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Preparation of a fine-structured TiC–Co composite by high-energy milling and subsequent heat treatment of a Ti–Co alloy

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Abstract

A fine-structured TiC–Co composite was prepared from a Ti–Co alloy by high-energy milling and subsequent heat treatment. The nanosized TiC and amorphous Co powders were synthesized by mechanical alloying of a Ti–Co alloy/graphite mixture. The amorphous Co phase was crystallized during the subsequent heat treatment. The DSC study revealed that Co in the nanosized TiC–Co powders melts at a lower temperature than that in conventional mixed TiC–Co powders. The coalescence of the nanosized TiC grains was effectively suppressed by the finely-dispersed Co phases making it possible to maintain the fine microstructure throughout the liquid-sintering process. The mechanical properties of the fine-structured TiC–Co composite were superior to not only the conventionally prepared TiC–Co composite but also to the previously reported TiC–Ni composites.

Keywords: A. Sintering; C. Hardness; Cermet; Titanium carbide; Coalescence

1. Introduction

Generally, cermets are TiC/Ti(CN) based composites which are produced by the sintering of a mixed powder of TiC/Ti(CN) and metallic binder phases (Ni or Co) [1]. TiC/Ti(CN) is largely responsible for the improved mechanical properties in cermets because TiC/Ti(CN) has excellent mechanical and chemical properties (high hardness, wear resistance, and chemical stability) [2]. The metallic binder phase is responsible for compensating for the low toughness of the TiC/Ti(CN). The metallic binder phase also functions as an additive to improve the sinterability of the cermets.

As mentioned above, the cermets consist of TiC/Ti(CN) and a metallic binder phase. Thus, the densification of the cermets can be divided into two sections depending on the sintering temperature. Below the metallic binder melting point, the cermets are sintered by solid state sintering. Although solid state sintering should not be neglected, the major densification of the cermets occurs by liquid phase sintering. Liquid phase sintering allows a faster and more complete penetration of the metallic binder phase into the pores. Therefore, the sintering of cermets is promoted by the addition of a metallic binder phase. However, it is not easy to fully densify cermets as much as WC–Co by liquid phase sintering because the wetting property of Ni and Co on the TiC/Ti(CN) (wetting angle $\approx 30^\circ$) is not excellent compared to that of Co on WC (wetting angle $\approx 0^\circ$) [3,4]. Consequently, the sintering temperature of TiC/Ti(CN) based cermets is higher (over 1500 °C) than that (below 1400 °C) of the WC–Co [5–8].

The poor wettability of Ni and Co on the TiC/Ti(CN) can also be the reason for the accelerated growth of the TiC/Ti(CN) particles during sintering because Ni and Co do not wet on the surface of TiC/Ti(CN) well; as a result, the possibility of coalescence between TiC/Ti(CN) particles increases. The enlarged TiC/Ti(CN) grains have a bad influence on the mechanical properties (especially hardness) of cermets [1]. If the particle size of raw TiC/Ti(CN) is ultrafine or nanosized, the grain growth rate of the particles by coalescence becomes much higher due to a larger surface area [9]. Thus, many studies on grain growth of TiC/Ti(CN) in cermets during sintering have been performed with the purpose of inhibiting

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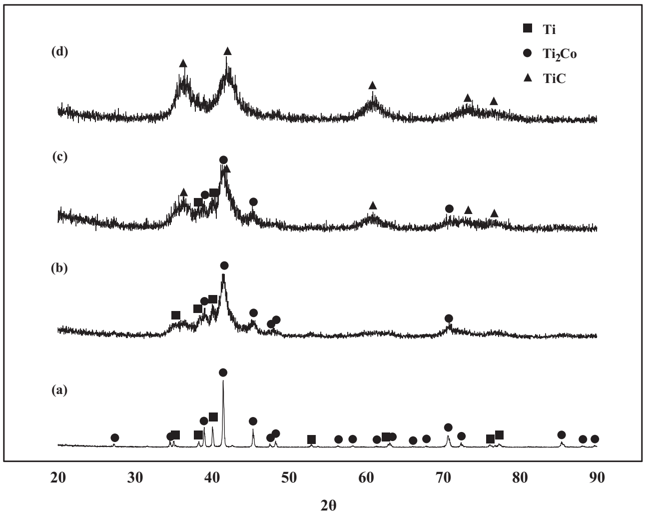

Fig. 1. XRD profiles for (a) the Ti–Co raw material and the Ti–Co and graphite powders milled for (b) 5, (c) 10, and (d) 20 h.

grain growth. Shin et al. found that the TiC grain size remained small in other carbides (Mo_2C and WC)-added systems after sintering [10]. It was also found that nanosized TiN particles distributed at the interface of the TiC/TiC grains impeded the grain growth of TiC in the TiC–Ni cermet effectively, and the grain refinement resulted in improved mechanical properties of the cermet [11]. These results on the grain refinement by the addition of other carbides and nanosized TiN are attributed to the decreased contiguity of the TiC grains and restricted diffusion between the carbides.

