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The sequence of phase formation during mechanical alloying of chromium and silicon powders

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The sequence of phase formation during mechanical alloying of chromium and silicon powders has been studied using high-energy ball milling of mixtures of elemental powders with different Si/Cr atomic ratios. X-ray diffactometry and transmission electron microscopy have been utilized to identify the phases and to characterize the microstructure of the powders. All four equilibrium phases in the Cr–Si system can form. With a Si/Cr atomic ratio equal to or higher than 3/5, $CrSi_2$ is always the first phase to form, and then $CrSi_2$ can react with chromium to form CrSi or Cr_5Si_3, depending on the Si/Cr atomic ratio. This is similar to the sequence of phase formation during annealing of multilayer chromium and silicon thin films. However, with low Si/Cr atomic ratio close to 1/3, Cr_3Si is the first and only phase to form during mechanical alloying.

1. Introduction

If chromium and silicon are joined as a diffusion couple at a temperature below 1000 °C, one would expect the formation of four equilibrium Cr silicides (Cr_3Si, Cr_5Si_3, CrSi and $CrSi_2$), together with the two respective terminal solid solutions, as shown by the binary Cr–Si phase diagram (Fig. 1) [1]. The heats of formation of these four silicides are very close (all in the range of -28 to $-26\,\mathrm{kJ\,mol^{-1}}$) [2], hence the particular silicide which could form directly from the reaction between chromium and silicon is determined by the kinetic conditions required by the formation of each of the phases. If the available kinetic conditions are highly constrained, none of the silicides may be able to form; instead metastable phases such as supersaturated solid solutions and/or amorphous phases may form. Under the constrained kinetic conditions accompanying annealing of multilayer elemental chromium and silicon thin films at a relatively low temperature (500–700 °C), Colgan *et al.* [3] and Sundstrom *et al.* [4] have shown that $CrSi_2$ is always the phase which forms directly from the Cr/Si reaction. This indicates that the kinetic conditions required by the formation of $CrSi_2$ are the most accessible of all the possible equilibrium and metastable phases during the diffusional solid-state reaction between chromium and silicon. In addition, Colgan *et al.* [3] have also shown that after consuming all the available silicon, $CrSi_2$ can react with unconsumed chromium to form Cr_5Si_3, and then Cr_5Si_3 can react either with $CrSi_2$ to form CrSi or with chromium to form Cr_3Si depending on the starting Si/Cr atomic ratio.

Similar to annealing of multilayer thin films, phase formation during mechanical alloying is also a result of diffusional solid-state reactions between different starting phases [5, 6]. However, unlike annealing of thin films, mechanical alloying involves dynamic deformation and fracturing of the powders which may render different thermodynamic and kinetic conditions from those accompanying thermal annealing of thin films. Under these circumstances, the phase formation behaviour during mechanical alloying and thermal annealing of multilayer thin films may show both similarities and differences. To illustrate this comparison, the sequence of phase formation during the mechanical alloying of chromium and silicon elemental powders has been studied, and the results of this investigation are presented here.

2. Experimental procedure

Mixtures of elemental powders of 99% pure chromium and 99.999% pure silicon (both with an average grain size of $\sim 50\,\mu\mathrm{m}$), corresponding to different nominal Si/Cr atomic ratios, were subjected to ball milling using a Spex 8000 Mixer/Mill. A hardened steel vial containing stainless steel balls (10 mm diameter, and 3.5 g weight) and a charge of 3 g premixed powder, were sealed in each case in a glove box under a helium gas atmosphere. The milling was performed inside the same glove box filled with helium gas. The weight ratio between the steel balls and the powder charge was approximately 5.7:1. The milling was interrupted at different times to remove the powder for characterization. The phases present in the powder were identified using X-ray diffractometry (XRD), and the structure of the powder was characterized using transmission electron microscopy (TEM).

All X-ray diffraction runs were done in a Rigaku diffractometer using CuK_α radiation and a nickel single-crystal monochromater. The TEM specimens were prepared by mounting the powder with epoxy and then thinning the slices of powder/epoxy composite using a Gatan twin ion mill. The TEM examination was performed using a Jeol 120CX TEM operated at 120 kV.

