

Microstructure and mechanical properties of TiC–WC–(Ti,W)C–Ni cermets

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ABSTRACT

(Ti_{0.93}W_{0.07})C solid-solution powder is synthesized via high-energy milling and carbothermal reduction. When the solid-solution carbide is sintered after blending with Ni and commercial single-phase carbides such as TiC and WC, a complex microstructure is developed, typically featuring a core–rim structure along with the initial solid-solution phase. Furthermore, an increase in total volume of the solid-solution phase with (Ti_{0.93}W_{0.07})C in the cermets results in significantly enhanced mechanical properties: fracture toughness (K_{IC}) is 7.5–12.7 MPa m^{1/2} and hardness (H_v) is 11.9–14.1 GPa. These properties are in contrast with those of conventional cermets, which yield K_{IC} = 6 MPa m^{1/2} and H_v = 12.6 GPa.

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1. Introduction

TiC- or Ti(CN)-based cermets are important cutting-tool materials in metal cutting and finishing operations because of their excellent wear resistance and chemical stability under high temperatures [1]. However, the poor wettability of Ni binder on carbides and low toughness values limit the broad application of TiC- or Ti(CN)-based cermets compared with WC–Co. Commercial cermets contain various carbide and nitride phases, including TiC, TiN, Ti(C,N), WC, TaC, and Mo₂C. Such cermets typically consist of carbonitride hard-phase particles embedded in the metal binder phase [2]. Most cermets have a core–rim structure consisting of an undissolved Ti(CN) core surrounded by a rim phase of (Ti,W,Ta, . . .)(CN) solid solution [3].

Cermets consisting of only (Ti,W)C- or (Ti,W)(CN)-type solid-solution phase microstructures have been investigated since the 1980s with the aim of overcoming the limitations of existing cermets. Recent studies have reported the microstructure of (Ti,W)C- or (Ti,W)(CN)-type solid-solution phase [4]. The microstructure of complete solid-solution phases is produced from an oxide mixture, resulting in vastly improved toughness compared with conventional TiC-based cermets. (Ti,W)C and (Ti,W)(CN) cermets are known to provide high toughness compared with conventional cermets [4,5]; however, the hardness is limited by a lack of hard TiC or Ti(CN) particles.

In the present study, cermets were prepared using a mixture of TiC single-phase carbide powder and solid-solution carbide powder, with the aim of utilizing the high hardness and wear resistance of TiC combined with high toughness. The microstructure is examined and explained in terms of the thermal stability of carbides and dissolution–reprecipitation phenomenon. The relationship between microstructure and mechanical properties is also considered.

2. Experimental procedure

(Ti,W)C–20 wt.%Ni powder was produced using anatase-TiO₂ (99+% purity), NiO (99% purity, 45 μm avg. particle size), and WO₃ (99+% purity, 20 μm avg. particle size). These ingredients were mixed with carbon to attain a target composition equivalent to TiC–15 wt.%WC–20 wt.%Ni. The powders were subjected to high-energy ball milling using a planetary mill (Model Pulverisette 7, Fritsch, Germany). Tungsten carbide balls were mixed with the oxide powders and carbon at a ball-to-powder weight ratio of 40:1. A tungsten carbide bowl was used, and all milling was conducted at a speed of 250 RPM for a period of 20 h. The (Ti,W)C–Ni solid-solution powder was prepared by carbothermal reduction at 1300 °C for 1 h.

Cermets were produced by mixing (Ti,W)C–Ni with WC (1.9 μm avg. particle size, Xiaman), TiC (1.0 μm avg. particle size, Treibacher), and Ni (4.0 μm avg. particle size, Inco). The compositions of cermets used in this study (cermets A–E) are listed in Table 1. All sample compositions were maintained equivalent to TiC–15WC–20Ni (in wt.%), regardless of (Ti,W)C content in the system. The slurry mixture was prepared with paraffin in acetone for

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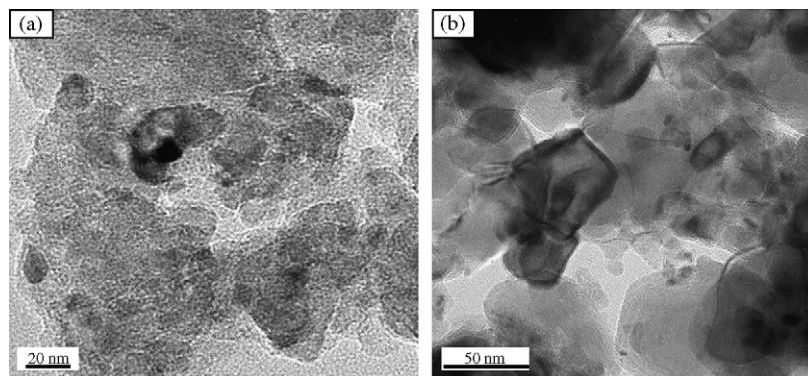


Fig. 1. TEM micrographs of (a) milled oxides and (b) (Ti,W)C-Ni powder.

Table 1
Compositions of the cermets investigated in this study.

