Fabrication of TiC-20 mass%Ni Cermet Using MA-PCS Process

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Mechanical alloying and pulsed-current sintering were used to synthesize TiC-20 mass%Ni cermet with ultra-fine TiC particles dispersed. The mixture, in which Ti and Ni elements were uniformly distributed, was prepared by mechanical alloying of Ti, Ni and graphite powders for 18 ks. TiC particles were produced in the mixture milled for longer than 18 ks through a combustion synthesis reaction during heating. The average grain size of TiC particles in the sintered body was 0.80 μm. The relative density of the sintered compact reached 92% of the theoretical one; its Vickers hardness was 2260 Hv.

1. Introduction

TiC-based cermet alloys are utilized for high-performance cutting tools because of their high hardness and chemical stability. It is important to enhance their mechanical properties, because the strength and toughness at room temperature for TiC-based cermet alloys are inferior to those of WC-Co hard metals. For that reason, new binders and effective additives for TiC-based cermet alloys have been required. Especially, miniaturization of TiC particles is one of the most effective techniques to improve the mechanical properties of TiC-based cermet alloys. Therefore, both synthesis of fine TiC particles and sintering of cermet alloys at low temperatures are indispensable for miniaturization of TiC particles in TiC-based cermet alloys.

In order to prepare TiC-Ni with fine TiC particles, mechanical alloying of elemental powders has been reported. However, TiC particles grow to be coarse during sintering even if the mechanically alloyed powder contains fine TiC particles. It has been reported that spark plasma sintering is a potential process to prepare cermet alloys at a lower temperature. The process can consolidate various powders in a short time under a pressure application at a relatively low temperature, leading to fine crystal grains. On the other hand, when a conductive material was sintered, plasma generation could not be confirmed. Then, this sintering process is called ‘pulsed current sintering (PCS)’ in this paper.

In this study, we investigated the synthetic behavior of TiC-20 mass%Ni cermet powder by mechanical alloying of elemental Ti, Ni and graphite powders. Subsequently, a TiC-20 mass%Ni cermet alloy containing ultra-fine TiC particles was fabricated by pulsed-current sintering of mechanically alloyed powder through TiC formation by a combustion synthesis reaction. Moreover, the microstructure of the obtained cermet alloy was investigated. The combustion synthesis reaction is an operative technique to fabricate fine-grained ceramics, composite materials, and intermetallic compounds.

2. Experimental Procedure

Using planetary ball milling for 18 and 36 ks, TiC-20 mass%Ni powders were synthesized from starting materials of commercial Ti powder (99.5 mass%Ti), Ni powder (99.9 mass%Ni), and graphite powder. The particle size was determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The powder after milling for 18 ks was poured into a 30-mm-deep graphite die of 10 mm internal diameter and 30 mm external diameter. The powder was consolidated using PCS at 1223 K under the pressure of 70 MPa. The sintered temperature was 20 : 1. The rotational speed of the planetary ball mill was 2.83 s⁻¹. The MA was performed under an argon gas atmosphere of reduced pressure 66 kPa to prevent the milled powder from oxidizing and nitriding. Microstructure and phase changes of the powder mixture with milling time were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Characterization of these obtained mixtures was carried out using differential scanning calorimetry (DSC) at a heating rate of 0.33 K/s under an argon gas flow in an alumina pan.

The powder after milling for 18 ks was poured into a 30-mm-deep graphite die of 10 mm internal diameter and 30 mm external diameter. The powder was consolidated using PCS at 1223 K under the pressure of 70 MPa. The sintered temperature was measured using an alumel-chromel type thermocouple with 3 mm inserted into the graphite die. The sintered compact was characterized by using XRD, SEM, Vickers hardness tester, and densimetry by Archimedes’ method.

The XRD data were obtained with a diffractometer using Cu Kα radiation (λ = 0.15418 nm) with a monochromator. The Vickers hardness was measured on the polished surface of the sintered compact with a load of 9.8 N and a loading time of 15 s.