3. Results

With an Si/Cr atomic ratio of 2/1 in the starting mixture of the elemental powders, $CrSi_2$ started to form during the first 4 h milling, as shown by the XRD pattern (Fig. 2a). At this stage of milling, most of the powders consisted of a mixture of chromium and silicon grains of sizes in the range of 10–20 nm, as shown by the selected-area diffraction patterns and the dark-field images such as those in Fig. 3a and b. The volume fractions of chromium and silicon grains varied considerably from powder to powder, with some powders containing a majority of silicon grains and a few chromium grains or vice versa. In the selected-area electron diffraction patterns, a few diffracted spots did not fall on the diffracted spotty rings corresponding to silicon or chromium (Fig. 3a). These spots were identified to be from the small amount of $CrSi_2$ which formed initially. Further milling up to a total time of 16 h only increased the volume fraction of $CrSi_2$, while consuming chromium and silicon, as shown by the XRD pattern (Fig. 2b). No change in chromium and silicon peak positions was observed

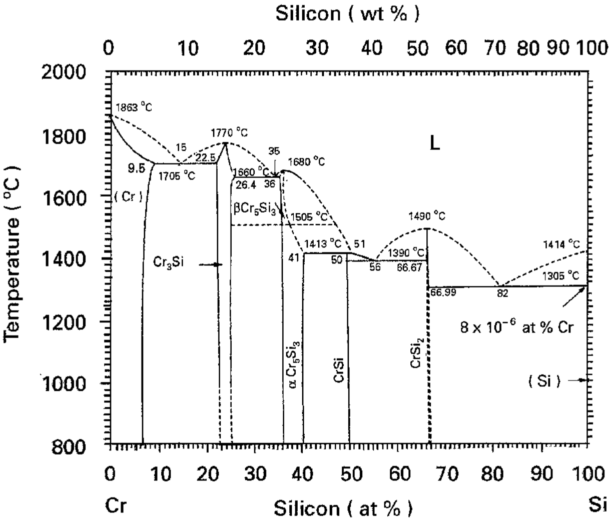

Figure 1 The binary Cr–Si phase diagram [1].

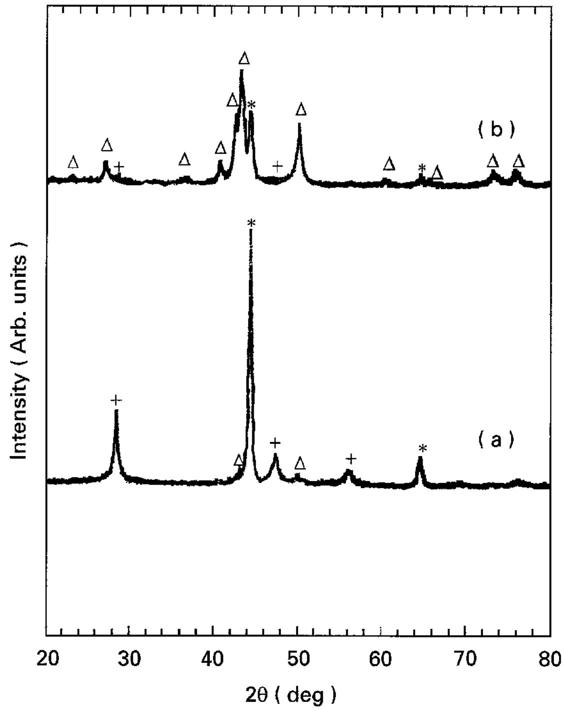

Figure 2 X-ray diffraction patterns of the powder with Si/Cr atomic ratio of 2/1 after milling for different times: (a) 4 h; (b) 16 h. (*) Cr, (+) Si, (Δ) $CrSi_2$.

