Sequence of phase formation during mechanical alloying in the Mo–Si system

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Abstract

In this work, the sequence of phase formation during mechanical alloying (MA) in the Mo–66.6 at.% Si, Mo–37.5 at.%Si, Mo–25at.%Si systems and the phase transition in $MoSi_2$ upon mechanical activation have been studied using electron microscopy, X-ray diffraction and differential thermal analysis.

It has been found that, in all the systems under study, molybdenum disilicide is the first phase to form during MA. In this case, during MA in the Mo–37.5 at.%Si and Mo–25at.%Si systems, molybdenum disilicide forms in the amorphous state. The phases Mo_5Si_3 and Mo_3Si form by the interaction of amorphous molybdenum disilicide with molybdenum under MA, which leads initially to the formation of amorphous molybdenum silicides the compositions of which are close to that of the crystalline phases Mo_5Si_3 and Mo_3Si, and then to the precipitation of crystalline phases.

It has been shown that MA in the Mo–66.6 at.%Si system and the mechanical activation of molybdenum disilicide are accompanied by the phase transition form α-$MoSi_2$ to β-$MoSi_2$.

Keywords: Phase formations; Mechanical alloying; Molybdenum disilicide

1. Introduction

The mechanical alloying (MA) method is of considerable current use for the synthesis of intermetallic compounds. The intermetallic compounds obtained using this method differ essentially in properties and structure from those intermetallides which are prepared by conventional solid state synthesis. In many cases, the use of MA results in the formation of unusual metastable states [1].

As in the solid state synthesis, during MA, the formation of a chemical compound is localized at the interface. Nevertheless, the sequence of formation of the intermetallic compound can differ from that in the isothermal synthesis owing to the non-equilibrium character of MA. It is particularly difficult to predict the course and results of MA in complex systems, the equilibrium phase diagrams of which show several intermetallic compounds in different polymorphous modifications.

Since the synthesis of intermetallic phases proceeds at the interface, this suggests that the process goes sequentially through the stages of formation of compounds differing in composition and structure. Experimental data of this kind are well known for the solid state isothermal synthesis [2] of substances and are essentially lacking for MA processes in the synthesis of intermetallic compounds.

In the present work, we attempted to establish the sequence of phase formation during MA in the Mo–Si system with the aim of comparing data on the variation in the phase composition in the synthesis of silicides by MA with the data for the solid state synthesis of the same compounds. The choice of the present subject of investigation is due to the availability of a great body of data on the sequence of phase formation during the solid state synthesis of this system [3–8] and to the possibility of preparing silicide phases by MA. Also a study of the formation of molybdenum silicide phases during MA is of interest from the practical standpoint because of the wide application of these phases in production processes.

The phase diagrams of the metal–silicon systems show, as a rule, more than three types of silicide. However, experimental data indicate that, during the formation of the silicide, not all of the equilibrium phases are present as dominating growth phases. Of course, this does not mean that some of the equilibrium phases cannot form at all; these simply do not grow to the size at which they could be identified.

The synthesis of silicides proceeds by a reaction between two contacting solid phases. In this case,

ordered intermetallic compounds form at temperatures much lower than the temperature at which the liquid phase forms [2].

In the Mo–Si system, the compounds Mo_3Si, Mo_5Si_3 and $MoSi_2$ are observed. The compound Mo_3Si has a cubic structure of the β-W type; the silicide Mo_5Si_3 has a b.c.t. W_5Si_3-type structure. The low temperature modification of disilicide, α-$MoSi_2$, has a tetragonal structure and the high temperature modification, β-$MoSi_2$, has a hexagonal $CrSi_2$ structure.

The majority of currently available studies on the synthesis of silicides by MA in the Mo–Si system treats the formation of the $MoSi_2$ phase. The following have been shown.

(1) During MA the formation of the $MoSi_2$ phase proceeds through a certain induction period and is similar to the self-propagation high temperature synthesis (SHS) [3].

(2) As well as the stable α-$MoSi_2$ phase, the high temperature β-$MoSi_2$ phase is formed during MA. Isothermal annealing brings about the crystallization of α-$MoSi_2$, the decomposition of β-$MoSi_2$ and the formation of the silicide Mo_5Si_3 [4–6].

