

# PREPARATION OF Ti-Al BASED NANOPHASE COMPOSITE POWDER BY MECHANICAL ALLOYING<sup>①</sup>

Wu Nianqiang, Wu Jinming, Li Wu<sup>†</sup>, Wang Guangxin, Li Zhizhang

*Department of Materials Science and Engineering,*

*Zhejiang University, Hangzhou 310027*

*<sup>†</sup> Hangzhou Institute of Applied Technology*

**ABSTRACT** A nanophase composite powder has been synthesized by ball milling of a mixture of elemental Ti, Al and graphite powder with the composition of  $\text{Ti}_{65}\text{Al}_{15}\text{C}_{20}$ . The nanophase TiC is distributed as ultrafine particles in an amorphous Ti-Al matrix. The present process combines alloying with solid-state reaction, which is controlled by interdiffusion of elements.

**Key word** composite Ti-Al-C system mechanical alloying

## 1 INTRODUCTION

During the past decade, extensive effort has been devoted to developing titanium aluminides ( $\text{Ti}_3\text{Al}$  and  $\text{TiAl}_3$  based alloys) because they possess an important combination of properties: low density, good oxidation resistance, as well as strength and modulus retention at high temperature<sup>[1]</sup>. These intermetallic compounds, however, have poor toughness near room temperature. Therefore, much attention has been focused on a ceramic-reinforced titanium aluminide matrix composite in order to solve this problem<sup>[2,3]</sup>. In particular, the in-situ particle-reinforced composites are most attractive, because the in-situ formed fine dispersoids are thermally stable and directly bonded with the matrix, assuring that the composite matrix has enough strength to transfer stress. Stiff ultrafine ceramic particles such as  $\text{TiB}_2$  and  $\text{Al}_2\text{O}_3$  are introduced in-situ into the intermetallics by an exothermic process termed XD<sup>TM</sup><sup>[4]</sup> and the self-propagating high-temperature synthesis (SHS)<sup>[5]</sup>.

Mechanical alloying, a non-equilibrium, low temperature, solid state reaction process, has been used successfully to produce numerous nanocrystalline intermetallic compounds and

amorphous alloys<sup>[6,7]</sup>. Moreover, mechanical alloying and the following consolidation provides with an innovative process of in-situ preparation of composite materials. Ultrafine grain size as well as uniform distribution of the constituting phases are expected to result in an improvement of mechanical properties for the composites prepared by this route. Suzuki *et al*<sup>[8,9]</sup> have reported that reaction milling of an equiatomic mixture of Ti and Al with n-heptane and following consolidation produce fine composite of TiAl and  $\text{Ti}_4\text{Al}_2\text{C}_2$  complex carbide. It has also been shown by Kesikinen *et al*<sup>[10]</sup> that mechanical alloying of  $\text{Ti}_x\text{Al}_{1-x}$  with hexane results in the formation of TiC and  $\text{TiH}_{2-x}$ .

In the present investigation, the nanophase composite powders were synthesized in-situ by mechanical alloying of the elemental Ti, Al and graphite mixture with the composition of  $\text{Ti}_{65}\text{Al}_{15}\text{C}_{20}$ . The nanophase TiC particles are distributed homogeneously in an amorphous Ti-Al matrix.

## 2 EXPERIMENTAL

The elemental titanium (< 150  $\mu\text{m}$ , > 99.5%), aluminum (< 150  $\mu\text{m}$ , > 99.5%)

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and graphite powder ( $< 50 \mu\text{m}$ ,  $> 99.5\%$ ) were mixed with the composition of  $\text{Ti}_{65}\text{Al}_{15}\text{C}_{20}$ . The powder mixture was sealed in a hardened stainless-steel vial in an argon-filled glove box. The milling media were the steel balls of 10 mm diameter and the weight ratio of the balls to the powder was 30:1. Milling was conducted in a QM-1SP planetary ball mill at a rotation speed of 230 r/min. At selected times, a small amount of the as-milled powders was taken for analysis. The progress of mechanical alloying was followed by a Rigaku D/max-3B X-ray diffractometer (XRD) with  $\text{CuK}\alpha$  radiation and a Phillips EM420 transmission electron microscope (TEM). The powders for TEM observation were scattered in ethanol and then the suspended powders were mounted on a copper microgrit.