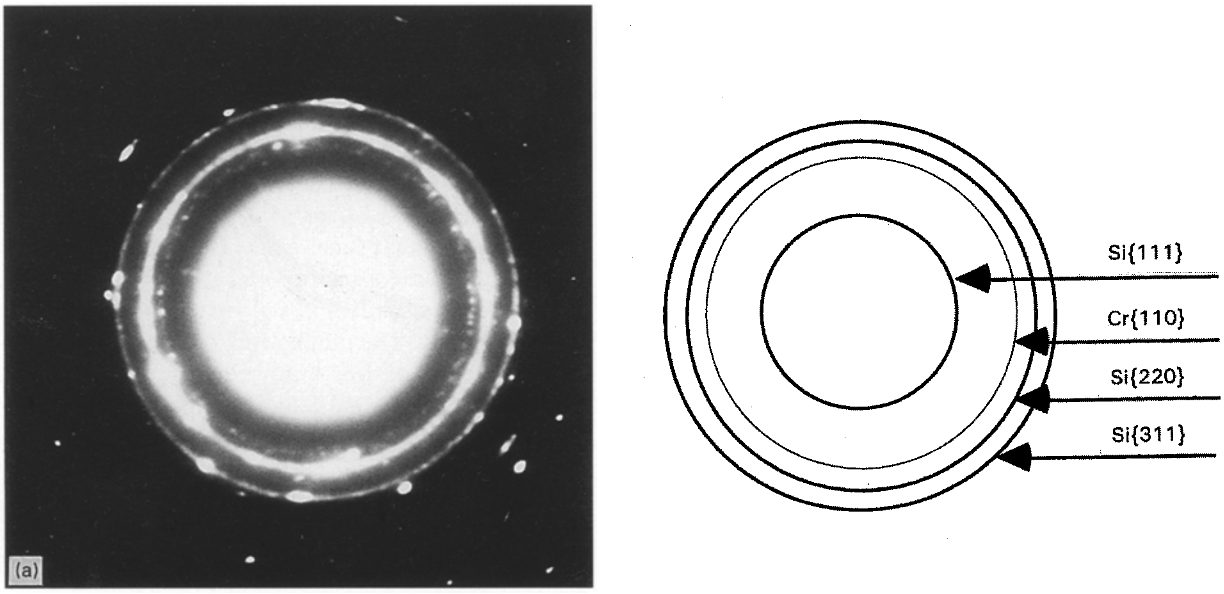

Figure 3 (a) Selected-area electron diffraction patterns of the 4 h milled powder with a Si/Cr atomic ratio of 2/1; (b) dark-field transmission electron micrograph imaged using a silicon diffracted spot.

