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Communication

Formation mechanism of Ti_5Si_3 powder by mechanical alloying

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Abstract: The formation mechanism of stoichiometry Ti_5Si_3 by mechanical alloying (MA) from elemental powders has been investigated. The results of XRD and SEM analyses of the powder show that Ti_5Si_3 can be synthesized by MA in a planetary mill with two different formation mechanisms. Ti_5Si_3 was formed gradually with the mechanical collusion reaction (MCR) mechanism under a lower impact energy, and the Ti_5Si_3 was formed abruptly with the self-propagating high-temperature synthesis (SHS) formation mechanism under a higher impact energy.

Key words: mechanical alloying; intermetallic; Ti_5Si_3; formation mechanism

1 Introduction

In recent years intermetallic Ti_5Si_3 has attracted more interest because a number of its properties have potential in materials applications. The combination of high melting point (2403 K), low density (4.32 g/cm^3), good strength at high temperature, good creep resistance, and high oxidation resistance makes Ti_5Si_3 an attractive candidate for high-temperature structural applications [1-7]. It can also be used in microelectronics as interconnections and diffusion barriers for integrated circuits, where low electrical resistivity and chemical compatibility with silicon substrates are needed [3].

Mechanical alloying (MA) is a promising method for producing intermetallics [8]. MA was developed in the late 1960s [9], mainly for production of the oxide dispersion strengthened superalloy powder. During ball milling, the diffusion couples form through a dynamic process of deforming, fracturing and cold-welding of the powders. Each powder consists of a large number of diffusion couples formed by sequential stacking of elemental nano-sized thin elemental layers or by agglomeration of equiaxed elemental particles [10]. The reaction occurs at low temperature. The phase formation mechanism of MA is self-propagating high-temperature synthesis (SHS) or gradual formation according to the enthalpy of the system and the variety of compositions. This had been observed in intermetallics $MoSi_2$ and Ni_3Si fabricated by mechanical alloying [11, 12]. But with regard to the intermetallics Ti_5Si_3, the study on the formation mechanism by MA was far from enough. The previous work has found Ti_5Si_3 formation in the mechanism of SHS [7]. In this paper we have investigated the formation mechanism of Ti_5Si_3 by mechanical alloying with a planetary ball mill at different rotational speeds and milling balls for various time. There are two different formation mechanisms that have been observed when MA with different milling balls.

2 Experimental procedure

Elemental powders of titanium with a purity of 99.5% and Si with a purity of 99.95% (both with an average grain size of 2-4 μm) were used. Mechanical alloying (MA) was performed by using a centrifugal planetary ball mill. A vacuum stainless steel vial (with 75 mm in diameter and 70 mm long) and ball (with 20 and 10 mm in diameter) were used for milling with the rotational speed (vials speeds) varying from 330 to 510 r/min. The elemental powders with the stoichiometric composition of Ti_5Si_3 were placed in the vial. The mass of the powder charge was 10 g, and the mass ratio between the steel balls and the powder charge was 30:1 for all cases. The powder sample and milling balls were loaded into the vial, then vacuumized and filled with purified Ar gas to avoid being contaminated. To ensure the same ball/powder mass ratio, the powder was completely removed and the new powder was loaded after every milling interval.

Structural evolution of the powder during the MA was monitored using a Philips X'pert x-ray diffraction (XRD) machine with Cu K_α radiation operated at 40 kV and 40 mA, the scanning speed used was 5°/min with a scan step of 0.03°.

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The morphologies of the milled powders were examined by scanning electron microscopy (SEM; Model S-570).

3 Results and discussion

The XRD patterns of Ti-Si powders milled for 16 h at different rotational speeds with the small milling balls are presented in **figure 1**. The XRD pattern in figure 1(b) shows that Ti and Si peaks remain in the pattern of the powder, and no compound is created, but the intensity of Si peaks have prominently decreased, and Ti peaks broaden. Changing the rotational speed to 420 r/min, as shown in figure 1(c), Ti peaks broaden and the intensity decreases more obviously, while a little Ti_5Si_3 reflections begin to appear. The intermetallic Ti_5Si_3 appears as a major composition when milled at a rotational speed of 510 r/min. The present result indicates that the mechanical alloying process relates to the rotational speed.