### 3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the samples after different milling times. After a milling time of 5 h, the intensities of the Al peaks decreased. The carbon peak disappeared, the peaks of Ti shifted toward higher Bragg angles due to dissolution of the Al atoms in the hcp Ti lattice. It was assumed that the contributions of the grain size and the internal strain to the integrated intensities of peaks follow the Cauchy and Gaussian distributions respectively<sup>[11]</sup>, the grain sizes of Ti and Al after milling for 5 h were then estimated to be 18 nm and 24 nm respectively, and the strains in the Ti and Al lattice were 1.1% and 1.3%, respectively. After 10 h of milling, XRD revealed a broad diffraction maximum superimposed by Bragg peaks of the Ti solid solution. This indicates that the material is partially amorphous. In addition, traces of TiC were observed in the XRD pattern. On further milling, the intensities of the peaks corresponding to TiC increased. And the lattice parameters of TiC were determined to be 0.4273 nm and 0.4315 nm for the samples milled for 20 h and 40 h respectively. This implies that the carbon content in TiC compound increased with milling time. Thus it can be deduced that this reaction is controlled by gradual diffusion of the components. On milling up to 40 h, the peaks of Al

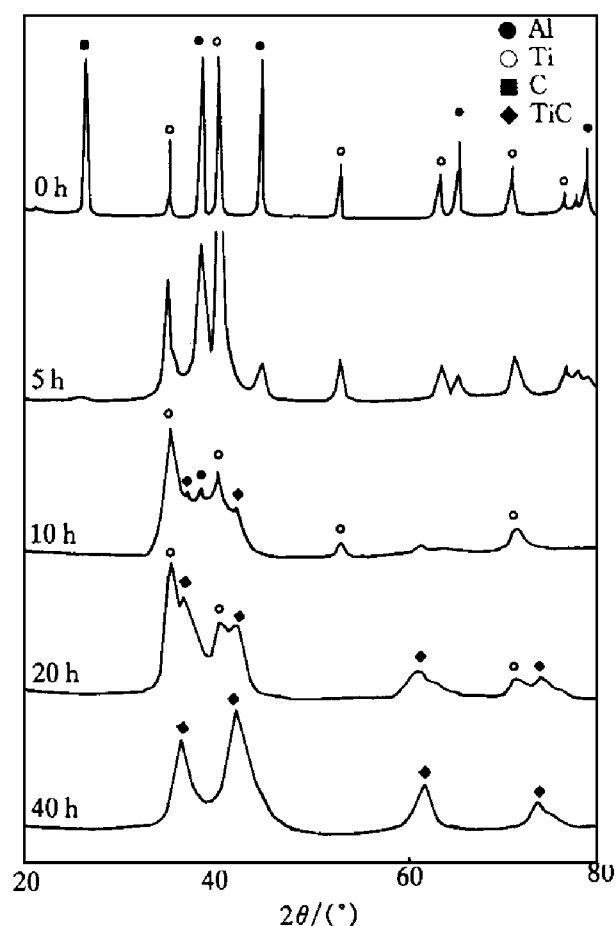
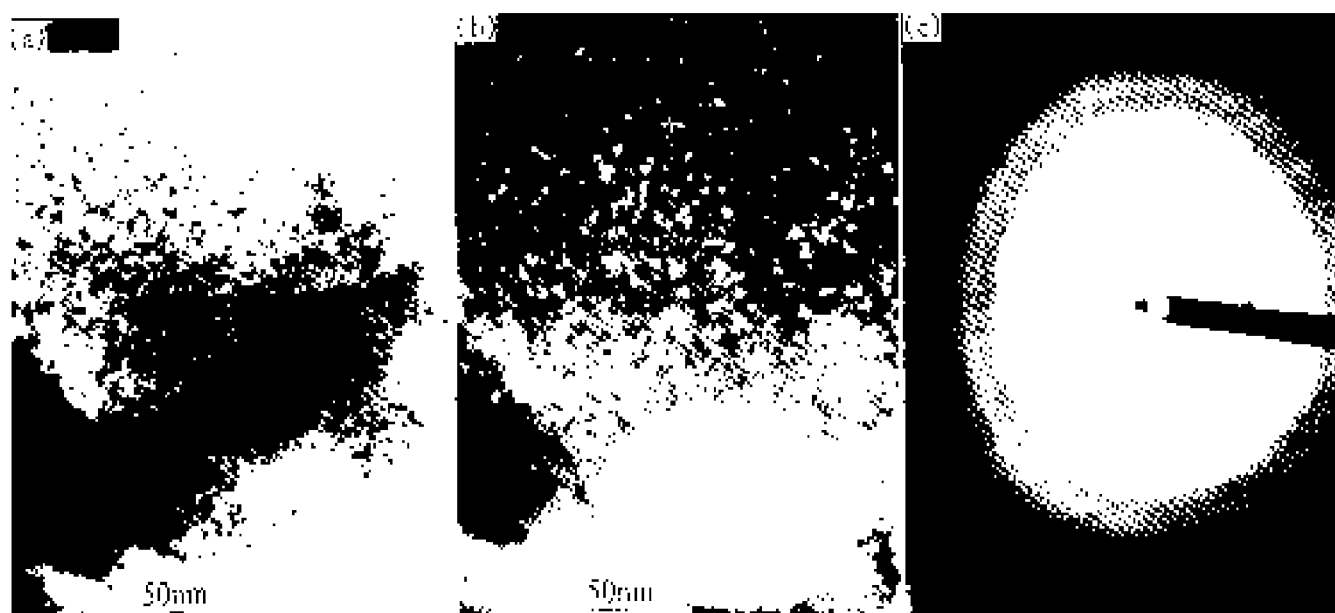


