

Reaction mechanism for the formation of intermetallic compounds from layered Sm/Fe powder obtained by mechanical milling

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Solid-state reactions in layered Sm/Fe powder particles with an overall composition of $\text{Sm}_{12}\text{Fe}_{88}$, obtained by ball milling, have been investigated by X-ray diffraction. During annealing at 500°C , one reaction, $\text{Sm} + 2\text{Fe} \rightarrow \text{SmFe}_2$ was observed in the time-range studied. However, during annealing at 800°C , five reactions were observed: $\text{Sm} + 2\text{Fe} \rightarrow \text{SmFe}_2$, $\text{Sm} + 3\text{Fe} \rightarrow \text{SmFe}_3$, $2\text{Sm} + 17\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$, $2\text{SmFe}_2 + 13\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$, and $2\text{SmFe}_3 + 11\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$. It is proposed that such reactions occur by a nucleation and growth process. Reactions of samarium with iron can be governed by nucleation; Sm/Fe interfaces possessing a higher free energy per unit area can play an important role in the nucleation. The observed results are discussed.

1. Introduction

Mechanical alloying is a powder processing technique used for producing powder with a fine microstructure [1, 2]. In this process, the elemental powders are mixed and milled for several hours in a ball mill. The milled powder particles undergo repeated fracture as well as cold-welding and form a lamellar structure of the starting constituents, the lamellar structure become finer and more convoluted with increasing milling time and finally solid-state reactions of layered metals on an extremely fine scale can lead to the formation of a variety of phases which include intermetallic compounds and amorphous alloys.

Several studies have been performed on the synthesis of intermetallic compounds using mechanical alloying. These studies have shown that intermetallic phases form by one of the two channels. First, intermetallic compounds form directly during milling [3]. Second, intermetallic compounds form after annealing of the milled materials, which may be amorphous phase [3, 4] or fine lamellar composites [5], or a mixture of both [6]. However, investigations of the mechanisms of solid-state reactions occurring during annealing and milling have received little attention. The present work attempted to elucidate thermodynamic and kinetic conditions for the formation of intermetallic compounds by solid-state reaction. We report here the solid-state reactions occurring in layered Sm/Fe powder particles. It is proposed that such reactions occur by a nucleation and growth process. Reactions of samarium with iron can be governed by nucleation and Sm/Fe interfaces can play an important role in the nucleation; the observed reactions may be explained in terms of this mechanism.

2. Experimental procedure

The iron powder and samarium powder (obtained by crushing samarium ingot and then sifting) were mixed to give an overall composition of $\text{Sm}_{12}\text{Fe}_{88}$. The mixture was placed in a cylindrical steel chamber under an argon atmosphere and milled in a planetary ball mill for 7 h. The milled powder was removed under an air atmosphere and then annealed under a vacuum of 1.5×10^{-4} torr at various temperatures for different time intervals. X-ray diffraction analyses were performed using a Philips PW-1700 diffractometer with CuK_α radiation.

3. Results

Fig. 1a shows the X-ray diffraction pattern of as-milled powder which is composed of a mixture of samarium and iron. Their crystallite sizes can be roughly estimated using the Scherrer formula $d = 0.9\lambda/\Delta(2\theta)\cos\theta_0$, where $\Delta(2\theta)$ is the width at half maximum of the diffraction peak, θ_0 the diffraction angle and λ the wavelength [7]. The estimated crystallite sizes are 18 nm from the samarium peak at $2\theta = 30.84^\circ$ and 24 nm from the iron peak at $2\theta = 44.98^\circ$, indicating that the as-milled powder particles possess a lamellar structure due to repeated fracture and cold-welding of the milled powder particles [1]. Fig. 1b shows the X-ray diffraction pattern of a specimen annealed at 500°C for 2 h. The annealing treatment results in the formation of an intermetallic compound, SmFe_2 . Fig. 1c is the X-ray diffraction pattern of a specimen annealed at 800°C for 2 h. The pattern, which can be indexed as $\text{Sm}_2\text{Fe}_{17}$ having $\text{Th}_2\text{Zn}_{17}$ structure, is almost the same as patterns obtained using mechanical alloying by Kuhrt *et al.*

