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The synthesis of amorphous M–Si (M = transition metal) alloy powders by mechanical alloying

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Crystalline powders of Si and M(transition metal) in the composition ratio Si:M = 2:1 were mechanically alloyed by a laboratory ball mill in an inert atmosphere. The progress of the mechanical alloying was identified by X-ray diffraction. The amorphization reaction between Si and M proceeded according to a second-order reaction. The sequence of the rate of amorphization reaction for the Si–M system was Mn > Ti > V > Ni > Co. The sequence of the rate was correlated to the volume ratio (V_M/V_{Si}) of the Si–M system except for Si–Ni system. The crystallization of Si–Mn, of which the MA rate was fastest, was studied by means of X-ray diffraction, differential thermal analysis (DTA) and electrical resistivity measurement. We observed parallel changes on crystallization between the thermal event in the DTA tracing and the change of electrical resistance.

1. Introduction

Herd *et al.* [1] and Schwarz and Johnson [2] obtained amorphous alloys by a novel method, called mechanical alloying (MA). Mechanical alloying is the technique for the production of bulk amorphous material and a new process that has some advantage compared to alloying by melting. Since MA is based on the solid-state amorphization reaction, the problems of the different melting temperature and the different specific gravity would be overcome by using this technique. It has been reported that various amorphous intermetallic compounds were obtained by using this reaction [3]. Weeber and Bakker [4] has reviewed the many amorphous alloy systems which could be prepared by MA. However, a solid-state amorphization reaction for the transition metal–silicon system has been rarely reported. In this paper we reported the synthesis of metal silicides by mechanical alloying of mixtures of transition metal and silicon powders.

2. Experimental procedure

The MA was carried out in a laboratory ball mill using a stainless steel vial (57 × 40 mm diameter) and balls (27 balls, 9 mm and 12 mm diameter). The starting materials were silicon (99.9999%) and M (Ti, V, Mn, Ni, Co; 99.9%) powder. The fine powders (*ca.* 325 mesh) were mixed before grinding and loaded into a stainless steel vial with an elastomer O-ring in a high purity nitrogen-filled glove box. The ball-to-powder weight ratio was 64:1. The mixer agitated the ball mill at 60 revolutions per second with an amplitude of 40 mm. The structure of the mechanically alloyed powders was characterized by X-ray diffraction (XRD) (Rigaku Denki RAD-2B). Thermal analyses were performed by means of a computerized differental thermal analysis (Shimazu DTA-50). The electrical resistivity of the amorphous metal silicide pellets was measured by a conventional d.c. resistivity technique over the range 298–873 K under vacuum (*ca.* 1.0×10^{-4} Pa).

3. Results and discussion

3.1. Reaction rate

Fig. 1 shows the X-ray patterns of Si–Ti system as an isolated example with increasing milling time. Curve (a) shows the XRD pattern of a mixture of crystalline Si and Ti powder. Curves (b)–(d) reveal the diffraction patterns of the same sample, after 18 ks (5 h), 36 ks (10 h) and 54 ks (15 h) of MA, respectively. The silicon (1 1 1) peak and the titanium (0 1 1) peak decreased with milling time. After 90 ks (25 h) of milling these peaks almost disappeared and a broad diffuse diffraction maximum which has to be attributed to the mechanically alloyed amorphous powder is shown. The halo patterns which are characterized by the MA powder are exhibited in Fig. 2, together with results on other systems. The peak maximum of these halo patterns are located at the lower angle of diffraction. It is found that the peak maximum shifts from $2\theta = 20.0°$ for Si–Co to $2\theta = 22.5°$ for Si–Ti. This would be attributed to a progressive decrease of the nearest neighbour distance as the metallic radius of M increases going from Co ($r_{Co} = 0.125$ nm) to Ti ($r_{Ti} = 0.147$ nm Å). The half-widths of these diffraction peaks are broader