Fig. 1 XRD patterns of samples after different milling times

and Ti completely vanished. The TiC peaks, together with a trapped halo peak corresponding to an amorphous phase, are visible in the XRD pattern. Further milling up to 80 h did not cause any significant variation. The lattice parameters of TiC are constant at the milling duration of 40 ~ 80 h. The estimated lattice parameter of TiC ( $a = 0.4315 \text{ nm}$ ) is slightly smaller than that ( $a = 0.4327 \text{ nm}$ ) given by the JCPDS database (32 - 1383).

The sample milled for 40 h was investigated by TEM. The selected area electron diffraction pattern (Fig. 2(c)) exhibits the smooth fcc rings of TiC with a lattice parameter of 0.432 nm, together with the superimposed halo pattern corresponding to an amorphous phase. The bright-field (Fig. 2(a)) and dark-field image (Fig. 2(b)) show that nanophase TiC is distributed homogeneously as ultrafine particles with diameters of about 10 nm in an amorphous matrix. The XRD and TEM analyses show that a nanophase composite powder was synthesized by ball



**Fig. 2 Bright image (a), dark image (b) and selected area electron diffraction pattern (c) for sample milled for 40 h**

milling of  $\text{Ti}_{65}\text{Al}_{15}\text{C}_{20}$  elemental powder mixture.

Since the temperature rise induced by collision of balls was estimated to be  $450 \sim 573 \text{ K}$ <sup>[12, 13]</sup>, the thermodynamic functions in the Ti-rich Ti-Al-C system ( $\text{Al} < 50\%$ ,  $\text{C} < 25\%$ , Ti bal, mole fraction) at 500 K have been analyzed and calculated<sup>[14]</sup>. The results show that the free energy of formation of TiC is much larger than those of the other possible formed phases ( $\text{Ti}_3\text{Al}$ ,  $\text{TiAl}$ , supersaturated  $\alpha\text{-Ti}(\text{Al}, \text{C})$  solid solution, and amorphous Ti-Al-C phase). Thermodynamically, carbon atoms are preferably bonded with Ti atoms and TiC forms favorably. Carbon and some titanium are consumed in the matrix phase due to formation of TiC. Thus, the matrix is mainly composed of titanium and aluminum, and the content of titanium is roughly estimated to be around 75% Ti (mole fraction). The formation of amorphous phase in the Al-Ti system by MA had been reported to occur in the composition range from 40% to 80% Ti (mole fraction)<sup>[15–18]</sup>. Hence, it is reasonable to conclude that an amorphous matrix phase is formed in the matrix.

The reaction ( $\text{Ti} + \text{C} \rightarrow \text{TiC}$ ) usually completes above  $1800^\circ\text{C}$ , whereas TiC is gradually formed via an interdiffusion-controlled reaction at relatively low temperature, which indicates that a unique condition occurs during mechanical alloying. It is known<sup>[19]</sup> that the fundamental

action of mechanical alloying is the repeated cold welding and fracture of the powder particles. Cold welding brings about intimate contact of atoms, while fracture decreases the particle size and creates new clean interface. As a result, this interplay between welding and fracture effectively kneads the internal structure so that the diffusion distance required for reaction is reduced. Moreover, at the early stage of mechanical alloying, plastic deformation leads to a large number of defects such as dislocations and grain boundaries, providing an excess of short-circuit diffusion pathways. At the late stage of mechanical alloying, an amorphous phase is formed. Following Chaudhari *et al.*<sup>[20]</sup>, in the amorphous alloy the small atoms diffuse interstitially through the skeleton formed by the large atoms and it seems that the diffusion rate is rather high. In addition, we believe that the heat released during formation of TiC not only provides thermodynamic driving force but also favors the reaction kinetically. Because the heat generated by the formation of initial TiC raises the temperature, the diffusivity of atoms is enhanced.

A previous investigation<sup>[21]</sup> has shown that ball milling of binary elemental Ti and graphite powders results in formation of TiC by an abrupt combustion reaction. However, in the present work no combustion reaction is observed. This may be attributed to dilution of the reactants be-

cause of addition of Al. Dilution of reactants can lead to an increase of the ignition temperature for combustion reaction and separation of reactants<sup>[22]</sup>.

#### 4 CONCLUSIONS

A nanophase composite powder has been synthesized by ball milling of the elemental Ti, Al and graphite powder mixture with a composition of  $\text{Ti}_{65}\text{Al}_{15}\text{C}_{20}$ . The nanophase TiC is distributed as ultrafine particles in an amorphous Ti-Al matrix. The present process combines alloying with solid-state reaction, which is controlled by interdiffusion of elements.

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