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Solid-state reaction in nanocrystalline Fe/SiC composites prepared by mechanical alloying

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Different solid-state reactions, i.e. $Fe + SiC \rightarrow Fe_3C + Fe(Si)$, and $Fe + SiC \rightarrow Fe_3Si + Fe_2Si + C$, were found in mechanically alloyed nanocrystalline Fe/SiC composites induced by prolonged milling or heat treatment, respectively. The solid-state reaction between nanocrystalline iron and SiC upon heating is greatly enhanced when compared with that between bulk iron and SiC. It is believed that the prolonged milling-induced reaction is related to the changed thermodynamics and kinetics while the heat-treatment-induced reaction, completed during a short time, is attributable to the changed reaction kinetics.

1. Introduction

Nanocrystalline metals and ceramics, which have been widely studied in recent years [1–7], are novel materials with properties significantly different from those of conventional polycrystalline materials. In order to obtain nanocrystalline structures, different techniques are available which may lead to certain modified properties of the final materials. Among these, mechanical milling/alloying offers the possibility of producing nanocrystalline structures in different alloy systems and of producing relatively larger powders (>10 μm) with a homogeneous nanocrystalline structure which is often difficult to obtain with alternative techniques such as inert-gas condensation. The mechanical milling/alloying technique has been used to prepare various kinds of nanostructured materials, such as pure elements [8–13], solid solutions [14–24], intermetallic compounds [8, 25–29], and dispersion-strengthened alloys [30–34]. The starting materials employed for the mechanical milling process are single-phase components whereas those for mechanical alloying are typically two-, or more than two-, component powders. There are many potential applications for silicon-based structural ceramics such as SiC and metal–ceramic composites in advanced engineering components. In particular, some metal–ceramic systems find use not only as a composite material but also in the joining of ceramics and metals. Therefore, a considerable amount of work has been performed to investigate the preparation, structures and/or properties of metal–ceramic systems [35–48]. In view of these considerations, there is a substantial interest in studying preparation and properties of nanocrystalline composites, such as metal–ceramic systems. In a previous work, we have studied the formation, structure and magnetic properties of nanocrystalline Fe/SiC composite by mechanical alloying [49]. In the present work, we sought to investigate the solid-state reaction in mechanically milled nanocrystalline Fe/SiC composites induced by a prolonged milling and heat treatment.

2. Experimental procedure

The mechanical alloying was carried out in a conventional planetary ball mill. Powders of iron (99.5%, average particle size less than 50 μm) and SiC (99.9%, average particle size 5 μm) were mixed with a starting composition of $Fe_{50}(SiC)_{50}$ (at %) and put into a hard bearing steel vial under a dry, pure argon atmosphere. The total weight of the powders was about 10 g. The mechanical alloying was performed with a ball-to-powder weight ratio of 40. The rotation rate of the vial was 720 r.p.m. The ball-milled powders were analysed by X-ray diffraction (XRD) and differential thermal analysis (DTA). The XRD experiments were carried out by a Rigaku X-ray powder diffractometer with CuK_α radiation ($\lambda = 0.154$ nm). The DTA experiment was performed at a heating rate of 20 K min^{-1}. The samples employed (80 mg) for DTA were put in Al_2O_3 pans and the heating was carried out in a vacuum better than 1.3×10^{-4} Pa.

3. Results

Fig. 1 shows a sequence of X-ray diffractograms of a ball-milled powder mixture of iron and SiC for various times. The initially sharp crystalline diffraction peaks are considerably broadened after 8 h milling as a result of the refinement of grain size and the increase of internal strain. Further milling results in

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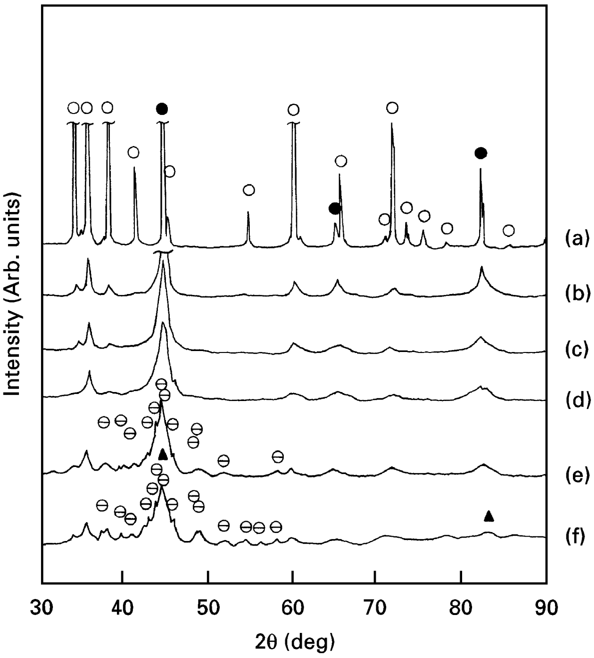

Figure 1 X-ray diffraction patterns of an equiatomic powder mixture of iron and SiC after (a) 0 h, (b) 8 h, (c) 24 h, (d) 40 h, (e) 60 h, and (f) 100 h milling under an argon atmosphere. (●) Fe, (○) SiC, (⊖) Fe_3C, (▲) Fe(Si).