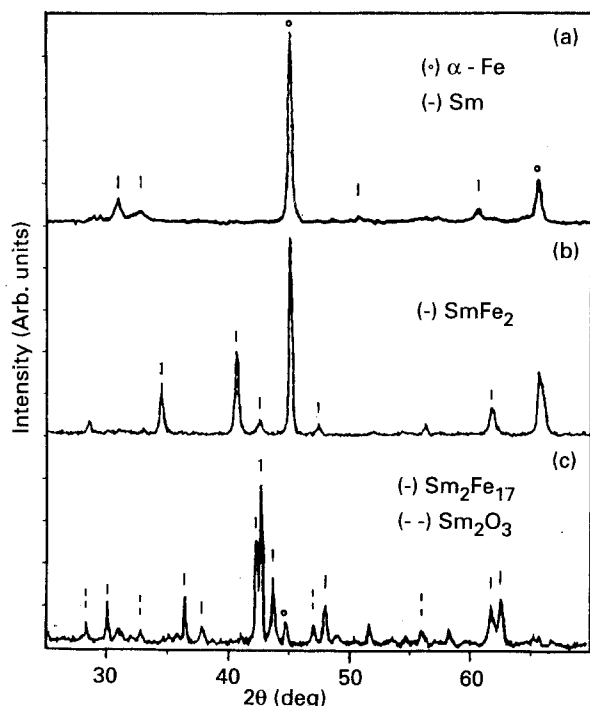


Figure 1 X-ray diffraction patterns for $\text{Sm}_{12}\text{Fe}_{88}$ specimens: (a) as-milled; (b) annealed at 500°C for 2 h; (c) annealed at 800°C for 2 h.

[8] and using melt-spun methods [9]. The diffraction peak at $2\theta = 37.8^\circ$, however, is higher than that reported in the literature [8, 9] but lower than that of $\text{Sm}_2\text{Fe}_{17}$ ingot [10]. Moreover, there is a small amount of Sm_2O_3 in all the annealed specimens.

Fig. 2 shows the X-ray diffraction patterns of specimens annealed at 800°C for various time intervals. An annealing at 800°C for 7 min leads to the appearance

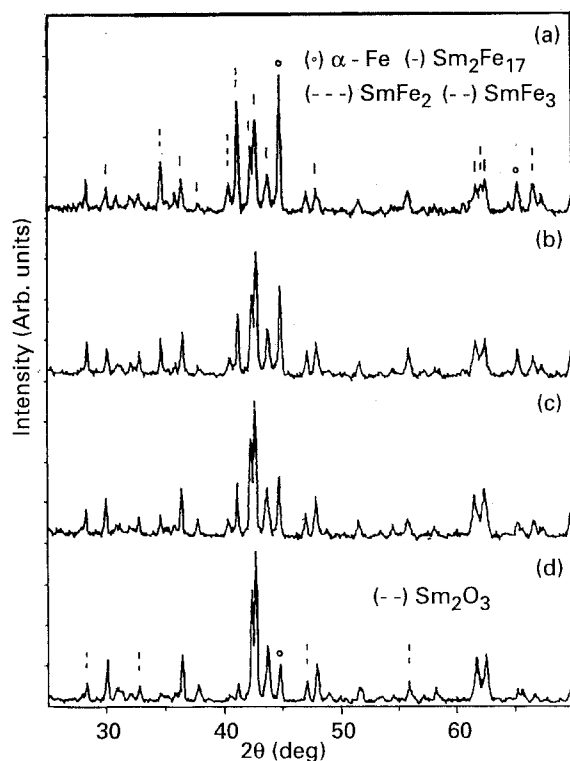


Figure 2 X-ray diffraction patterns for $\text{Sm}_{12}\text{Fe}_{88}$ specimens annealed at 800°C for different time intervals: (a) 7 min; (b) 15 min; (c) 30 min; (d) 1 h.

of diffraction peaks corresponding to three phases: SmFe_2 , SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$. The peak heights of the phases SmFe_2 , SmFe_3 and bcc iron decrease with increasing annealing time, while the peak heights of the phase $\text{Sm}_2\text{Fe}_{17}$ increase, demonstrating that two reactions, $2\text{SmFe}_2 + 13\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$ and $2\text{SmFe}_3 + 11\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$, occur during extended annealing. When the annealing time interval reaches 2 h, the peaks of the phases SmFe_2 and SmFe_3 disappear and the specimen is almost single-phase $\text{Sm}_2\text{Fe}_{17}$ (Fig. 1).