2. Experimental procedure

Elemental powders with a purity of 99.9% or better and a particle size in the range 5–7 μm were used for the present experiments. The MA was performed in a centrifugal planetary ball mill with an acceleration of 600 m s^{-2} using stainless steel vials and balls with a ball-to-powder ratio of 20 to 1. The experiments were carried out under an argon atmosphere to avoid oxidation. After different milling times, a small quantity of powder was removed for X-ray, transmission electron microscopy and differential thermal analysis (DTA). The X-ray investigation was performed on a diffractometer using Cu Kα radiation. Electron microscopy was performed with a JEOL JEM-2000FX2 microscope at an acceleration voltage of 200 kV.

3. Results and discussion

3.1. The formation of the Mo_3Si phase during mechanical alloying

A study of the sequence of phase formation in the Mo–Si system where the starting powders were taken in a ratio of 3 to 1 has shown that, as the time of MA increases, the following changes are observed in the X-ray diffraction patterns (Fig. 1).

(1) An increase in the time of MA produces a decrease in the intensity of the X-ray reflections of crystalline silicon, and after 4 min the reflections of silicon completely disappear.
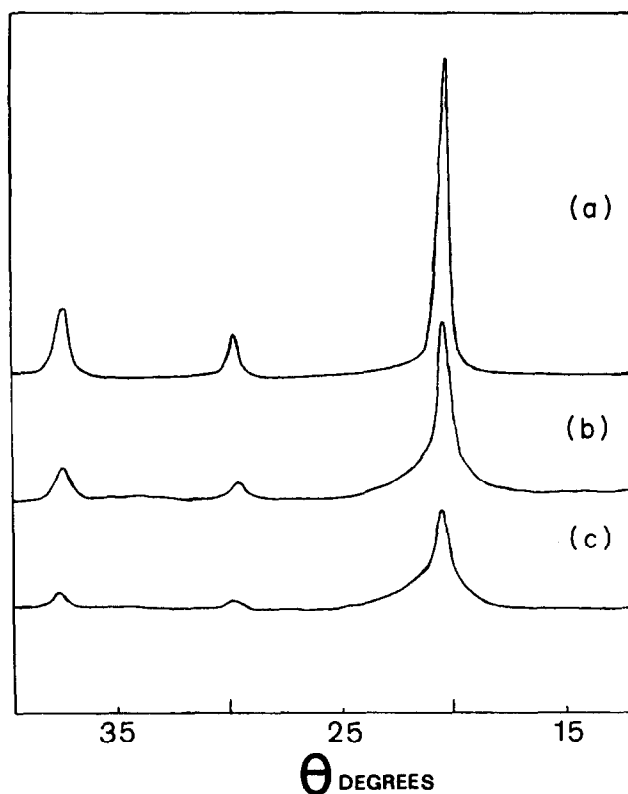

Fig. 1. Evolution of phases in the Mo–25at.%Si powder as a function of milling time, as shown by XRD patterns of the powders after 4 min MA (curve a), 10 min MA (curve b) and 30 min MA (curve c).

(2) The MA process is accompanied by a decrease in the intensity of the Mo reflections, and by the broadening and insignificant shift of these reflections to the large-angle region.

The changes observed in the X-ray diffraction patterns (broadening and shift of the diffraction peaks) correspond to the diffraction patterns of powders in a stressed state. Also a decrease in the particle size of molybdenum upon mechanical treatment can also contribute to the broadening of the X-ray peaks [9].

(3) After 10 min treatment, the background in the angle range $2\theta = 36$–$48°$ increases, which indicates the formation of the amorphous state of the substance.

