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Characterization of Ti-based solid solution cermets prepared by mechanically induced self-sustained reaction and subsequent pressureless sintering

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ABSTRACT

Nanocrystalline (Ti,Mo)C and (Ti,W)C solid solution powders were obtained by mechanically induced self-sustained reaction through high-energy ball milling of Ti, Mo, W and graphite powders under an argon atmosphere. The synthesis process of the solid solution powders and the microstructure of the solid solution cermets were investigated. The solid solution powders formed between 2 h and 3 h of ball milling. After 8 h of milling, Mo dissolved in TiC completely but W did not. (Ti,Mo)C–Ni cermets had a weak core–rim structure, and (Ti,Mo)C solid solution grains showed a poor wettability with the binder. (Ti,W)C–Ni cermets contained some grains without a core–rim structure and showed a superior toughness. The addition of Mo improved hardness and transverse rupture strength of the solid solution cermets but reduced the toughness, and the solid solution cermets showed greater toughness than conventional cermets.

1. Introduction

TiC- or Ti(C,N)-based cermets are made of TiC or Ti(C,N) as the main hard phase and Ni or/and Co as the binder phase. They are kind of promising materials for high speed cutting because of their excellent properties such as low density and high values of melting point, hardness, mechanical strength, thermal conductivity, oxidation resistance, creep resistance as well as low friction coefficient to metals [1,2]. They have improved surface finishing, ensuring at the same time excellent chip and tolerance control as well as the dimensional accuracy of workpieces, compared with conventional WC–Co tools [3].

A variety of additives such as Mo/Mo_2C, WC, TaC or NbC are added in TiC- or Ti(C,N)-based cermet system to improve the sinterability, hot hardness and thermal shock resistance of cermets [2–4]. It is well known that the microstructure of TiC/Ti(C,N)–MC–Ni (M = W, Mo, Ta, et al.) cermets exhibit a typical core–rim structure. The cores are undissolved TiC or Ti(C,N) particles and the rims are (Ti,M)C or (Ti,M)(C,N) solid solution [5–9]. In general, the rim phase consists of two regions: an inner rim is close to the core–rim boundary and richer in heavy metals; an outer rim is close to the rim-binder phase boundary and contains less heavy metal than the inner rim. The interface between the core and the inner rim phase can be highly strained, and probably became potential sites for crack initiation and propagation, which results in the decrease of fracture toughness for cermets [10–13]. Therefore, TiC- and Ti(C,N)-based cermets show lower fracture toughness than WC–Co cermets in practical cutting due to the poor wettability of liquid Ni on TiC and Ti(C,N) and the complex microstructures along with a large number of interfaces, which limits their industrial applications [10–15].

The solid solution rim phases are known to improve the toughness in TiC- and Ti(C,N)-based cermets [10,11,16,17]. Solid solution cermets have less interfaces in the microstructures [10,11], thus many studies have sought to enhance the toughness of cermets by producing single-phase and homogeneous solid solution as the hard phase, such as (Ti,W)C, (Ti,W)(C,N) and (Ti,W,Mo)(C,N) solid solution cermets [10,11,16,17]. All of these solid solutions were prepared by carbothermal reduction method. Mechanically induced self-sustaining reaction (MSR) proposed by Yen et al. [18] takes advantage of the strong exothermic characteristic of the carbide and nitride formation from the elemental powders to promote self-propagating reactions during milling and obtains complex carbonitrides powders with homogeneous and controlled chemical composition by adjusting milling parameters and the metal-to-carbon atomic ratio in the starting mixture [3,18–21]. This is a novel, high-efficiency and cost-effective method to produce ultrafine (even nano-structured) carbides or carbonitrides solid solution powders. Córdoba et al. [22–26] have employed MSR to prepare several carbonitride solid solutions such as (Ti,Ta)(C,N),

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Table 1
Summary of starting elemental mixtures, ignition time and properties of the synthesized phases.

Sample	Raw powders Ti/M/C (atomic ratio)	Ignition time	Phase	D (nm)	a (nm)
P1	Ti/Mo/C (0.9/0.1/1)	147 min	(Ti.Mo)C	44.9	0.43218
P2	Ti/W/C (0.95/0.05/1)	141 min	(Ti,W)C	33.2	0.43321
P3	Ti/C (1/1)	136 min	TiC	39.4	0.43275

D – crystalline size ; a – lattice parameter.

Table 2
Nominal composition of cermets.

Cermet	Synthesized ceramic powders + binder (wt%) + 3rd phase (wt%)
C1	(Ti, Mo)C + Ni (20 wt%)
C2	(Ti, W)C + Ni (20 wt%)
C3	TiC + Ni (20 wt%)
C4	(Ti, Mo)C + Ni (20 wt%) + Mo (10 wt%)
C5	(Ti, W)C + Ni (20 wt%) + Mo (10 wt%)
C6	TiC + Ni (20 wt%) + Mo (10 wt%)

(Ti,Nb)(C,N) and (Ti,Hf)(C,N). But few studies investigated the synthesis of (Ti,Mo)C and (Ti,W)C solid solution by MSR.

In this work, (Ti,Mo)C and (Ti,W)C solid solution powders were synthesized by high-energy ball milling of element Ti, Mo, W and graphite powders. The synthesized solid solution powders were mixed with metal Ni and then were sintered to prepare cermets. The phase structure and the morphology of milled powders were characterized, and the formation process and mechanism of solid solution as well as the microstructure and mechanical properties of sintered cermets were also investigated.