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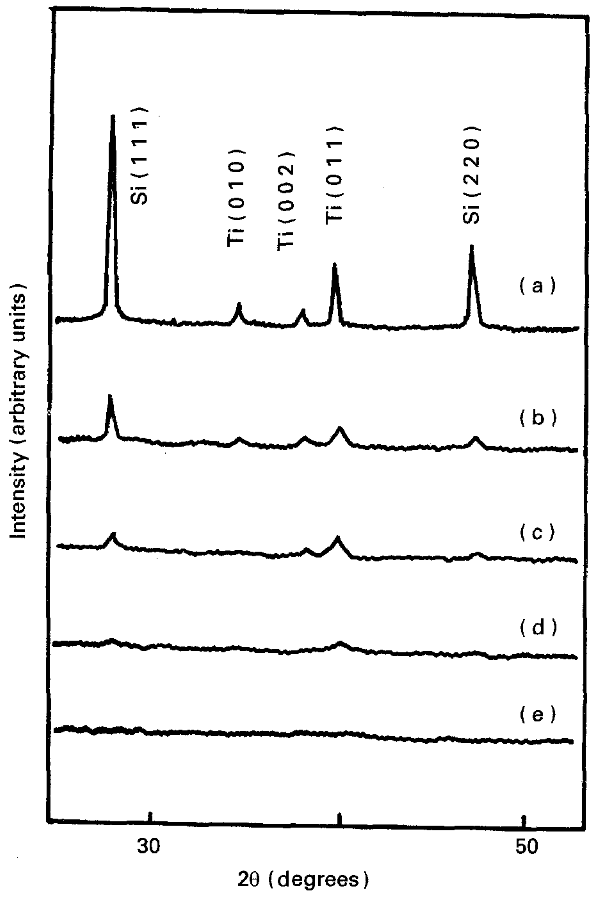

Figure 1 XRD intensities for Si–Ti system. Curve (a) is from a mixture of pure Si and Ti. Curves (b), (c), (d) and (e) are after mechanical alloying for 18, 36, 54 and 90 ks, respectively.

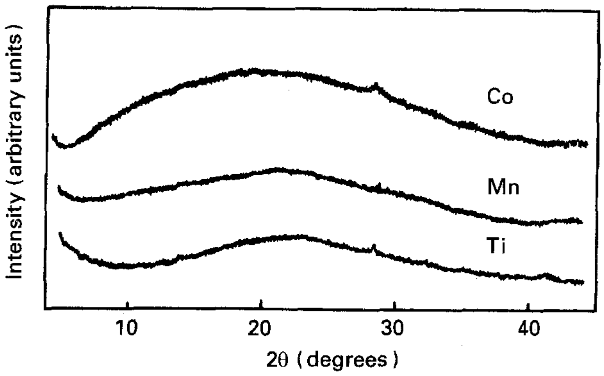

Figure 2 XRD pattern of Si–M samples after milling (M = Ti, Mn, Co).

than those of the MA powders for Ti–M (M = V, Cr, Mn, Fe, Co, Ni, Cu) or Zr–M (M = Cu, Fe, Mn, Cr, V) [5].

It was reported that the MA rate was related to "the energy input into the alloy" and this assumption led to a MA rate which was linear with time [6]. It has become apparent in the MA of Ni, Co, and Fe with Ti, that the rate of the growth of the amorphous phase was represented by a square root of the time law [7]. We examined the MA reaction rate of a Si–M system by using the rate of the disappearance of starting materials.

If the amorphization reaction between Si and M proceeds according to a second-order reaction, the rate equation is

$$[1/(a - b)]\ln[b(a - x)/a(b - x)] = kt \quad (1)$$

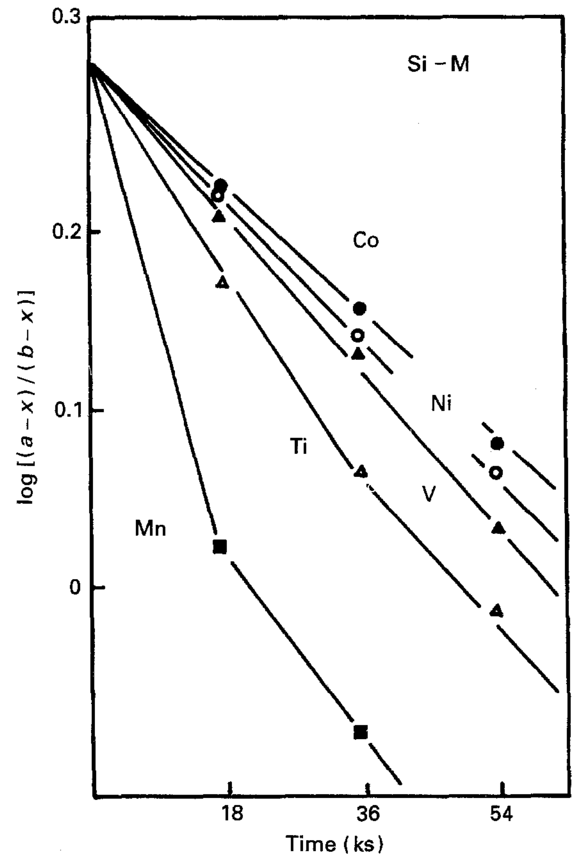

Figure 3 $\log[(a - x)/(b - x)]$ versus time. It is assumed that the rate of which the binary crystalline powders are amorphized by mechanical alloying follows the second-order reaction.