The data obtained in a study of the MA process using electron diffraction agree well with those obtained using X-ray analysis. However, the disappearance of the Si reflections in electron diffraction patterns occurs somewhat later than in X-ray diffraction patterns. The Si reflections are recorded even after a 6 min MA. Also, the electron diffraction patterns of Mo–25at.%Si samples after 20 min MA show two amorphous haloes: the first in the region of 3.7 Å and the second at 2.2 Å (Fig. 2(a)). It should be noted that the second amorphous halo is detected in X-ray diffraction patterns by the increased background in the angle range
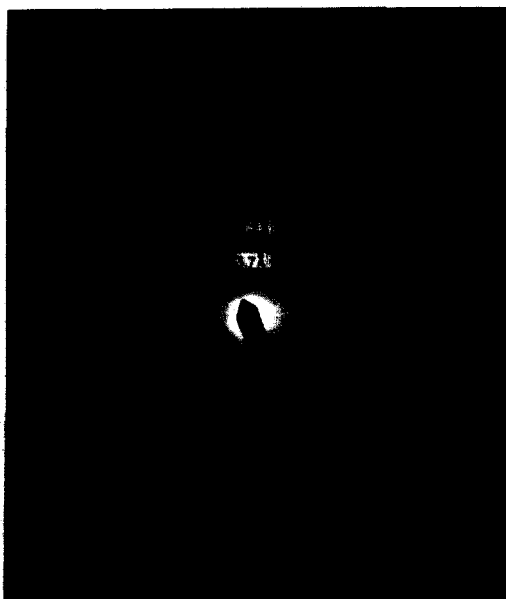
(a)
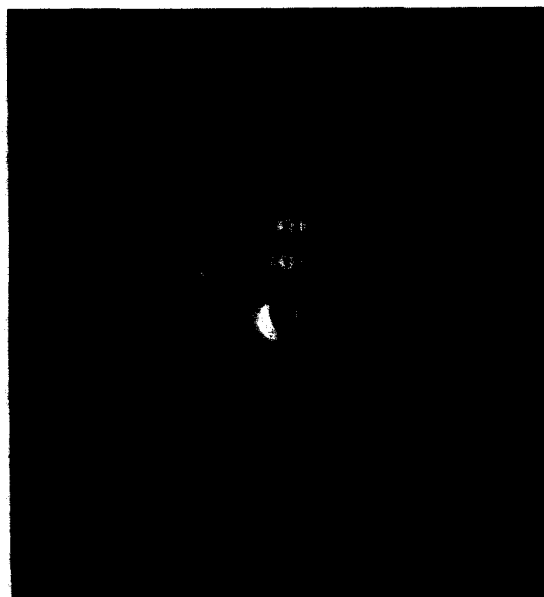
(b)

Fig. 2. Selected-area electron diffraction pattern of Mo–25at.%Si powder (a) after 10 min MA and (b) after 30 min MA.

$2\theta = 36$–$48°$, whereas the first amorphous halo is observed only in the electron diffraction patterns. As the time of MA increases, the first amorphous halo disappears in the electron diffraction patterns. The electron diffraction patterns show only the amorphous halo with a center at 2.2 Å (Fig. 2(b)).

A transmission electron microscopy study of the Mo–25at.%Si powders during the progress of MA has shown that the process is accompanied by aggregation of Mo and Si particles. In this case, during the MA process a decrease in the size of the crystalline blocks

of molybdenum and silicon occurs. After 20 min MA, the characteristic particle size of molybdenum in aggregates amounts to several tens of nanometers.

The annealing of the Mo–25at.%Si samples obtained by 10 min MA at 600 °C brings about the formation of a small amount of the β-MoSi$_2$ phase whereas, after the samples which had been mechanically activated for 20 min were annealed at this temperature, no silicide phases are detected. The X-ray diffraction patterns of the samples prior to and after annealing are essentially identical. Changes are detected only by the disappearance of the first amorphous halo with a center at 3.7 Å in the electron diffraction patterns. These data suggest that, during the MA of molybdenum and silicon of such a stoichiometry, two amorphous silicides of different compositions form sequentially. The first is of the approximate composition MoSi$_2$ and the second is enriched with molybdenum. The fact that the β phase of molybdenum disilicide crystallizes at 600 °C suggests that the amorphous phase producing a halo at 3.7 Å has the approximate composition of silicon disilicide. The disappearance of this phase during MA appears to be due to the progress of a reaction between amorphous molybdenum disilicide and unreacted molybdenum with the formation of amorphous disilicides high in molybdenum content [10] (from Mo$_{70}$Si$_{30}$ to Mo$_{60}$Si$_{40}$).