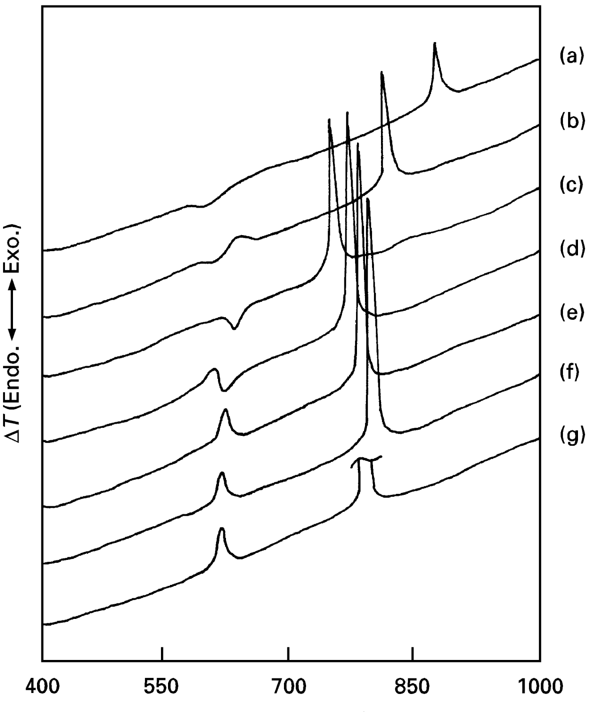

Figure 2 DTA traces of an equiatomic powder mixture of iron and SiC powders after (a) 4 h, (b) 8 h, (c) 16 h, (d) 24 h, (e) 40 h, (f) 60 h, and (g)100 h milling.

the formation of Fe_3C intermetallic compound (60 and 100 h) and Fe(Si) solid solution (100 h), as shown in Fig. 1e and f. The crystallite size, which is calculated from the XRD profiles [39], is less than 40 nm for both iron and SiC after 8 h milling. Furthermore, a structural study by transmission electron microscopy (TEM) reveals that an abundance of nanocrystalline grains, with sizes ranging from 4–20 nm, exists in the powder mixture mechanically alloyed for 24 h [39]. These experiments confirm the formation of a nanocrystalline Fe/SiC composite by ball milling because it is usually recognized that the grain size for nanostructured materials ranges from 1–100 nm.

Shown in Fig. 2 are the DTA curves obtained from the powder mixture of iron and SiC ball milled for various times. All of the curves show an endothermic peak and/or an exothermic peak around 610 °C. For the subsequent peaks which are clearly exothermic, the heat release increases while the position of the peak changes (ranges from 750–867 °C) with increasing milling time. For a more distinct comparison, the temperatures of these subsequent large exothermic peaks are shown in Fig. 3. Also shown in Fig. 3 are the average crystallite sizes of iron and SiC crystals. The average crystallite sizes were calculated from the XRD profiles by the method suggested previously [49].

Fig. 4 shows the XRD patterns of heat-treated Fe/SiC composites mechanically alloyed for 8, 24 and 100 h, respectively. The heat treatment consists of heating to 925 °C at 20 K min^{-1} and then cooling to room temperature in the DTA. After the heat treatment, the reaction products are Fe_3Si, Fe_2Si and carbon (C), as shown in Fig. 4.

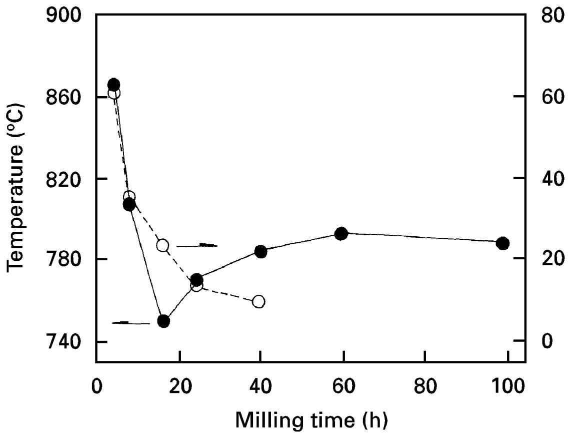

Figure 3 (- - -) The average size (AVS) of iron and SiC crystals and (——) the reaction temperature in a mechanically milled Fe/SiC powder mixture as a function of milling time.