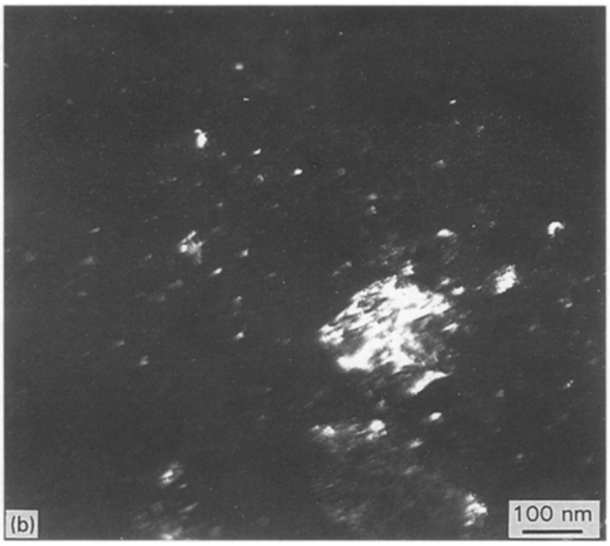

Figure 3 Continued

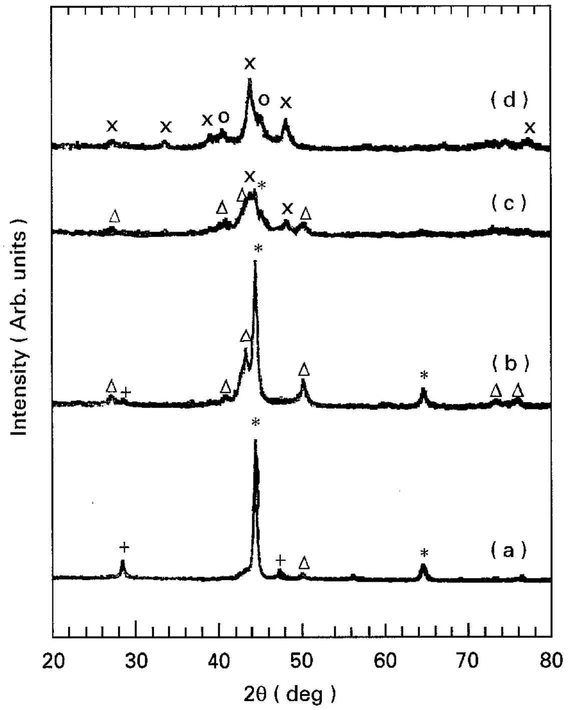

Figure 4 X-ray diffraction patterns of the powder with Si/Cr atomic ratio of 1/1 after milling for different times: (a) 4 h; (b) 8 h; (c) 16 h; (d) 32 h. (+) Si, (*) Cr, (Δ) $CrSi_2$, (×) CrSi, (O) Cr_5Si_3.

during all stages of milling. After 4 h milling, the intensity of the silicon peaks became much smaller than that of the chromium peaks in the XRD patterns.

With a Si/Cr atomic ratio of 1/1, $CrSi_2$ started to form during the first 4 h milling (Fig. 4a). The fraction of $CrSi_2$ increased and most of the silicon was consumed after milling up to 8 h (Fig. 4b). After continued milling for a total time of 16 h, the amount of $CrSi_2$ decreased to a very low level and at the same time CrSi formed, apparently by a reaction between $CrSi_2$ and unconsumed chromium (Fig. 4c). After 24 h milling Cr_5Si_3 also formed, and after 32 h milling the powder mainly consisted of a majority of CrSi with a small amount of Cr_5Si_3 (Fig. 4d).

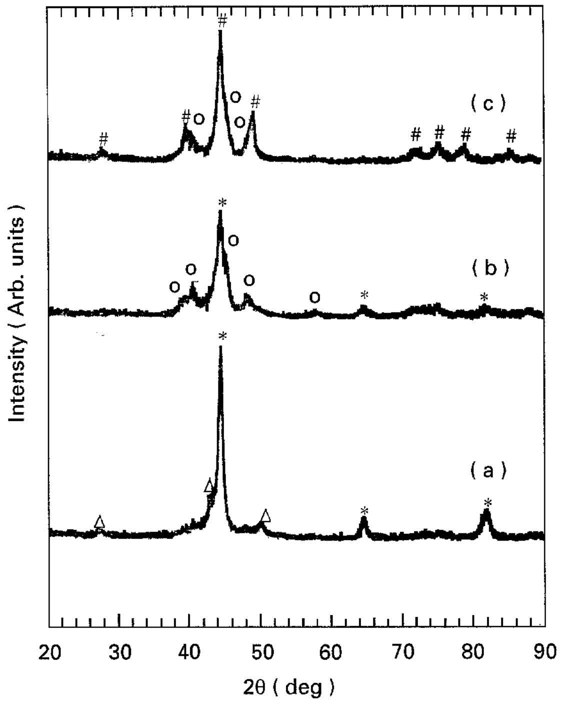

Figure 5 X-ray diffraction patterns of the powder with Si/Cr atomic ratio of 3/5 after milling for different times: (a) 8 h; (b) 16 h; (c) 36 h. (*) Cr, (Δ) $CrSi_2$, (O) Cr_5Si_3, (#) Cr_3Si.

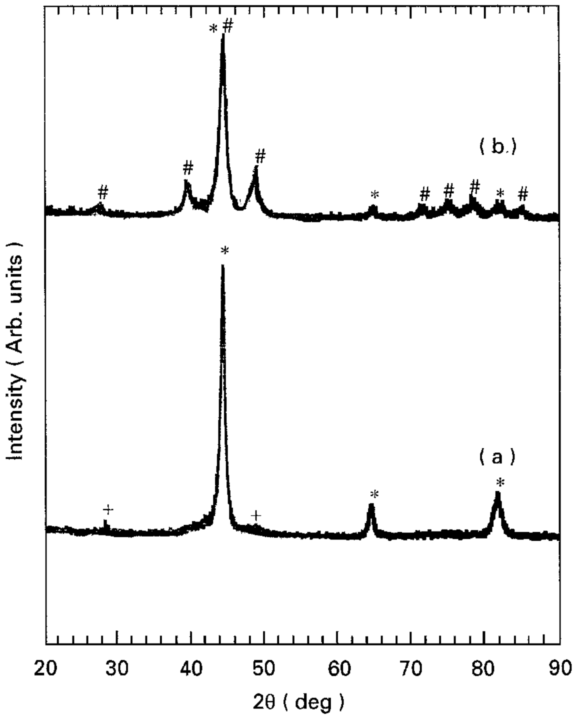

Figure 6 X-ray diffraction patterns of the powder with Si/Cr atomic ratio of 1/3 after milling for different times: (a) 8 h; (b) 16 h. (+) Si, (*) Cr, (#) Cr_3Si.