Variations in the phase composition of the samples during MA is accompanied by changes in the DTA curves. Two exothermic peaks are observed in the DTA curves of the samples subjected to mechanical treatment (to 10 min) (Fig. 3, curve a). The first has a maximum at 600 °C and the second in the region 700–800 °C. The DTA curves of the samples obtained after 30 min MA (Fig. 3, curve b) show only the second exothermic peak in the temperature range 700–800 °C. The annealing of such samples at 1000 °C results in the crystallization of the Mo$_3$Si phase, the reflections of which are seen in the X-ray diffraction patterns.

Such changes in the DTA curves during MA agrees well with the above data on changes in the phase composition of the products during MA. At the initial stages of MA, amorphous molybdenum disilicide forms. It crystallizes into β-MoSi$_2$ at 600 °C. Then, during the MA, MoSi$_2$ interacts with Mo to form amorphous silicides enriched with the metal. The temperature of crystallization of this amorphous silicide is higher than the temperature of crystallization of amorphous MoSi$_2$, which manifests itself as changes in the shape of the DTA curves.

3.2. The formation of the silicide Mo$_5$Si$_3$ during mechanical alloying

The study of the MA process during the formation of Mo$_5$Si$_3$ from a mixture of powdered Mo and Si taken in a ratio of 5 to 3 has shown that in this case the
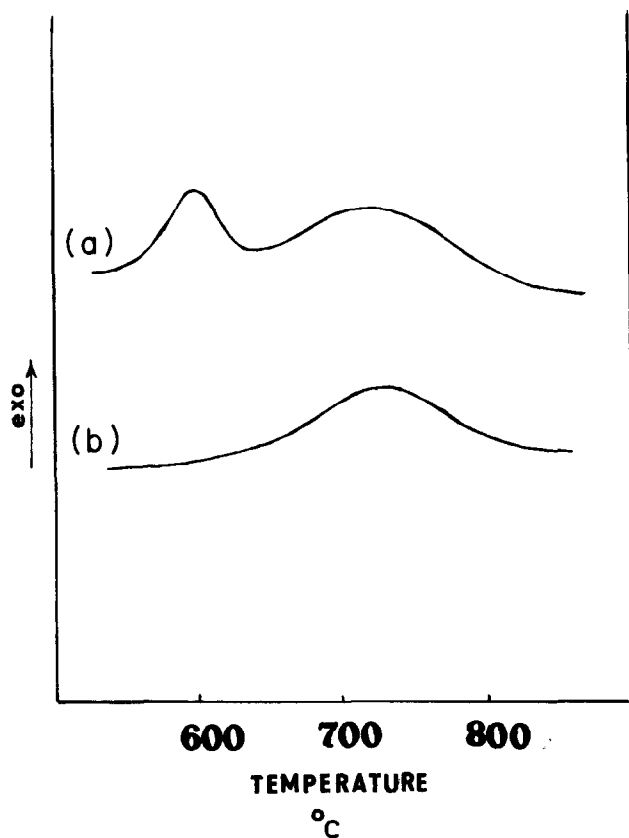
Fig. 3. DTA curves of Mo–25at.%Si powders milled for various times: curve a, 10 min; curve b, 30 min.
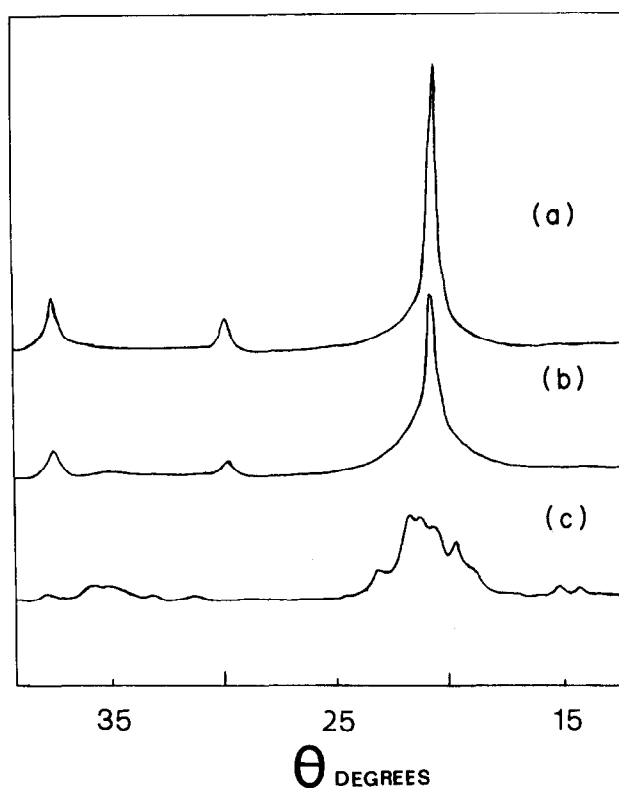