3. Results and Discussion

3.1 Synthesis of TiC-20 mass%Ni powders by mechanical alloying and the characterization

Respective microstructures of TiC-20 mass%Ni powders
milled for 18 and 36 ks are shown in Figs. 1(a) and (b). In the powder milled for 18 ks, coarse flat powders and fine powders are found. On the other hand, large agglomerates are observed in the powder milled for 36 ks. The diameter of the largest agglutinate reached about 1 mm. The XRD patterns of TiC-20 mass%-Ni powders milled for 18 and 36 ks are shown Fig. 2. The XRD pattern of the powder milled for 18 ks (Fig. 2(a)) shows Ti and Ni peaks, without graphite peaks. Peaks of compounds such as TiC and TiNi are invisible. Therefore, the flat powder shown in Fig. 1(a) suggests the deformed solid metal of Ti and/or Ni. On the other hand, Fig. 2(b) shows the powder milled for 36 ks consists of TiC and Ni phases. It is suggested that TiC was formed through a combustion synthesis reaction in the vessel during mechanical alloying in the time range between 18 and 36 ks. The cross-sectional observation of the large agglomerate in the powder milled for 36 ks by SEM revealed fine TiC particles with the average particle size of 1.54 μm were dispersed in Ni matrix. According to the fluorescent X-ray analysis, the amount of Fe in the powder milled for 36 ks was 1.0 mass%, which corresponded to be more than three times as much as that in the powder milled for 18 ks. The detected Fe suggests the contamination from the vessel and balls during the mechanical alloying.

The peaks of Ni in the XRD pattern of the powder milled for 36 ks are shifted to the low angle side and broadened. At the early stage for MA of Ti, Ni and graphite powders, the peaks arising from graphite have disappeared. This suggests graphite would be amorphous phase and forced to diffuse in Ni matrix by MA. In other words, TiC has been already synthesized in the powder milled for 36 ks with carbon remained in Ni matrix. On the other hand, the generation of amorphous Ti-Ni phase in the mechanical alloying of TiC-Ni has been reported. It can be concluded that the peak shift of Ni is caused by the existence of Ni-C solid solution and Ti-Ni amorphous phase.

The DSC curves of TiC-20 mass%-Ni powders prepared by milling for 18 and 36 ks, and mixing by mortar, are shown in Fig. 3. The curves of the two milled powders reveal an exothermic reaction below 750 K. In the powder milled for 18 ks, the exothermic reaction includes two peaks: one at 573 K and another at 728 K. Because the peak of 573 K is not observed in the powder milled for 36 ks, in which TiC has already been synthesized, this peak is probably due to the exothermic reaction of TiC synthesis. For the mixture of Ti, Ni, and graphite powders by using a mortar, a higher temperature is necessary to synthesize TiC because the exothermic reaction is not completed below 900 K as shown in Fig. 3(c). The synthetic reaction of TiC probably progresses slowly at the low temperature in mechanically alloyed powders, even though the combustion synthesis reaction of Ti + C → TiC spreads instantaneously along with the great generation of heat. The peaks of graphite were not observed in the XRD pattern of the powder milled for 18 ks. It has been reported that graphite becomes amorphous at early stages of MA, and has partly dissolved in Ni powder. Therefore, TiC would be synthesized in the powder milled for 18 ks at the lower temperature than 573 K. The exothermic reaction of 728 K is thought to reflect stabilization of the nonequilibrium phase, such as Ni-based amorphous phase. It is inferred that the nonequilibrium phase was generated at the interface of Ti and Ni through mechanical alloying for 18 ks.
Therefore, this exothermic reaction at 728 K was observed in both mechanical alloyed powders. It is expected that TiC-20 mass%Ni powder milled for 18 ks can be sintered completely at the low temperature after synthesizing TiC at the early stage of sintering.