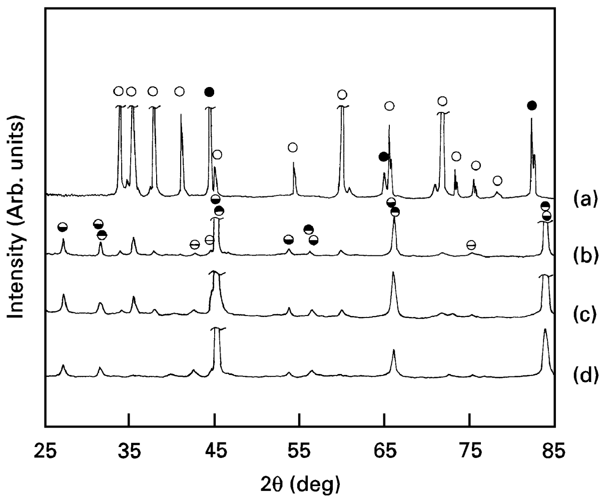

Figure 4 X-ray diffraction profiles of a powder mixture of iron and SiC milled for (a) 0 h, (b) 8 h, (c) 24 h and (d) 100 h, respectively, then heated to 925 °C at 20 K min^{-1} and cooled to room temperature. (●) Fe, (○) SiC, (◒) Fe_3Si, (◓) Fe_2Si, (⊖) C.

4. Discussion

The XRD profiles shown in Fig. 1 reveal that the prolonged milling of nanocrystalline Fe/SiC composites results in the formation of Fe–C compounds. The solid-state reaction between a metal and SiC, however, usually produces metal silicides and carbon [41, 46, 48, 50]. It is believed that the formation of metal silicides is thermodynamically favoured while that of metal carbides is not. For example, the Gibbs free energies of formation of Fe_3C and Fe_3Si at 298 K are $+20.1$ and $-94.6\ \mathrm{kJ\,mol^{-1}}$, respectively [51]. Furthermore, the solid-state reaction between iron and SiC generally occurs at high temperature because the nucleation and growth of the products at room temperature are rather difficult. Therefore, the prolonged milling (60 and 100 h) of nanocrystalline Fe/SiC composites has changed the thermodynamics and kinetics of this solid-state reaction.

It was reported [1] that the excess Gibbs free energy at 500 K for chromium atoms located in a nanocrystalline grain boundary may be as high as $+180\ \mathrm{kJ\,mol^{-1}}$. Based on this, it may be reasonable to assume that a similar magnitude excess Gibbs free energy may also be obtained for the iron and SiC located in a nanocrystalline grain boundary. The enthalpy of formation of SiC in the standard state is only $-67.0\ \mathrm{kJ\,mol^{-1}}$ [52], which is obviously lower (in absolute) than the above-mentioned excess Gibbs free energy. Therefore, some SiC located at the grain boundaries may decompose into elemental silicon and carbon at room temperature because of the high-energy state of SiC may make it become positive in free energy. Kinetically, the rate of diffusion of iron into SiC at room temperature is very low. However, if the diffusion of carbon and silicon in nanocrystalline iron is considered and their diffusion activation energies are hypothesized to be 40% of those for carbon and silicon in ordinary crystalline α-Fe [1, 53], the chemical diffusion coefficients for carbon and silicon in nanocrystalline iron at 298 K are calculated to be 9.4×10^{-13} and $2.5\times10^{-20}\ \mathrm{m^2\,s^{-1}}$, respectively. Because there are no data for the diffusion of silicon in α-Fe at room temperature, the data [53] from 900–1400 °C are extrapolated to room temperature to make the above calculation. It can be seen that the former coefficient is much larger than the latter one. In addition, the solubility of carbon in α-Fe at room temperature is very small (0.007 wt %) [54]. Furthermore, the Gibbs free energy of formation of Fe_3C from nanocrystalline iron and carbon may be negative at room temperature when the solid-state reaction occurs at a nanocrystalline grain boundary because of the highly positive excess Gibbs free energy of iron in the grain boundaries. Therefore, Fe_3C can be formed, from the viewpoint of the changed thermodynamics and kinetics, after 60 and 100 h milling. After 100 h milling, we also find the formation of a solid solution of silicon in α-Fe, as indicated by the shift in the position of Fe(2 1 1) Bragg peak. The reaction in nanocrystalline Fe/SiC composites induced by a prolonged ball milling at room temperature, i.e. $Fe + SiC \rightarrow Fe_3C + Fe(Si)$, is obviously different from the heat- activated reaction between bulk iron and SiC, which yields Fe–Si compounds and carbon [41, 46, 48, 50].