Fig. 4. Evolution of phases in Mo–37.5at.%Si powder as a function of milling time as shown by XRD patterns of the powders after 5 min MA (curve a), 10 min MA (curve b) and 30 min MA (curve c).

changes in the X-ray diffraction patterns at the early stages of treatment are analogous to the changes observed in the Mo–37.5at.%Si system during MA (Fig. 4).

(1) After 5 min MA no reflections of crystalline silicon are observed in the X-ray diffraction patterns (Fig. 4, curve a).

(2) The intensity of the Mo reflections decreases, and the reflections broaden and shift slightly (Fig. 4, curve b).

(3) The background in the angle range $2\theta = 36$–$48°$ increases (Fig. 4, curve c).

However, in contrast with MA in the Mo–25at.%Si system, during the MA of Mo–37.5at.%Si, the formation of Mo_5Si_3 is detected by the appearance of reflections of this phase in the X-ray diffraction patterns after 30 min MA.

After 20 min MA of Mo_5Si_3, the isothermal annealing of the samples at 500 °C gives rise to weak β-$MoSi_2$ reflections in the X-ray diffraction patterns together with the broadened reflections of molybdenum. The annealing of these samples at 1000 °C for 1 h causes the crystallization of the Mo_5Si_3 phase, which is detected by the appearance of reflections of this phase in the X-ray diffraction patterns.

In contrast with the X-ray data, the electron microscopy study has shown that the reflections of crystalline silicon are still observed in the electron diffraction patterns of Mo–37.5at.%Si after 10 min MA, whereas after 20 min MA the electron diffraction patterns show no silicon reflections. In this case, an amorphous halo in the region of 3.7 Å and reflections of Mo are seen (Fig. 5). The isothermal annealing of such samples at 600 °C gives rise to the β-$MoSi_2$ phase, which is accompanied by the disappearance of the amorphous halo in the region of 3.7 Å, and the annealing at 900 °C brings about crystallization of the Mo_5Si_3 phase.

During the MA of Mo–37.5at.%Si powders, DTA curves change (Fig. 6). For short MA times, two exothermic effects are observed: the first at 600 °C and the second in the temperature range from700 to 900 °C (Fig. 6, curve a), whereas for the times of mechanical treatment longer than 20 min, only a broad exothermic peak is observed at 700–900 °C (Fig. 6, curve b).

