm), Mo (>99 wt.%, ~2.8 μm) and C (>99 wt.%, <80 μm) powders. Nominal compositions of four experimental (Ti,W)C solid solutions were given in Table 1. Raw powder mixtures were ball-milled for 48 h before heat treating at a ball-to-powder weight ratio of 40:1 and a speed of 400 rpm. The milling was conducted in a full-ranged planetary ball mill (QM-QX4, Nanjing university instrument plant, China). Cemented carbide ball and nylon jar were used in mechanical milling. Sieved by 100 mesh sieve, the as-milled mixtures were then heated 1450 °C for 2 h with a heating rate 5 °C/min in vacuum (1–30 Pa).

Ni_3Al powder used in this research was produced by mechanical alloying, which was depicted in earlier paper [11]. The nominal compositions of cermets were 60($Ti_{1-x}W_x$)C-30Ni_3Al-10Mo (wt.%) ($x = 0.05, 0.15, 0.25, 0.35$). For simplicity, the cermets were labeled as S005, S015, S025 and S035, respectively. The cermets mixtures were planetary ball-milled for 48 h with ethyl alcohol at a ball-to-powder weight ratio of 7:1 and a speed of 220 rpm, and then dried, sieved by 100 mesh sieve. Green compacts were prepared by uniaxially pressed at a pressure of 400 MPa for 90 s, and then sintered at 1430 °C, 1450 °C and 1480 °C for 1 h in vacuum (10^{-2} ~ 10^{-1} Pa).

Phase identification was conducted by X-ray diffractometer (XRD; XRD-7000S, Shimadzu, Japan) using Cu Kα radiation (λ = 1.5406 Å) and 10°/min. Microstructural investigations were performed by scanning electron microscopy (SEM; QUANTA 200, FEI, Netherland), field emission scanning electron microscopy (FSEM; JSM-7600F, JEOL; Japan), equipped with an energy dispersive spectrometer (EDS) analysis system, and field emission transmission electron microscopy (FTEM; Tecnai G2 F30, FEI, Netherland) technique. Sample for FTEM testing were prepared by ion milling (691, Gatan, America) after polishing to ~50 μm. Fast Fourier transforms (FFT) of HRTEM images was obtained using Gatan Digital Micrograph 3.9 software package.

Archimedes principle was employed to measure the density of cermets. The transverse rupture strength (TRS) at room temperature was measured by a three-point bending test (span 14.5 mm) on a universal electron material testing machine model WE-10. Vickers hardness and fracture toughness testing were conducted on Electric Vickers Hardness Tester (432SVD, Wilson, America). Fracture toughness (K_{1C}) of as-sintered cermet was measured by indentation method and calculated as follows [20]:

$$K_{1C} = 0.15\sqrt{\frac{HV30}{\sum_{i=1}^{4} l_i}} \quad (1)$$

Where l_i (mm) is the length of the crack tip from hardness indentation, HV30 is the Vickers hardness (N/mm^2) under 30 kg loads for 15 s, $\sum_{i=1}^{4} l_i$ is the total crack length (mm) from each corner of an indent to the tip of the corresponding crack.

Table 1
Raw powder composition ($Ti_{1-x}W_x$)C synthesized by carbothermal reduction.

Sample-no.	Target constituent	C(g)	TiO_2(g)	WO_3(g)
A	$(Ti_{0.95}W_{0.5})C$	11.45	24.46	3.74
B	$(Ti_{0.85}W_{0.15})C$	10.45	19.33	9.90
C	$(Ti_{0.75}W_{0.25})C$	9.55	15.28	14.78
D	$(Ti_{0.65}W_{0.35})C$	8.91	11.99	18.73

3. Results

3.1. Preparation of (Ti,W)C solid solution by carbothermal reduction

In this study, ($Ti_{1-x}W_x$)C ($x = 0.05, 0.15, 0.25, 0.35$) solid solutions were synthesized by carbothermal reaction from oxides and graphite. The synthesis mechanism of carbothermal reduction would not be depicted in this paper for its detailed study in previous research [21]. The XRD patterns of ($Ti_{1-x}W_x$)C after carbothermal reducing at 1450 °C are shown in Fig. 1. Clearly, there were mainly TiC phase (i.e. the (Ti,W)C phase as they have identical crystal structure) in all four powders and a small amount of WC existed in powder C and D. It has been reported that the formation energy of solid solution is positive and the stability of solid solution would decline when x>~26 at.% in ($Ti_{1-x}W_x$)C [22]. Therefore, in powder C and D with high W content, WC would precipitate during heat treatment. The existence of small amounts of WC, which is inevitable in this case, has little effect on properties and microstructure of subsequent cermets. In consequence, these powders were used as raw powders of cermets.

The morphologies of ($Ti_{1-x}W_x$)C powders after carbothermal reducing at 1450 °C and their corresponding SEM-EDAX spectrums are shown in Fig. 2. The SEM- EDAX results are listed in Table 2 and the phase constituent of powders were also given from the ratio of Ti and W content. It can be seen from Fig. 2 that the particles showed round and were agglomerated as large particles. Obviously, agglomeration of particles occurred in the process of heat treatment. After carbothermal reducing, submicron level particles were obtained and the particle size decreased with W content in solid solution increasing. Furthermore, the size of small grains approaches nano-scale as W ≥ 25 at.%. The phase constituents of heat-treated powders were almost in accordance with target constituents.

3.2. Microstructure and phase constituent of ($Ti_{1-x}W_x$)C-Ni_3Al cermets

The XRD patterns of cermet S025 before and after sintering are shown in Fig. 3 and XRD patterns of other cermets were not given for their similar results. After milling, the intensity of WC peaks increased due to introduction of part WC from cemented carbide ball during milling. XRD phase analysis revealed that the as-sintered specimens mainly consisted of TiC-type phase and Ni_3Al

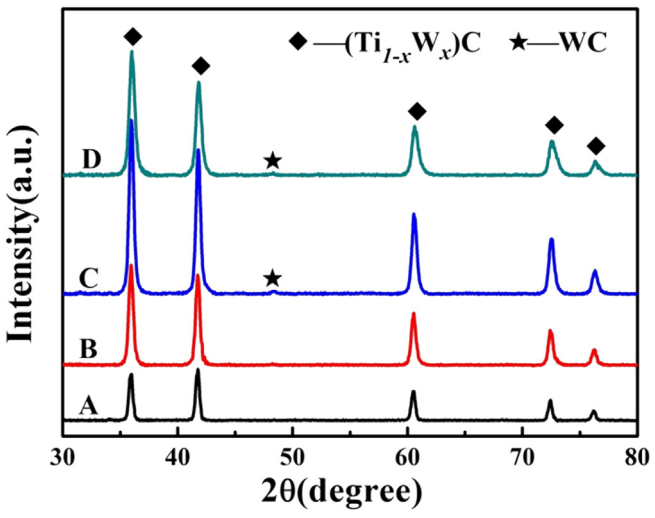

Fig. 1. XRD patterns of ($Ti_{1-x}W_x$)C after carbothermal reduction at 1450 °C.