4. Discussion

It has been established that for a ductile/ductile alloy system, repeated fracture and cold-welding of powder particles during milling results in layered composites of the starting constituents [1, 2, 5] and that such layered particles possess sizes of $\sim 100 \mu\text{m}$ [1]. X-ray data show that our samples are composed of nano-sized crystallites of samarium and iron, whose sizes are related to the lamellar spacings. It is therefore concluded that those powder particles possess a layered structure.

It is proposed that solid-state reactions occur by a nucleation and growth process: thermal fluctuations occurring at a/b interfaces create stable new-compound nuclei; these nuclei grow by atom diffusion as well as interfacial reaction. The thermodynamic driving force for such reactions is the free energy difference between a mixture and an appropriate crystalline phase. Interphase interfaces play an important role in determining the kinetics of the reactions. The free energy change associated with the formation at an a/b interface of a volume, V_c , of the c phase is approximately given by

$$\Delta G = -(V_a G_b + V_b G_c - V_c G_c) + S_{a/c} \gamma_{a/c} + S_{b/c} \gamma_{b/c} - S_{a/b} \gamma_{a/b} \quad (1)$$

where V_a and V_b are the volumes of phases consumed during nucleation, and V_c is the volume of phase created; G_a , G_b and G_c are the free energies per unit volume of a, b and c phases; $S_{a/c}$, $S_{b/c}$ and $S_{a/b}$ are the areas of a/c, b/c and a/b interfaces; $\gamma_{a/c}$, $\gamma_{b/c}$ and $\gamma_{a/b}$ are the free energies per unit area of a/c, b/c and a/b interfaces. The first part of this equation is a volume free energy reduction during the nucleation process and represents the driving force for reaction. The second part is three interfacial energy contributions. The first two are positive because they arise from interfaces created during the nucleation. Third, however, is due to the destruction of the a/b interface and results in a negative energy contribution. Fig. 3 gives the hypothetical variation of volume energy, interfacial energy and ΔG with radius, r , for a spherical nucleus at an a/b interface. For r smaller than r^* , the interfacial energy increase is larger than the volume free energy decrease and the free energy change ΔG increases with increasing r . There is a critical size at which ΔG reaches a maximum. This ΔG^* represents a free energy barrier for nucleation. Thermal fluctuations can cause local rearrangements of atoms. It is assumed that when such thermal fluctuations with

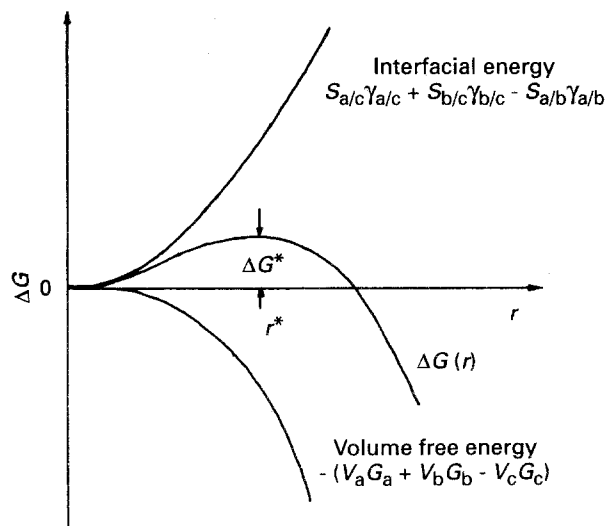


Figure 3 Schematic plots of the variation of volume free energy, interfacial energy and ΔG with radius r for a spherical nucleus at an a/b interface.

energy higher than ΔG^* take place at a/b interfaces, stable nuclei of a compound will appear.

Analogous to the growth of a compound occurring in thin film diffusion couples [11], the growth of compounds in our samples could be determined by a combination of two types of processes: (1) the diffusion of matter through the compound formed and along interfaces surrounding the compound formed; (2) the rearrangement of the atoms at the interfaces required for the growth of the compound which may involve a reaction barrier. Therefore, reactions for the formation of compounds depend upon three kinetic parameters: activation energy for nucleation, activation energy for diffusion and activation energy for interfacial reaction.