As a whole, the data obtained show that the formation of silicide phases during the MA of Mo–25at.%Si and Mo–37.5at.%Si are similar. At the initial stages of MA an amorphous silicide with the approximate composition of molybdenum disilicide forms and then the formation of amorphous molybdenum silicide enriched with the
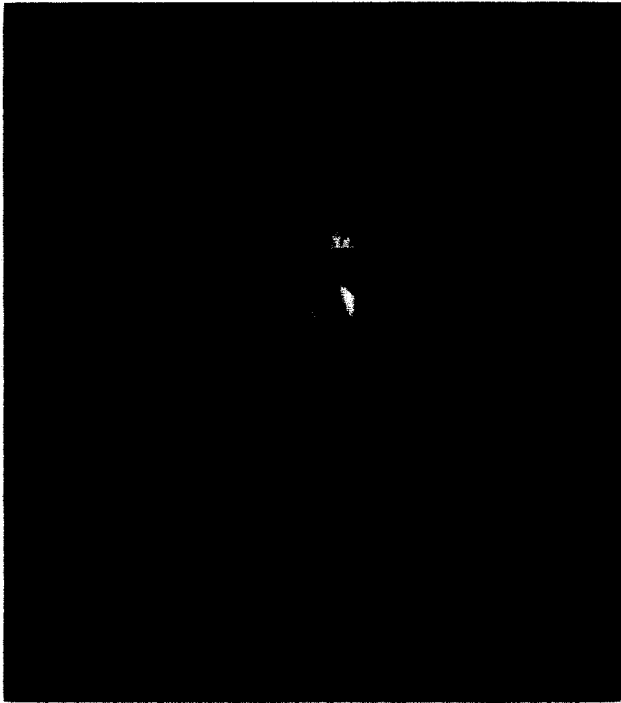
Fig. 5. Selected-area electron diffraction pattern of Mo–37.5at.%Si powder after 20 min MA.
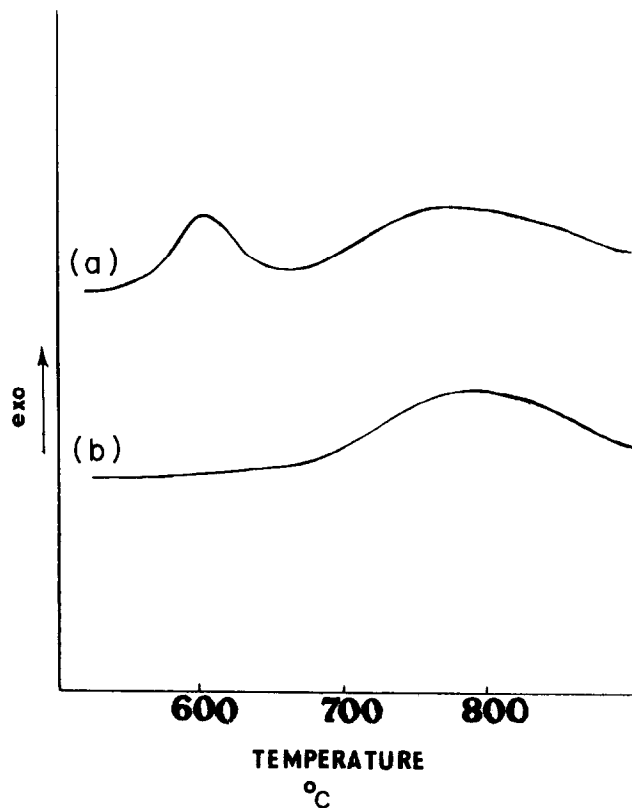

Fig. 6. DTA curves of Mo–37.5at.%Si powders milled for various times: curve a, 10 min; curve b, 30 min.

metal occurs. A distinctive feature of the process is the possibility of formation of the crystalline Mo₅Si₃ phase during MA, which appears to occur because the

energy of formation of the Mo_5Si_3 phase is higher than that of the Mo_3Si phase.

3.3. Formation of the $MoSi_2$ phase during mechanical alloying

The formation of molybdenum disilicide ($MoSi_2$) during MA shares a number of traits with the formation of the intermetallides Mo_5Si_3 and Mo_3Si during MA; yet at the same time these processes differ from one another.

As in the above processes of formation of silicide phases, during the MA of powdered molybdenum and silicon taken in a ratio of 1 to 2, the following changes are observed (Fig. 7).

(1) For mechanical treatment times less than 5 min, no reflections of silicide phases are detected in the X-ray diffraction patterns. For these treatment times, an abrupt decrease in and broadening of the reflections of crystalline silicon and insignificant broadening of the reflections of molybdenum are observed (Fig. 7, curve a).