In the DTA curves of the Fe/SiC powder mixture, ball milled for 16, 24 and 40 h, respectively, there are weak exothermic peaks at about 310 °C which have not been shown in Fig. 2. These exothermic peaks may be attributed to the crystallization of a small amount of amorphous Fe–C alloy formed by the ball milling into carbide phases, e.g. Fe_3C [55]. However, there is no similar peak for the powder mixture milled for 60 and 100 h, respectively. This may be related to the transition from the amorphous Fe–C alloy into carbide phases by further milling [55]. The exothermic peaks around 610 °C in some scans may be related to the decomposition of various carbides [55] while the endothermic peaks around 610 °C in some scans may be related to an unknown solid-state reaction. The evidence for this is that the XRD profiles show a small amount of Fe_3C phase existing in the Fe–SiC composite, which is ball milled for 40 h, then heated to 510 and 680 °C, respectively, at $20\ \mathrm{K\,min^{-1}}$, and cooled to room temperature. In comparison, there are no similar endothermic and/or exothermic peaks in the DTA curves of iron or SiC powder, ball milled separately. Further study is needed to verify the solid-state reaction related to the endothermic and/or exothermic peaks around 610 °C.

The relatively large exothermic peaks ranging from 750–867 °C are related to the solid-state reaction between iron and SiC. Fe_3Si, Fe_2Si and carbon (C) are formed after the solid-state reaction, as revealed in Fig. 4 which shows the XRD patterns of milled Fe/SiC composites heated to 925 °C and cooled to room temperature. This heat-treatment-induced reaction in nanocrystalline Fe/SiC composites corresponds well to that in bulk Fe/SiC couples, except that the former occurs at a much more rapid rate [41] and/or much lower temperature [48]. The remaining SiC phase in the heated composites is attributed to the lack of iron because for the completion of the above-mentioned reaction the mole ratio of iron to SiC should at least be 2 : 1. A chemical analysis shows that the composition of Fe/SiC composites is $Fe_{53}(SiC)_{47}$, $Fe_{61}(SiC)_{39}$ and $Fe_{65}(SiC)_{35}$, corresponding to milling times of 8, 24 and 100 h, respectively. The increased content of iron in the milled powder mixture is related to the wear of ball and vial. In fact, there is only a small amount of SiC in the heated Fe/SiC composite which had been ball milled for 100 h, as shown in Fig. 4d. In addition, it was reported [41] that the reaction at 925 °C for a Fe/SiC diffusion couple (disc 9 mm diameter by 5 mm thick) showed an incubation time of about 18 h. In comparison, the solid-state reaction in the nanocrystalline Fe/SiC composites is completed when they are heated to 925 °C at $20\ \mathrm{K\,min^{-1}}$ (the total heating time is less than 1 h). The high reactivity in the nanocrystalline Fe/SiC composites may be explained as follows.

It was reported [56] that for the ball milling of ductile/brittle systems, the brittle particle phase (e.g. SiC) is usually evenly distributed through the ductile matrix (e.g. iron). The dispersion of the brittle phase in the ductile matrix is enhanced with increasing milling time. Therefore, when the powders of iron and SiC are ball-milled, a great number of Fe/SiC reaction couples are created. This results in a large decrease in the atomic diffusion distances. In the meantime, severe plastic deformation during the ball milling generates nanocrystalline crystallites with many grain boundaries and other defects (point defect, dislocation, interphase boundary, etc.). Hence, the atomic diffusion rate can be greatly enhanced due to the formation of the nanocrystalline structural defects. Therefore, the solid-state reaction in nanocrystalline Fe/SiC composites can take place at a fast rate.

It is interesting to note that the temperature for the transition from iron and SiC into Fe_3Si, Fe_2Si and carbon does not decrease continuously with decreasing crystallite size, as shown in Fig. 3. This may be related to the Fe_3C barrier layer formed at the interface of iron and SiC by further ball milling. It is shown, however, by Fig. 3 that the reaction temperature for the solid-state reaction between nanocrystalline iron and SiC have been decreased compared with those between bulk iron and SiC crystals [41]. The reaction temperature for nanocrystalline Fe/SiC composites ball milled for 16 h is 750 °C, which is obviously smaller than the temperature, 925 °C, for the start of solid-state reaction of bulk Fe/SiC diffusion couples [41].

5. Conclusion

In this report, we have described the solid-state reactions in nanocrystalline Fe/SiC composite induced by prolonged ball milling and heat treatment. A prolonged milling of the nanocrystalline Fe/SiC composite produces Fe_3C and Fe(Si) phases. In addition, the solid-state reaction, which is induced by heat treatment, between nanocrystalline iron and SiC produces Fe_3Si, Fe_2Si and carbon. This heat-treatment-induced reaction exhibits a much decreased reaction time compared with that between bulk iron and SiC crystals. Both the formation of Fe_3C and Fe(Si) phases by ball milling and the much decreased reaction time are attributed to the changed thermodynamics and/or kinetics of the solid-state reaction between nanocrystalline iron and SiC.

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