where k is the rate constant, a and b represent the identical concentration of Si and M, respectively. A weighed quantity of Si or M was used as an initial concentration. Also $(a - x)$ or $(b - x)$ was estimated by the intensity of the XRD line of each component at several milling times. A plot of the reciprocal of the logarithm of $[(a - x)/(b - x)]$ versus time is linear with slope K as shown in Fig. 3. Thus it is clear that the amorphization reaction between Si and M by MA proceeds according to a second-order reaction. The sequence of the rate of amorphization reaction for Si–M system was Mn > Ti > V > Ni > Co, judging from the slope of the initial straight line. In general, it can be predicted from the volume ratio of M_A and M_B (M_A/M_B) for a $M_A - M_B$ system whether M_A is a fast diffuser in M_B or not [8]. Since $V_{Mn}/V_{Si} = 4.42$, silicon is a fast diffuser in manganese. However, because the volume ratios (V_M/V_{Si}) of other systems are 0.25 for Ti, 0.18 for V, 0.27 for Ni and 0.16 for Co, M is a diffuser in silicon. In any event the sequence of rates is correlated with the volume ratio of a Si–M system except for a Si–Ni system, judging from the value of the volume ratio. Although the change of the diffraction intensity can be explained by several factors, the apparent decrease of Si peak in Si–Mn system during the initial stage of alloying may be due to the large difference in the volume. Also, it is considered that in Si–Ni system a thin layer of oxide

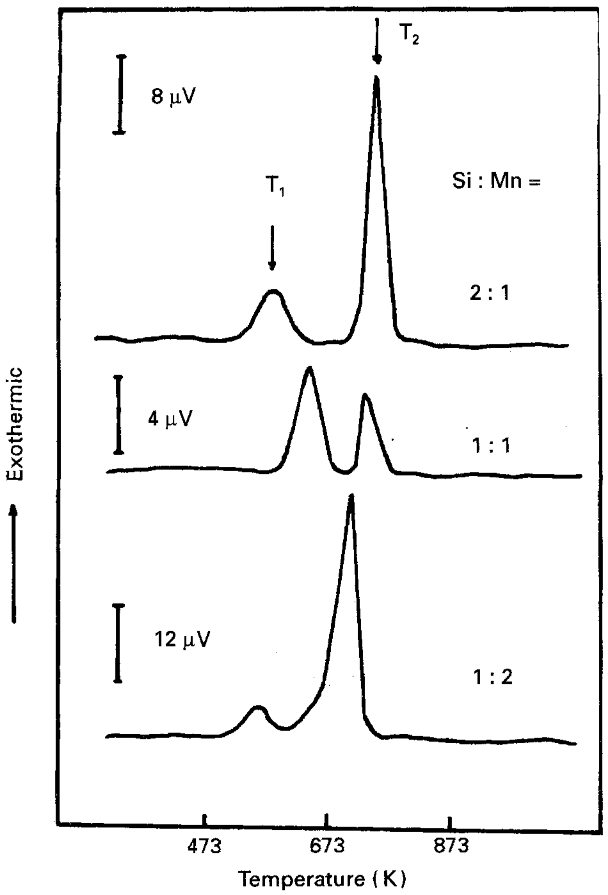

Figure 4 DTA tracings obtained from amorphous alloys at a heating rate of 20 K min^{-1}.

on the surface of the nickel particles may be strongly affected by the rate of MA reaction.

3.2. Crystallization

We investigated the crystallization of amorphous powders obtained by MA reaction. Si–Mn system, in which the rate of MA was fastest, was selected. Results of the DTA measurements for the Si–Mn system are shown in Fig. 4. Two exothermic heat effects were observed. The peak of the first transition curve is designated T_1. The peak of higher temperature exothermal curve is designated T_2. When the amorphous samples were heated to a temperature above T_2, the intermetallic crystalline was first identified by XRD as described below. The enthalpy change in crystallization ΔH_c can be determined from the crystallization DTA peak area. The compositional dependence of ΔH_c is shown in Fig. 5. ΔH_c consists of the sum of the two exotherms. The position of the minimum is about $x = 0.5$. The enthalpy change is almost entirely a change of internal energy, since the contribution of external pressure may be neglected. The change of internal energy is related to the integral of the atomic forces over the interatomic distance change from the amorphous to the crystalline phase. Thus, one would expect that MnSi is not a stable single phase. That is, we would expect that the intermetallic crystalline having lower or higher Si concentration can be obtained. The results of XRD studies of amorphous Si–Mn system which were heated to a temperature above T_2 are summarized in Table I.