With a Si/Cr atomic ratio of 3/5, $CrSi_2$ was also the first phase to form within 8 h milling (Fig. 5a). During further milling up to a total time of 16 h, the amount of $CrSi_2$ decreased to an undetectable level and at the same time Cr_5Si_3 formed by a reaction between $CrSi_2$ and chromium (Fig. 5b). During further milling up to 36 h, Cr_3Si also formed, while at the same time the amount of chromium decreased to an undetectable level. The amount of Cr_5Si_3 remained at the low level (Fig. 5c).

When the Si/Cr atomic ratio in the starting powder mixture was reduced to 1/3, the $CrSi_2$ was not detected, and Cr_3Si was the first and only phase to form during milling (Fig. 6a and b).

4. Discussion

The results of the mechanical alloying experiments presented above clearly show that all the equilibrium phases predicted by the Cr–Si phase diagram can form during mechanical alloying of elemental chromium and silicon powders. Similar to annealing of chromium and silicon multilayer thin films [3, 4], there is a characteristic sequence of phase formation during mechanical alloying of chromium and silicon powders. With the Si/Cr atomic ratio in the starting mixture of elemental powders equal to or higher than 3/5, $CrSi_2$ is always the first phase to form, in other words, $CrSi_2$ is always the direct product of the reaction between elemental chromium and silicon phases. After all the silicon has been consumed by formation of $CrSi_2$ during mechanical alloying, $CrSi_2$ will react with unconsumed chromium to form either CrSi or Cr_5Si_3, depending on the starting Si/Cr atomic ratio. This sequence of phase formation is very similar to that observed by Colgan *et al.* [3] during annealing of multilayer chromium and silicon elemental thin films [3]. The only difference is that the reaction between $CrSi_2$ and chromium only produces Cr_5Si_3 during annealing of thin films, while during mechanical alloying, both Cr_5Si_3 and CrSi could be the products of this reaction. The above similarities in the sequence of phase formation during mechanical alloying and annealing of thin films shows that with a high Si/Cr atomic ratio (presumably equal to or higher than 3/5), these two processes render similar thermodynamic and kinetic conditions for phase formation.

With a low Si/Cr ratio close to 1/3, the Cr_3Si forms directly from the reaction between chromium and silicon. Similarly, the Cr_3Si which forms at the last stage of milling of the powder mixture with an Si/Cr atomic ratio close to 3/5 (Fig. 5c), is also likely to be the result of the Cr/Si reaction. This is in clear contrast with annealing of thin films with similar Si/Cr atomic ratio where $CrSi_2$ is still the direct product of the Cr/Si reaction. This shows that, unlike annealing of chromium and silicon thin films, reaction during mechanical alloying of chromium and silicon is dependent on the Si/Cr ratio. This type of dependence has also been found in the mechanical alloying of elemental palladium and silicon powders [7] : an amorphous phase is the direct product of the reaction between palladium and silicon with a low Si/Pd atomic ratio of 1/5, while equilibrium Pd_2Si is always the direct product of this reaction with a Si/Pd atomic ratio equal to or higher than 1/2.

The difference in the phase formation behaviour during mechanical alloying and the annealing of multilayer thin films may be associated with the fact that more complicated factors are involved in the formation of diffusion couples in the process of mechanical alloying. During mechanical alloying, diffusion couples between the two elemental phases are formed through dynamic deformation, fracturing and cold welding of the powders, and then the solid-state reaction occurs within these diffusion couples by enhanced diffusion of the species. Decrease in Si/Cr atomic ratio in the starting powder mixture means that the volume fraction of the silicon phase is lowered. When the volume fraction of silicon is lower than a critical value, ball milling may facilitate the formation of Cr/Si diffusion couples which have very different thermodynamic and kinetic conditions from those formed by multilayer thin films with same silicon volume fraction, and this may cause different reactions.

