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Highly toughened dense TiC–Ni composite by in situ decomposition of (Ti,Ni)C solid solution

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Abstract

A highly-toughened TiC–Ni composite was produced by the in situ decomposition during sintering of a nonequilibrim (Ti,Ni)C solid-solution phase. The solid solution was synthesized by the mechanical milling of Ti–Ni alloy/graphite mixtures, which then decomposed to finely dispersed TiC and Ni upon heating in a vacuum. To take advantage of the fine microstructure, samples were sintered to facilitate the in situ decomposition. Densification of the (Ti,Ni)C during the sintering was achieved through the coalescence of fine particles and the concurrent decomposition of the nonequilibrium (Ti,Ni)C phase. Additional densification was obtained through liquid-phase sintering by the eutectic melting of Ni. The fracture toughness of the sintered TiC–Ni composite was notably higher than that of conventional TiC/Ti(CN)–Ni or of comparable Ti(CN)–WC–Ni composites. Its fine and dense microstructure is believed to account for the enhanced toughness. The method suggested here might represent a valuable option for the preparation of TiC–Ni composites with desirable mechanical properties.

Keywords: B. Composites; C. Hardness; D. Carbides; E. Cutting tools

1. Introduction

TiC/Ti(CN)–Ni composites are widely used in cutting tools owing to their high hardness, wear resistance, chemical stability, and low density. They are generally produced by the liquid-phase sintering of a mixture of TiC/Ti(CN) and Ni powders. Nevertheless, the formation of a dense TiC/Ti(CN)–Ni composite by liquid-phase sintering is generally difficult due to the relatively poor wettability of Ni on a TiC/Ti(CN) surface. (The wetting angles are 30° and 17° in a vacuum and in hydrogen, respectively.) The poor wettability is attributed to the formation of surface oxide; therefore, the elimination of pores by the penetration of liquid Ni into the TiC/Ti(CN)–Ni system becomes difficult [1–3]. In some cases, Mo_2C is added to improve the wettability of Ni on the TiC/Ti(CN). The full densification of TiC/Ti(CN)–Ni composites requires their sintering at above 1450 °C [4–6]. This difficulty in sintering often limits the applicability of the TiC/Ti(CN)–Ni composites in cutting tools despite Ti and Ni being less expensive than the more commonly used W and Co.

Mechanical alloying is a useful method for the synthesis of various nonequilibrium phases such as supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys [7]. It has widely been used to fabricate supersaturated binary solid-solution such as Zr–Al, Fe–Cu, Al–Mn, Al–Fe, Al–Si, Al–Ge, and Ni–Ag, which exhibit very limited mutual solubility [8–15]. Such supersaturated solid solutions decompose exothermically to thermodynamically stable phases with sufficient activation energy. Beyond the binary alloys, the ternary solid-solution phase of the constituents of the TiC–Ni composite (i.e., Ti, Ni, and C) does not exist at equilibrium [16–18]. Therefore, if a nonequilibrium solid-solution phase of Ti, Ni, and C

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(i.e., (Ti,Ni)C) could be synthesized by mechanical alloying, it would spontaneously decompose into TiC and Ni upon proper heat treatment.

This work reports a new method to produce a dense TiC–Ni composite via the decomposition of a nonequilibrium (Ti,Ni)C phase. A (Ti,Ni)C phase, the nonequilibrium solid-solution phase of Ti–Ni–C, was initially synthesized by the mechanical alloying of a Ti–Ni alloy/graphite mixture. The sintering behavior of (Ti, Ni)C powders was investigated in terms of the shrinkage rate and microstructure evolution and compared with that of Ti(CN)–Ni prepared by conventional mixing. The mechanical properties of the TiC–Ni composites prepared by the sintering of (Ti,Ni)C powders were compared with previously reported properties of TiC–Ni and Ti(CN)–WC–Ni composites.

2. Experimental procedure

Nonequilibrium solid-solution (Ti,Ni)C powders were produced using powders of a Ti–Ni alloy (Ti:Ni weight ratio=7:3; purity > 99%; particle size < 75 μm) and of graphite (purity > 99%; average particle size: 7–10 μm; Alfa Aesar). The Ti–Ni alloy powders were obtained by the hydrogenation and dehydrogenation of a Ti–Ni alloy ingot, which was prepared by the arc melting of Ti and Ni (purity > 99.5%; average size: 3–20 mm; RNDKOREA) under an Ar atmosphere. The Ti–Ni alloy was transferred into a vacuum furnace for hydrogenation at a temperature of 873 K. Hydrogen gas (99.9999%) was introduced into the furnace to maintain a pressure between 5×10^5 and 7×10^5 Pa for 2 h. The hydrogenated Ti–Ni alloy was mechanically crushed into a size of < 75 μm. To remove the hydrogen, the Ti–Ni alloy powder was annealed at 973 K for 2 h in vacuum. The amount of graphite was adjusted to match the molar ratio of Ti in the Ti–Ni alloy, thus allowing TiC to form when the (Ti,Ni)C decomposed into TiC and Ni. The powders were then subjected to high-energy milling using a planetary mill (Pulverisette 5, Fritsch, Germany). Tungsten carbide balls were mixed with the Ti–Ni and graphite powders in a ball-to-powder weight ratio of 40:1. The powders were milled in a stainless steel bowl at 250 rpm in an argon atmosphere for 20 h. The phases of the milled powders were analyzed using X-ray diffraction (XRD) (SmartLab, Rigaku, Japan) with monochromated Cu Kα radiation (λ=1.5418 Å), which employed Si as a calibration standard. Differential scanning calorimetry (DSC) (SETSYS Evolution, SETARAM, France) was carried out in an Ar flow to analyze the reactions that occurred during the heat treatment of the (Ti,Ni)C phase. Heating rate of 5 °C/min was applied to all samples for the DSC analysis. The chemical composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, OPTIMA 5300DV, PerkinElmer) and CNO analysis (TCH-600, CS-600, LECO, Michigan, USA).