Cermets	(Ti _{0.93} W _{0.07})C–20Ni: TiC–15WC–20Ni (in wt.%)
A	1:0
B	1:1
C	1:3
D	1:5
E	0:1

All cermet compositions are equivalent to TiC–15 wt.%WC–20 wt.%Ni.

24 h and then dried in an oven for 24 h. Disk-type compacts of 1 cm in diameter were prepared under a pressure of 125 MPa and sintered at 1510 °C for 1 h in a graphite furnace at 0.133 Pa.

The synthesized powders were analyzed using an X-ray diffractometer (M18XHF-SRA, Macscience, Japan) with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and Si as the standard. Powder morphology was studied using high resolution transmission electron microscopy (Model JEM-3000F, JEOL, Japan). Sintered specimens were ground and their microstructure observed by scanning electron microscopy (Model JSM-5600, JEOL, Tokyo, Japan). Energy dispersive spectrometer analysis was performed by high resolution transmission electron microscopy (Model F20, FEI, USA). Vicker's hardness was measured with an indenter load of 30 kg, and fracture toughness was calculated using the expression derived by Shetty et al. [6].

3. Results and discussion

3.1. Microstructure

Fig. 1 shows TEM images of milled powder of oxide mixture and (Ti,W)C–Ni powder. (Ti,W)C–20 wt.%Ni cermet powder was synthesized by carbothermal reduction at 1300 °C for 1 h. The particle size of milled oxide and (Ti,W)C powders was maintained in the ~50 nm range even after carbothermal reduction. The XRD result shown in Fig. 2 reveals that the oxide mixture was reduced and fully carburized to (Ti,W)C. Unexpectedly, particle growth was not significant

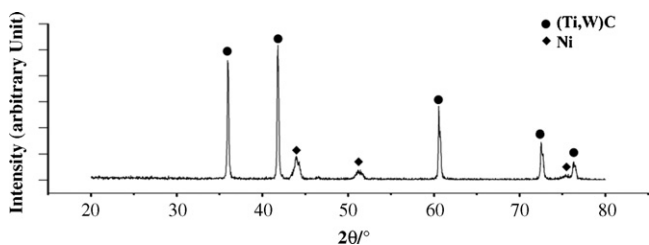


Fig. 2. XRD spectra of (Ti,W)C–Ni powders after carbothermal reduction at 1300 °C for 1 h.

under the conditions employed for carbothermal reduction. The broadening of (Ti,W)C peaks in Fig. 2 supports the presence of fine crystallites, as indicated by TEM observations.

Fig. 3 shows SEM micrographs of cermets with varying amounts of (Ti_{0.93}W_{0.07})C–20Ni. As the content of the TiC phase increases in the order of cermets A–D, the amount of TiC (black grains in Fig. 3) increases. Furthermore, when (Ti_{0.93}W_{0.07})C–20Ni was added to conventionally prepared cermet powder (TiC–15 wt.%WC–20 wt.%Ni), the content of the solid-solution rim phase exceeded 75% in volume after sintering. It is commonly observed that conventional cermets such as cermet E contain a rim phase that makes up ~60% in volume, excluding the binder portion.

Interestingly, there is a significant increase in the rim phase from cermets E (conventional cermet) to D (<20% addition of the solid solution); however, further addition of (Ti_{0.93}W_{0.07})C to TiC–15 wt.%WC–20 wt.%Ni has little effect on the rim content, as seen from cermets D to C or from C to B. This result is possible explained by the small difference in thermal stability (i.e., dissolution tendency in Ni melt) between the (Ti_{0.93}W_{0.07})C and TiC phases, as discussed below. In addition, the microstructure of the cermets (Fig. 3a–d) appears simple compared with that of the conventional cermet (Fig. 3e).

3.2. Phase formation

Fig. 4 shows TEM images of cermets A and B. As expected, cermet A comprises a single solid-solution phase: (Ti,W)C. In contrast, cermet B comprises three different carbide structures (Fig. 3b): a TiC-based core–rim, (Ti,W)C-based core–rim, and single-phase (Ti,W)C particles (Fig. 4a–c). The core–rim structure typically consists of a core, inner rim, and outer rim. The core and rim phases are visually distinct in TEM bright field micrographs, depending on W content: a relatively high concentration of heavy elements such as W results in a relatively dark appearance.

In TiC- or Ti(CN)-based conventional cermets, W content is generally higher in the inner rim than in the outer rim. The outer rim, which obviously forms later than the inner rim, possibly forms at a sintering temperature or low temperature during the cooling stage [7].

TEM/EDS results are listed in Table 2. W concentrations in the rims of TiC core–rim structure are similar to those in the rims of solid-solution core–rim. This finding indicates that the rim phases around the TiC- and (Ti,W)C-based cores are formed at the same time and from the same sources.

The outer rims are enriched in W compared with the originally added solid-solution phase (8.4 at.%; Table 2). This finding raises the possibility that the outer rims around the TiC- and (Ti,W)C-based cores formed via the dissolution of WC and original solid-solution

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