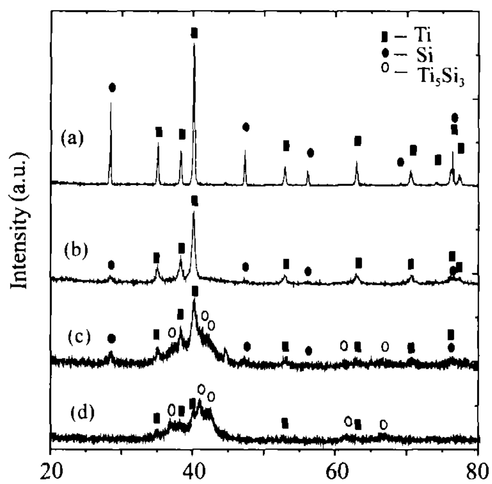

Figure 1 XRD patterns of Ti-Si powders milled for 16 h at different rotational speeds: (a) as-blended; (b) 330 r/min; (c) 420 r/min; (d) 510 r/min.

It is noticed that the $\{101\}_{Ti}$ peak position is not shifted to a large angle direction to form a Ti(Si) solid solution [4]. On the contrary, the $\{101\}_{Ti}$ peak position shifts slightly to a small angle direction, which may be just induced by Ti particles undergoing compress deformation.

Figure 2 shows the XRD spectra of Ti_5Si_3 MA for different time at a rotation speed of 510 r/min. It shows that there are the diffraction peaks of the intermetallic Ti_5Si_3 when the powder is milled for 8 h. While the intensity of $\{101\}_{Ti}$ diffraction peaks is in the highest position, the Si diffraction peak exists also. Figure 2(b) shows that a mass of intermetallic Ti_5Si_3 formed when milled for 12 h, and the Si peak becomes barely visible. Figure 2(c) indicates that the major diffraction peaks are Ti_5Si_3 when milled for 24 h, the diffraction peaks of Ti become very weak, and no diffraction peak of Si is found. Prolonging the milling time to 48 and 96 h, as shown in figures 2(d) and (e), there are two amorphous halos at 2θ = 35-46°, which indicates that the intermetallic Ti_5Si_3 becomes amorphous phase. This phenomenon has also been observed in the Mo-Si system [13], and the mechanism that the new compound creation needs long time during MA may be attributed to such a mechanical collision reaction (MCR) with the every suitable impact.

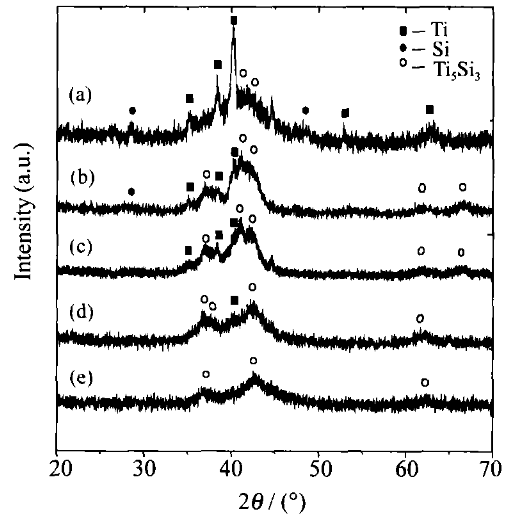

Figure 2 XRD patterns of Ti-Si powders milled at 510 r/min with small milling balls for 8 h (a), 12 h (b), 24 h (c), 48 h (d), and 96 h (e).