The (Ti,Ni)C powder was then compacted at 125 MPa into discs. The sintering behavior of the (Ti,Ni)C compacts was monitored using a dilatometer (DIL 420 PC, Netzsch Geraetebau GmbH, Selb, Germany). The compacts were sintered at 1250 °C and 1330 °C for 5 min and 30 min. Their microstructures were examined using field-emission scanning electron microscopy (FE-SEM) (MLA650F, FEI, Oregon, USA) and field-emission transmission electron microscopy (FE-TEM) (JEM-2100 F, JEOL, Tokyo, Japan). Vickers hardness was measured with an indenter load of 30 kg, and fracture toughness was calculated using the expression derived by Shetty et al. [19]. The sintering behavior and the microstructure of the (Ti,Ni)C compact were compared with those of a Ti(CN)–Ni sample prepared by the conventional mixing of powders of Ti(CN) (molar ratio of C:N = 1:1; purity > 99%; average particle size: 1 μm) and Ni (purity > 99%; average particle size: 4.2 μm).

3. Results and discussion

3.1. Preparation of the nonequilibrium (Ti,Ni)C phase

The nonequilibrium (Ti,Ni)C phase was synthesized by high-energy milling. Fig. 1 shows X-ray diffraction patterns of the phases evolved during the high-energy milling and the subsequent heat treatment of a mixture of Ti–Ni alloy and C. The as received Ti–Ni alloy was composed of Ti_2Ni and pure Ti (Fig. 1 (a)). The sample milled for 20 h revealed only a B1-structured phase (NaCl-like structure), suggesting that the reaction for carbide formation had run to completion (Fig. 1(b)). It was found that the amount of contaminants introduced from the jar and balls were not much (Table 1). Milling for 20 h led to the formation of a (Ti,Ni)C phase, as evidenced by its lattice parameter being smaller than that of TiC, thus indicating the participation of Ni in the reaction (Table 2). Fig. 1(c) shows the XRD pattern of the (Ti, Ni)C powder after heat treatment at 1200 °C. Only TiC and Ni peaks are present, suggesting that the (Ti,Ni)C phase decomposed to TiC and Ni during the heat treatment. The lattice parameter of the B1-structured phase after the heat treatment was larger than that of the milled powder. The extraction of Ni from the (Ti,Ni)C phase increased the lattice parameter, because the atomic size of Ni is smaller than that of Ti. The lattice parameter of the heat-treated B1-structured phase was smaller than that of the TiC phase (i.e., 4.3274 Å). This may be explained by the formation of

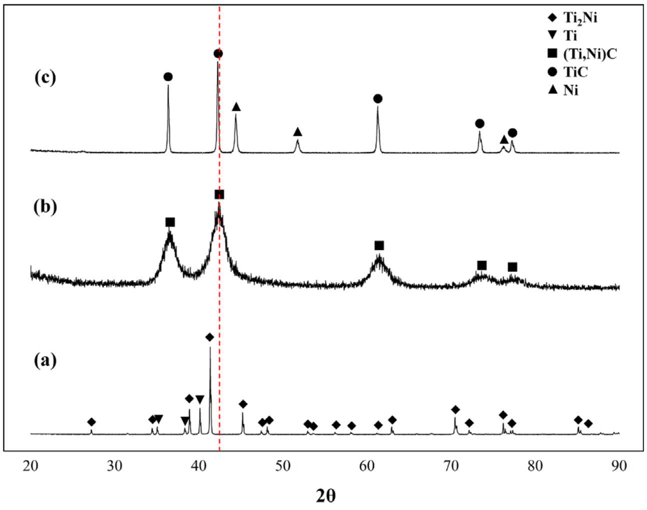

Fig. 1. X-ray diffraction patterns of (a) Ti–Ni raw material, (b) synthesized (Ti,Ni)C powder, and (c) (Ti,Ni)C powder heat treated for 2 h at 1200 °C.