No signs of amorphous phase formation have been observed. It is also unlikely for a metastable supersaturated Si(Cr) solid solution to form simply because, with high Si/Cr atomic ratio, the strong competition from the formation of $CrSi_2$ will rule out this possibility. The question is whether a supersaturated solid solution could form prior to formation of Cr_3Si when the Si/Cr atomic ratio is low (less than 3/5). X-ray diffraction patterns from the milled powder show that the chromium peak positions were left unchanged in all stages of the mechanical alloying. However, this is hardly evidence to rule out the formation of a supersaturated Cr(Si) solid solution, because an extrapolation of the Cr(Si) lattice parameters as a function of silicon content (Fig. 7) measured by Chang [8] shows that the $\{1\,1\,0\}$ Cr(Si) peak position shifts only for 0.2° in 2Θ (where Θ is the diffraction angle) with the silicon content increasing from 0 to 20 at %. A silicon content of 20 at % is already well above the equilibrium limit (Fig. 1). This slight shift of peak positions cannot be unambiguously measured with the broadened X-ray diffraction peaks from the nanocrystalline powders. It has been observed that the intensity of silicon peaks in the XRD patterns decreased much faster than that of the chromium peaks before Cr_3Si started to form, indicating that a supersaturated Cr(Si) solid solution may form. In a study of mechanical alloying of molybdenum and silicon, Schwarz *et al.* [9] also observed that the intensity of silicon peaks decreased much faster than that of molybdenum peaks, but the

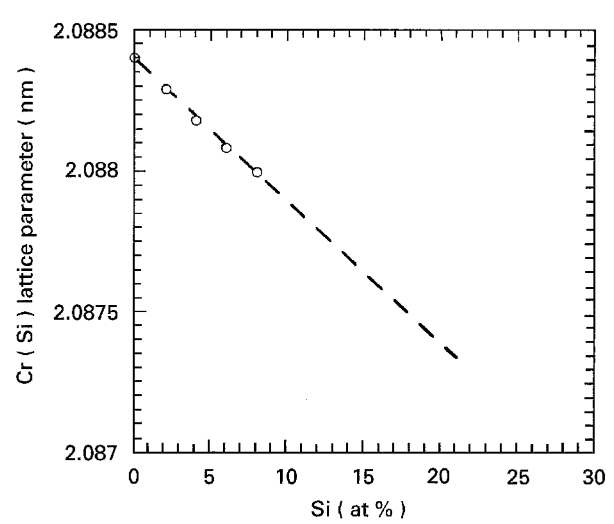

Figure 7 Lattice parameter of the Cr(Si) solid solution as a function of silicon content [8].

molybdenum lattice parameter was left unchanged. They speculated that a supersaturated Mo(Si) solid solution formed as a result of the mechanical alloying. It is apparently desirable to conduct more detailed characterization before a firm conclusion can be made. If a metastable supersaturated Cr(Si) solid solution forms prior to the formation of Cr_3Si, Cr_3Si may form from a solid-state precipitation reaction of this solid solution.

Mechanical alloying of chromium and silicon elemental powders with a low Si/Cr ratio close to 1/3, has also been investigated by Bampton *et al.* [10]. Unlike the current work, where Cr_3Si forms directly from mechanical alloying, in their study no new phases could form without subsequent annealing of the mechanically alloyed powder. This discrepancy may be due to the fact that they used a low-energy ball mill instead of a high-energy ball mill which has been used in the present study.

5. Conclusions

All four equilibrium phases in the Cr–Si system can form during mechanical alloying of elemental chromium and silicon powders. With a Si/Cr atomic ratio equal to or higher than 3/5, $CrSi_2$ is always the first phase to form, and then $CrSi_2$ can react with chromium to form CrSi or Cr_5Si_3 depending on the Si/Cr atomic ratio. This is similar to the sequence of phase formation during annealing of multilayer chromium and silicon thin films. However, with a low Si/Cr atomic ratio close to 1/3, Cr_3Si is the first and only phase to form during mechanical alloying.

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