It is suggested on the basis of the result shown in Fig. 1b that for the reactions of samarium with iron, the activation energy for nucleation can be predominant over the rest and that the Sm/Fe interfaces can play an important role in the nucleation. During nucleation, the Sm/Fe interfacial energy contribution is $-S_{\text{Sm/Fe}}\gamma_{\text{Sm/Fe}}$ and the destruction of a larger amount of Sm/Fe interfaces having high energy will reduce the free energy barrier for nucleation. The eliminated relative area for the creation of a stable nucleus of SmFe_2 should be larger than that of SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$. This is illustrated by Fig. 4. Nuclei of SmFe_2 , SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$ are assumed to have equal radii; thus these three nuclei also have identical interfacial areas but the areas eliminated are different. The interfacial energy arises from broken bonds or distorted bonds and an interphase interface with a relatively open structure possesses a relatively high energy [12]. Sm/Fe interfaces created by cold-welding should possess more free volume than other interfaces created during nucleation (because the structure of the interfaces created during nucleation should be identical to the interfacial structure of the ingot which has the highest density); hence the Sm/Fe interfacial energy per unit area can possess a value higher than two

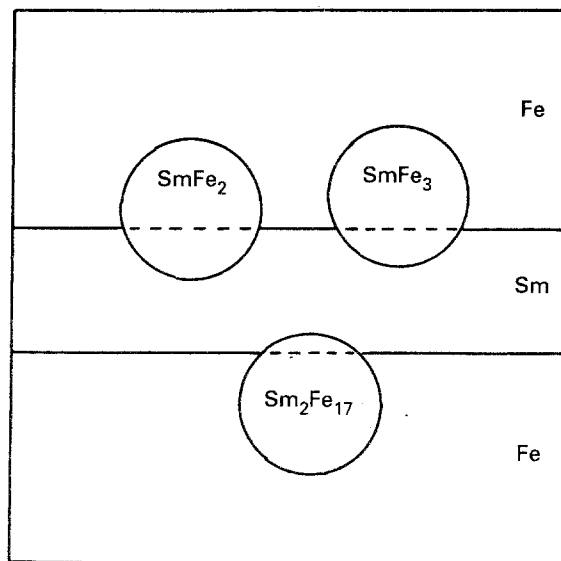
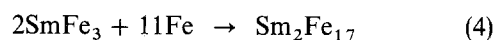
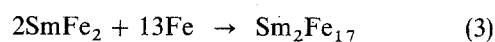
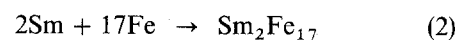


Figure 4 Schematic plots of the cross-section of the Sm/Fe interfacial areas eliminated during the nucleations of SmFe_2 , SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$. The eliminated area for the nucleation of SmFe_3 should be slightly smaller than that of SmFe_2 but larger than that of $\text{Sm}_2\text{Fe}_{17}$ if these nuclei are assumed to have equal radii.

other created interfaces. Therefore, the relative interfacial energy increase for the nucleation of SmFe_2 can be smaller than for the nucleation of SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$, and the free energy barrier for the nucleation of SmFe_2 can be smaller than that of SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$. The reason why the reaction leading to the formation of SmFe_2 is dominant may be that thermal fluctuations at 500°C are small, so that it is difficult for SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$ to nucleate.

The results shown in Fig. 2 also support the above suggestions. The nucleations of three phases can be activated at an appreciable rate by thermal fluctuations at 800°C . The free energy barrier for the nucleation of SmFe_3 should be smaller than that of $\text{Sm}_2\text{Fe}_{17}$; thus in competing reactions the reaction rate in $\text{Sm} + 3\text{Fe} \rightarrow \text{SmFe}_3$ should be higher than in $2\text{Sm} + 17\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$. The data in Fig. 2a show that the fraction of SmFe_3 in a specimen annealed at 800°C for 7 min is comparable with the fraction of $\text{Sm}_2\text{Fe}_{17}$. However, the amount of $\text{Sm}_2\text{Fe}_{17}$ results from three reactions



