

Ti-based nanocrystallites formation by high-energy milling

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ABSTRACT

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties. Since nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, considerable attention has been paid to the application of nanomaterials. In this study, Ti-based nanocrystallites including solid-solution phase were designed and prepared by high-energy milling. Especially, Ti-based alloys as starting materials were used to prepare the nanocrystallites.

Keywords: titanium, carbide, nanocrystallite, solid-solution, hard material

1 INTRODUCTION

It has been shown that the hardness of a cermet increases with increasing volume portion of the hard phase as well as decreasing grain size and increasing contiguity [1]. Lee & Gurland developed the relationship between hardness and microstructural parameters based on the well-known Hall-Petch relationship for bulk materials [2]. Meanwhile, cermets with a complete solid-solution phase have high levels of toughness, in contrast to conventional Ti-based cermets. Therefore, cermets with high hardness and high toughness can be obtained if the solid-solution cermet with nano-sized grains is prepared.

2 EXPERIMENTAL PROCEDURE

Ti-based nanocrystallites were produced using Ti-based alloy and oxide powders (99.9% purity). These were mixed with graphite to attain target compositions and the mixtures were subjected to high-energy ball milling using a planetary mill (Model Pulverisette 5, Fritsch, Germany). Tungsten carbide balls were mixed with Ti-based alloys/oxides and graphite at ball-to-powder weight ratios of 20:1 and 40:1. The milling times were varied from 10 hr to 20 hr. A stainless steel bowl was used, and all milling was conducted at a speed of 250 RPM. The milled powders were heat-treated at 1200 °C for 2 hr in a graphite furnace under a vacuum.

The phase evolutions during the milling process were analyzed using an X-ray diffractometer (Smartlab, Rigaku, Japan) with monochromatized Cu-K α radiation ($\lambda=1.5418$ Å) and Si (SRM640D, NIST, USA) as a standard. The crystallite sizes of the synthesized powders were calculated

using XRD peak broadening by the Halder-Wagner method [3]. The powder morphologies were observed by transmission electron microscopy (JEM-2100F, JEOL, Japan).

3 RESULTS AND DISCUSSION

3.1 Phase evolution during high-energy milling

As shown in Table 1, although all the transition metals have similar electro-negativity and electron valence values, the atomic sizes of Zr, Hf, Nb, Ta are much larger and Al is much smaller than those of Ti (0.176 nm), V (0.171 nm). Therefore, it is more difficult to form (Ti,Zr)C, (Ti,Hf)C, (Ti,Nb)C, (Ti,Ta)C, (Ti,Al)C than (Ti,V)C and more energy is needed to create the (Ti,Zr)C, (Ti,Hf)C, (Ti,Nb)C, (Ti,Ta)C, (Ti,Al)C phases as compared to the (Ti,V)C phase during the milling process. Thus, it is thought that the difference in the ability to form a solid solution in the B1 structure (NaCl-like structure) can explain why the mechanical energy for (Ti,Zr)C, (Ti,Hf)C, (Ti,Nb)C, (Ti,Ta)C, (Ti,Al)C formation is greater than that required for the formation of (Ti,V)C. This can be also confirmed by the XRD patterns of the annealed powders.

Fig. 1 shows images of the crystallites as observed by TEM. All of the synthesized powders are mainly composed of agglomerates of nano-sized crystallites. The figure also shows that the crystallite sizes of the synthesized powders by high-energy milling are ~30 nm. In addition, the crystallite sizes become larger after annealing at 1200 °C. These crystallite sizes of the powders are similar to the values calculated for XRD peak broadening. If the crystallite size of the (Ti,V)C phase is compared to that of the (Ti,Al)C phase, it can be known that the crystallite size of the (Ti,V)C is larger than that of the (Ti,Al)C. This can be explained in terms of the milling effect. As mentioned above, the mechanical energy for the synthesis of the (Ti,Al)C phase during milling is greater than that of the (Ti,V)C phase due to the difference in the ability to form a solid solution with Ti in the B1 structure. This clearly indicates that the (Ti,Al)C phase is formed at a later stage under a more severe condition than the (Ti,V)C phase. In other words, the size of the (Ti,Al)C phase becomes smaller than that of the (Ti,V)C phase because the (Ti,Al)C phase forms later during the milling process.

4 CONCLUSIONS

Nanocrystalline solid-solution carbides with nano-sized crystallites were prepared by the high-energy milling of Ti alloys/oxides with graphite. The following conclusions can be drawn from this study. (Ti,Al)C was formed under a more severe condition than (Ti,V)C because the tendency of forming a solid solution with Ti affects the synthetic behavior of (Ti,Al)C and (Ti,V)C. The atomic size of V (0.171 nm) is similar to that of Ti (0.176 nm). This means that the formation of the (Ti,V)C phase occurs more readily than that of the (Ti,Al)C phase. As a result, (Ti,Al)C forms at a later stage of milling and the crystallite size of the (Ti,Al)C phase becomes smaller than that of the (Ti,V)C phase after milling.

Element	Atomic radius (nm)	Common valence	Crystal structure of carbide	Electro negativity
Ti	0.176	4	B1	1.54
Zr	0.206	4	B1	1.33
Hf	0.208	4	B1	1.3
V	0.171	5	B1	1.63
Nb	0.198	5	B1	1.6
Ta	0.2	5	B1	1.5
Al	0.118	3	Rhombohedral	1.61

Table 1: Atomic information about the tendency of solid-solution formation.

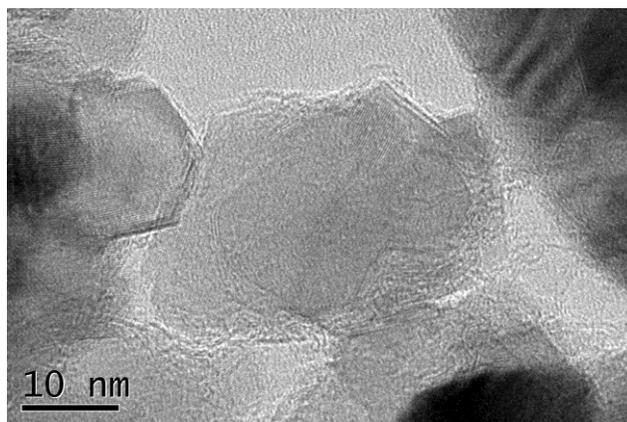


Figure 1: TEM images of the solid-solution nanocrystallites.

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