In this study, a TiC–Co composite with a fine microstructure is proposed using nanosized TiC particles containing a metallic binder phase (Co). The nanosized TiC particles with a finely dispersed Co phase were synthesized by high energy milling of the Ti–Co alloy and its subsequent heat treatment. The sintering behavior of the nanosized TiC–Co powders was examined in terms of the microstructural evolution. The mechanical properties of the fine-structured TiC–Co composite were also evaluated.

2. Experimental procedure

The nanosized TiC–Co powder was produced with Ti–Co alloy (weight ratio of Ti:Co = 7:3; purity > 99%; particle size < 75 μm), and graphite (purity > 99%; average particle size: 7–10 μm) powders. The Ti–Co alloy powder was obtained by the hydrogenation and dehydrogenation of the Ti–Co alloy ingot which was prepared by arc melting of the Ti and Co (purity > 99.5%; average size: 3–20 mm, respectively) under Ar atmosphere. The amount of graphite was adjusted to match the molar ratio of Ti in the Ti–Co alloy such that stoichiometric TiC was formed when the Ti reacted with the graphite. The powders were subjected to high-energy milling using a planetary mill (Pulverisette 5, Fritsch, Germany). Tungsten carbide balls were mixed with the Ti–Co and graphite powders in a ball-to-powder weight ratio of 40:1. A stainless steel bowl was used, and the powders were milled at 250 rpm in an argon atmosphere for 20 h. The milled powder was heat treated at 1000 °C for 1 h for the crystallization of the phases formed during milling. The phase of the synthesized powder was analyzed using X-ray diffraction (XRD) analyses (SmartLab, Rigaku, Japan). Monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å) was employed during the analyses, and Si was used as a standard to calibrate the diffractometer. Differential scanning calorimetry (DSC) (SETSYS Evolution, SETRAM, France) was done an Ar flow to analyze the reactions that occurred when the milled phase was heat treated. Additionally, the morphologies of the powders were observed with field-emission transmission electron microscopy (FE-TEM) (JEM-2100F, JEOL, Tokyo, Japan). Energy-dispersive spectrometry (EDS) was performed with a system using a FE-TEM attachment to observe the distribution of the elements in the powder.

The heat-treated powder was then compacted into discs with a pressure of 125 MPa. The compacts were sintered at 1200, 1300, and 1400 °C for 1 h. Then, the sintered specimens were polished, and their microstructures were observed with field-emission scanning electron microscopy (FE-SEM) (MLA650F, FEI, Oregon, USA). The Vickers hardness was measured with an indenter load of 30 kg, and the fracture toughness was calculated with an expression derived by Shetty et al. [12]. The sintering behavior and the microstructure of the compacts of the synthesized powder were compared to those of a TiC–Co sample (weight ratio of Ti:Co = 7:3) prepared by conventional mixing of TiC (purity > 99%; average particle size: 1 μm) and Co (purity > 99%; average particle size: 4.2 μm) powders.

3. Results and discussion

3.1. High-energy milling of Ti–Co alloy and C mixture

The high-energy milling of the Ti–Co alloy produced nanostructured TiC particles along with an amorphous Co phase. Fig. 1 shows the X-ray diffraction patterns of the phases evolved during the high-energy milling of the Ti–Co alloy and C mixture. The as-received Ti–Co alloy consisted of Ti_2Co and pure Ti (Fig. 1(a)). During the high-energy milling for 5 h, a reduction in the size of the Ti_2Co occurred while the Ti phase remained intact without reacting with C (See Fig. 2(b)). The metallic Ti reacted with C during the high-energy milling for 10 h, forming a TiC phase with a B1 structure (i.e., a NaCl-like structure) shown in Fig. 1(c). Ti_2Co phase decomposed afterwards to Ti and Co to form TiC because the reaction between Ti_2Co and C requires a higher activation energy than that between pure Ti and C [13]. Meanwhile, the peak intensity of the B1-structured phase dominated after milling for 20 h as the reaction between the Ti_2Co phase and C finishes. Accordingly, the sample milled for 20 h exhibited only a B1-structured phase (Fig. 1(d)). At this stage, no diffraction peaks were observed related to metallic Co or Co carbide. Carbide phases of cobalt do not exist in the cobalt–carbon system even though cobalt has some solubility for carbon at elevated temperatures (~1000 °C) [14]. Therefore, we assumed that Co in the milled powder existed as an amorphous form. Here, it should be mentioned that it was not possible to obtain the mixture (nano-