Therefore, the amount of SmFe_3 resulting from $\text{Sm} + 3\text{Fe} \rightarrow \text{SmFe}_3$ should be larger than the amount of $\text{Sm}_2\text{Fe}_{17}$ originating from $2\text{Sm} + 17\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$. The smaller amount of SmFe_2 than SmFe_3 in the specimen annealed at 800°C for 7 min can be explained by the lower driving force for the reaction leading to the formation of SmFe_2 , which increases the free energy barrier for nucleation. The driving force for reactions is related to temperatures. It can be inferred from the Sm-Fe phase diagram [13] that SmFe_2 is likely to have a higher free energy than SmFe_3 at 900°C . It may be believed that SmFe_2 also possesses a

higher free energy at 800 °C; thus the driving force for $\text{Sm} + 2\text{Fe} \rightarrow \text{SmFe}_2$ can be lower.

Oxidation could be related to the exposure of milled powder to an air atmosphere when removing the samples, leading to the particle surface absorbing a very slight amount of moisture. The surfaces of these particles could be oxidized during annealing. We believe that such surface oxidation has no considerable effect on reactions occurring in particles; observed reactions are expected from the Sm-Fe phase diagram [13].

Ball milling results in a fine layered structure [1, 2], which increases nucleation sites and reduces the diffusion distance required for reactions. Ball milling also introduces defects [1, 2], which raise the free energy of the reactant phases and increase the effective driving force for reactions. Thus, the annealing temperature and time interval for the formation of $\text{Sm}_2\text{Fe}_{17}$ in milled samples (800 °C/2 h) are much lower and shorter than in as-cast samples (1000 °C/48 h) [14].

A full explanation of the reactions in the layered Sm/Fe powder requires a detailed understanding of the various interfaces as well as the temperature dependence of free energy of phases involved in such reactions. However, the knowledge of interfaces is very limited and the exact calculation of free energy of a compound is also very difficult. This work, therefore, can only give a rough discussion of the reaction mechanism. Much work remains to be done to achieve a thorough understanding of the mechanism.

5. Conclusions

One reaction, $\text{Sm} + 2\text{Fe} \rightarrow \text{SmFe}_2$, occurs in layered Sm/Fe powder particles obtained by ball milling during annealing at 500 °C; five reactions occur during annealing at 800 °C: $\text{Sm} + 2\text{Fe} \rightarrow \text{SmFe}_2$, $\text{Sm} + 3\text{Fe} \rightarrow \text{SmFe}_3$, $2\text{Sm} + 17\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$, $2\text{SmFe}_2 + 13\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$ and $2\text{SmFe}_3 + 11\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$. It is proposed that in lamellar Sm/Fe powder particles, reactions of Samarium with iron can be controlled by nucleation and that Sm/Fe interfaces can play an important role in the nucleation. The fact that the reaction leading to the formation of SmFe_2 is dominant during annealing at 500 °C may be explained by

two reasons: (1) the higher free energy barrier for the nucleation of SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$, which can be mainly attributed to the consumption of a smaller amount of Sm/Fe interfaces possessing higher free energy during nucleation; (2) small thermal fluctuations at 500 °C which cannot agitate the nucleations of SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$ at appreciable rates. The reason why the reaction rate at 800 °C of $\text{Sm} + 3\text{Fe} \rightarrow \text{SmFe}_3$ is higher than of $\text{Sm} + 2\text{Fe} \rightarrow \text{SmFe}_2$ and $2\text{Sm} + 17\text{Fe} \rightarrow \text{Sm}_2\text{Fe}_{17}$ could be that the free energy barrier for the nucleation of SmFe_3 , $\Delta G^*(\text{SmFe}_3)$, is lower than $\Delta G^*(\text{SmFe}_2)$ and $\Delta G^*(\text{Sm}_2\text{Fe}_{17})$. $\Delta G^*(\text{SmFe}_3) < \Delta G^*(\text{Sm}_2\text{Fe}_{17})$ can be related to the elimination of a larger number of Sm/Fe interfaces during the nucleation of SmFe_3 , and $\Delta G^*(\text{SmFe}_3) < \Delta G^*(\text{SmFe}_2)$ to the lower driving force for the reaction leading to the formation of SmFe_2 .

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