3.2 Consolidation of TiC-20 mass%Ni by pulsed current sintering and the characterization

Under 70 MPa pressure, the TiC-20 mass%Ni was consolidated using PCS. Figure 4 shows the relationship between the amount of shrinkage and the die temperature. After the compact expanded slightly to 400 K, it gradually shrunk with increasing the die temperature. The shrinkage is due to the combustion synthesis reaction of TiC, according to the DSC profile as shown in Fig. 3(a). It is thought that local heat generation was caused by the combustion synthesis reaction, and that the formation of necks among powder particles occurred at a low temperature. Considerable shrinkage at the temperatures of more than 1100 K is attributed to be typical densification of TiC-20 mass%Ni cermet. TiC-20 mass%Ni cermet fabricated by PCS at 1223 K had metallic luster and the relative density was 92% of the theoretical one of TiC-20 mass%Ni. On the other hand, TiC-20 mass%Ni cermet prepared at 1223 K by PCS of the powder milled for 36 ks had a metallic luster, but did not improve the compact density. As the powder milled for 36 ks has already generated TiC during the MA, the necking among particles would not be formed at the low temperature. In addition, because the powder milled for 36 ks has a rough and large particle size relative to that milled for 18 ks as shown in Fig. 1, larger energy would be necessary for the densification of the compact.

The XRD pattern of TiC-20 mass%Ni sintered by PCS process at 1223 K is shown in Fig. 5. The sintered body consists mainly of TiC and Ni. Compounds except for TiC are not synthesized though the synthetic temperature of TiC in the powder milled for 18 ks is low as shown in Fig. 3(a).

The microstructure of TiC-20 mass%Ni cermet sintered by PCS at 1223 K is shown in Fig. 6. The dark region corresponds to TiC and the bright one Ni. Ni pools of about 10 μm in length are observed. This is probably because liquid Ni appears at the high temperature and penetrates into the empty space. Figure 7 shows SEM images of the part where TiC is rich and the Ni pool. Ultra-fine TiC particles are exactly combined with Ni in the part where TiC is rich (Fig. 7(a)). This part would be formed during the combustion synthesis reaction that occurs at the low temperature. Since the Ni pool contains few TiC particles in Fig. 7(b), it was probably formed without accompanying the combustion synthesis reaction. A few pores are included in the Ni pool. Therefore, it is presumed that Ni pool was formed at a higher
temperature than that at which Ni softened. The existence of Ni pool makes the microstructure of TiC-Ni cermet inhomogeneous, leading to the decrease of its strength. It is necessary to optimize PCS sintering conditions (compaction pressure or heating rate) to produce a homogeneous compact at lower sintering temperature.

4. Conclusion

TiC-20 mass%Ni powder was synthesized rapidly through mechanical alloying of elemental Ti, Ni and graphite powders. The mechanically alloyed powder without TiC synthesized was consolidated with pulsed current sintering at a low temperature. The reaction path during pulsed current sintering and microstructures of TiC-20 mass%Ni were investigated. Results indicate the following:

1. TiC was synthesized by mechanical alloying of elemental Ti, Ni, and graphite powders using planetary ball mill for 36 ks with a ball-to-powder weight ratio of 20 : 1. The mechanically alloyed powder milled for 18 ks consisted of Ti and Ni phases without reacted compounds. Graphite became amorphous at the early
stage of mechanical alloying, and partially dissolved in 
Ni.
(2) The TiC-20 mass%Ni powder milled for 18 ks showed
exothermic reactions at 573 and 728 K. The powder
milled for 18 ks generated TiC in the pulsed current
sintering. The relative density of TiC-20 mass%Ni
sintered at 1223 K of the powder milled for 18 ks was
92%.
(3) The TiC-20 mass%Ni produced via the combustion
synthesis of TiC during pulsed-current sintering was a
composite material containing TiC particles with the
average size of about 0.8 μm. The TiC-20 mass%Ni
sintered at 1223 K showed Vickers hardness of about
2260 Hv.

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