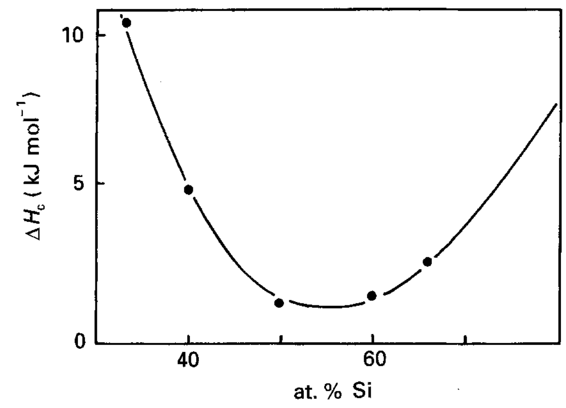

Figure 5 Enthalpy difference between amorphous and crystalline Si–Mn.

TABLE I Crystallization products of amorphous Si–Mn system

Mixture composition	Thermal treatment at 573 K	Final products
2:1	α-Mn + amorphous	$Mn_{27}Si_{47}$ + Mn_5Si_3
3:2	”	$Mn_{27}Si_{47}$ + Mn_5Si_3
1:1	”	Mn_5Si_3
2:3	”	Mn_5Si_3
1:2	”	Mn_5Si_3

The crystalline phases are observed for $Mn_{27}Si_{47}$ and Mn_5Si_3. Mn_5Si_3 were found only in the range of lower Si. These results are consistent with the interpretations as described above.

3.3. Electrical resistivity

It is well known that the crystallization features obtained from electrical resistivity are in excellent agreement with the DTA results [4, 9]. The results of electrical resistance measurements are shown in Fig. 6. The normalized change in electrical resistance is plotted as a function of temperature. The heating rate for all samples is about 20 K min^{-1}. The arrows in the figure correspond to the thermal effects observed in the DTA tracings.

The decrease of the resistivity was observed in all samples. When the resistance at 300 K was compared with that at 780 K, the drop in resistivity became small with increasing the content of Mn. Except for the sample (Si:Mn = 2:1), at first the large decrease in resistivity was observed in the temperature range below T_1. When all of the amorphous samples were treated *in vacuo* at 573 K, α-Mn as a crystallization product was identified by means of XRD as shown in Table I. Therefore, it is assumed that these decreases were related to the crystallization of α-Mn from the amorphous Si–M system, although the mechanism of the crystallization from the amorphous state to α-Mn is not clearly revealed. In the two samples (Si:Mn = 1:1, 1:2) the change of resistivity rarely occurred at T_2. Moreover, when the samples were cooled, the resistance did not return to the original values. From these results, it was found that the

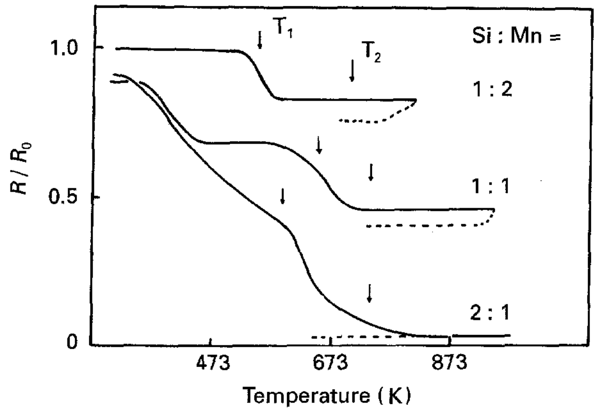

Figure 6 Change of electrical resistance with temperature at a heating rate 20 K min^{-1}, normalized to the value at room temperature.

resistivity behaviour was correlated with the thermal behaviour of DTA.

4. Conclusions

The mechanical alloying of mixtures of transition metal (M) and silicon powders was carried out by the use of a laboratory ball mill. The progress of the amorphization reaction between Si and M proceeded according to a second-order reaction. The reaction rate of Si–Mn system, which has the largest volume ratio (V_{Mn}/V_{Si}), was greater than that of the other systems. The sequence of the rate for Si–M system was Mn > Ti > V > Ni > Co.

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