2. Experimental

Ti powder (99% in purity, 45 μm), Mo powder (99.9% in purity, 2.80 μm), W powder (99.9% in purity, 3.80 μm), Ni powder (99.8% in purity, 2.25 μm) and graphite powder (99.9% in purity, 5.50 μm) were used in this work. Table 1 lists the composition of the raw powders mixtures (P3 is a comparison). The mixtures and stainless steel balls were put into a stainless steel vial and then filled with highly pure argon (99.999%) atmosphere. The powders mixture were planetary ball-milled with a ball-to-powder weight ratio of 25:1 and a rotate speed of 350 rpm. An infrared thermometer was used to monitor the temperature inside the vial during ball-milling. When the temperature raised sharply, MSR was ignited. Milling was interrupted at intervals and powder samples were removed for analysis.

The obtained solid solution powders were mixed with 20 wt% of Ni in ethanol by planetary ball milling (WC-Co balls were used for milling medium) for 24 h. As a comparison, 10 wt% of Mo was added to the cermets system. The composition of cermets is shown in Table 2. The mixed powder was dried at 85 °C and then sieved before compacting into rectangular shape under a uniaxial pressure of 300 MPa. Green compacts were sintered at 1415–1445 °C under vacuum (0.01 Pa) for 1 h.

Phases of milled powders and sintered cermets were identified by X-ray diffraction (XRD, X'Pert PRO, PANalytical). The crystallite size of milled powders was evaluated by Williamson–Hall method [27]. Data obtained from the XRD analysis were also used to estimate the lattice parameter by the Nelson–Riley extrapolation function [27,28]. The morphologies and microstructures of the milled powders and sintered cermets were observed by scanning electron microscopy (SEM, Sirion 200, Quanta 200, FEI) equipped with an energy dispersive X-ray spectrum (EDX, EDAX Inc.). The hardness was measured by a Vickers hardness tester (432 SVD, Wolpert wilison Instrument) with an indenter load of 30 kg over 15 s and fracture toughness was evaluated by a direct crack measurement using the expression derived by Shetty et al. [29]. The transverse rupture strength (TRS) was measured by a universal material testing machine (Zwick/Roell Z020) with a three-point bending method. The dimension of specimen was 20.00 mm × 6.50 mm × 5.20 mm (span 14.5 mm); the strain rate was 0.5 mm/min.

3. Result and discussion

3.1. Characterization of synthesized solid solution powders

The ignition time of MSR in each system is listed in Table 1. The reactions of Mo–C and W–C are low exothermic without enough adiabatic temperature to occur MSR, thereby the Mo and W played a role of diluents and prolonged the ignition time. Fig. 1(a) shows XRD patterns of P1 after milling with different durations. After 2 h

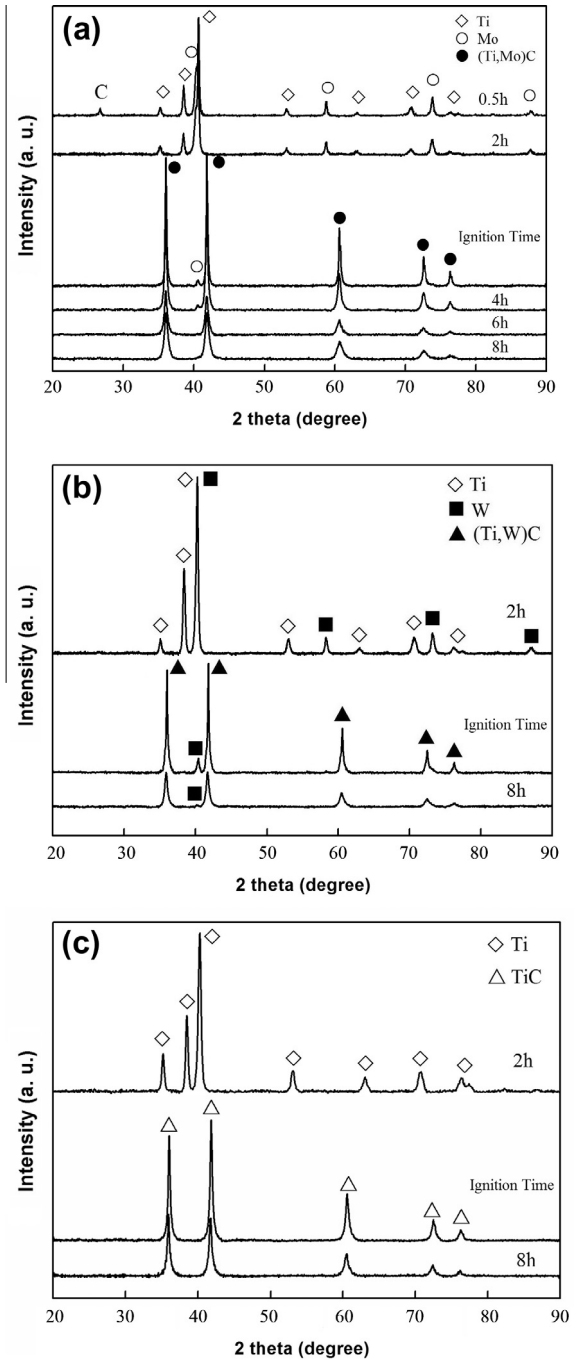

Fig. 1. XRD patterns of samples P1, P2 and P3 after milling with different durations: (a) P1; (b) P2; (c) P3.