In order to investigate the mill energy influence on the formation mechanism, we changed the small milling balls to big balls with the same mass ratio and rotation speed. Comparing with figure 2, **figure 3** shows that the abrupt reaction for Ti_5Si_3 occurs in a short time by using the big milling balls, and all the Ti and Si elements transform to intermetallic Ti_5Si_3. Such an explosive reaction indicates that the formation mechanism of Ti_5Si_3 in this state is attributed to SHS.

Figure 4 shows the difference of crystallite sizes of the milled powders by different milling energies. It can be seen that the crystallite size of milling with small balls is finer than that of milling with big balls. MA is a solid-state processing technique that consists of repeated fracturing and cold-welding of powder particles in a dry, high-energy ball mill. Flattening or fracturing of the powder particles creates an atomically clean surface, which has a higher surface energy. The system energy increases as the particle size decreases and the activation energy decreases. When the crystallite particle size decreases to a certain critical dimension during MA, the impact can increase the local temperature to match the reaction temperature, and a new compound is created. The reaction $5Ti + 3Si \rightarrow Ti_5Si_3$ is exothermic. A higher milling speed provides a higher impact energy. So the reaction occurs in powders with larger crystallite sizes, and it releases more heat. When the formation heat of Ti_5Si_3 is high enough to heat the circumambient particles to the reaction temperature, the reaction propagates and Ti_5Si_3 forms through the SHS mechanism. Otherwise, Ti_5Si_3 forms through the MCR mechanism.

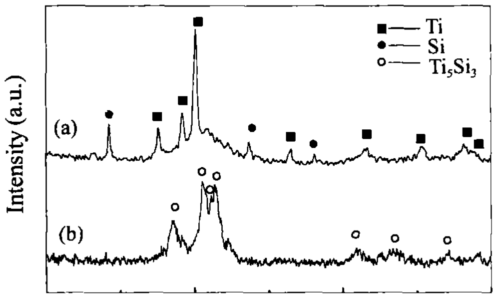

Figure 3 XRD patterns of Ti-Si powders milled at 510 r/min with big milling balls for 4 h (a), 5 h (b).

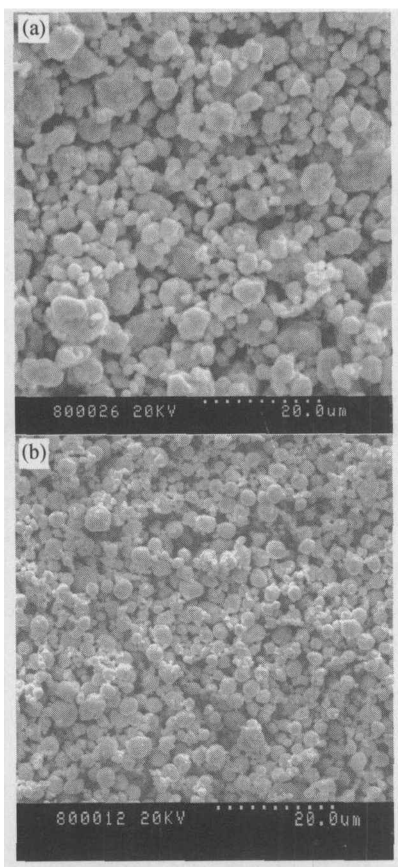

Figure 4 SEM micrographs of milled powders at 510 r/min: (a) Big balls for 5 h; (b) Small balls for 12 h.

4 Conclusions

(1) Ti_5Si_3 can be synthesized by using the mechanical alloying method from elemental powders (Ti_5Si_3 stoichiometry).

(2) Ti_5Si_3 was formed gradually with the mechanic collusion reaction (MCR) mechanism under a lower impact energy, such as small milling balls at rotational speeds of 420 and 510 r/min.

(3) Ti_5Si_3 was formed abruptly with the self-propagating high temperature synthesis (SHS) formation mechanism under a higher impact energy, such as big milling balls at the rotational speed of 510 r/min.

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