(2) During MA, considerable changes in the state of the substances are observed in X-ray diffraction patterns after 6 min treatment. In this case the X-ray diffraction patterns show rather intense reflections of α-$MoSi_2$ (Fig. 7, curve b). A further increase in the MA time gives rise to the reflections of the high
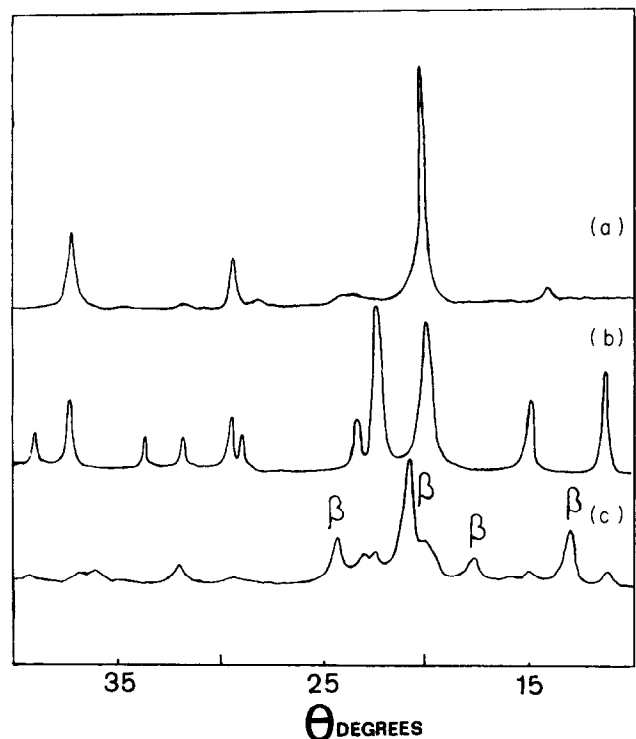

Fig. 7. Evolution of phases in the Mo–66.6at.%Si powder as a function of milling time, as shown by XRD patterns of the powders after 5 min MA (curve a), 10 min MA (curve b) and 30 min MA (curve c).

temperature β-MoSi$_2$ phase, together with the reflections of the stable low temperature phase of molybdenum disilicide, α-MoSi$_2$. During MA, a change in the ratio of the content of the α-MoSi$_2$ and β-MoSi$_2$ phases occurs; the α-MoSi$_2$ content decreases and the β-MoSi$_2$ phase increases. After 40 min MA, the X-ray diffraction patterns show mainly β-MoSi$_2$ reflections (Fig. 7, curve c).

An increase in the time of MA in the system Mo–66.6at.%Si produces changes in the DTA curves (Fig. 8). For the samples treated for 4 min, two exothermic peaks are detected: the first at 600 °C and the second rather broad peak in the region from 700 to 800 °C (Fig. 8, curve a). The thermal effect decreases as the time of mechanical treatment of the samples increases.

The DTA curves of the samples obtained after 40 min MA show only the wide exothermic peak in the region 700–800 °C (Fig. 8, curve b), characterizing the transformation of the metastable β-MoSi$_2$ into the stable α-MoSi$_2$ phase.

Several factors may be responsible for the first exothermic peak at 600 °C.

(1) The formation of molybdenum disilicide by the solid state synthesis is known to proceed at these temperatures.

(2) The existence of the exothermic effect is associated with the crystallization of amorphous molybdenum disilicide (analogously to the above examples of the synthesis of silicide phases in the Mo–37.5at.%Si and Mo–25at.%Si systems.

The lack of information about the formation of amorphous molybdenum disilicide may be associated with the fact that the formation of crystalline MoSi$_2$ from the amorphous state by MA proceeds with rather a high rate.

The transformation of low temperature α-MoSi$_2$ into high temperature β-MoSi$_2$ proceeds also during mechanical activation. In this case, as well as during MA, the concentration of β-MoSi$_2$ gradually increases and the α-MoSi$_2$ content decreases (Fig. 9). The transformation of the α phase of the disilicide into high temperature β-MoSi$_2$ is essentially completed after 30 min mechanical treatment. It can be suggested that the transformation of the stable α-MoSi$_2$ phase into metastable β-MoSi$_2$ can be caused by several factors.

(a) The transformation into high temperature β-MoSi$_2$ is due to a decrease in the particle size of disilicide. Similar stabilization processes of high temperature phases occur, for example, during the mechanical activation of zirconium oxide where the stable tetragonal phase ZrO$_2$ transforms into a metastable cubic phase [11]. In this case, the stabilization of the β-MoSi$_2$ phase proceeds at the cost of increased surface energy of the crystals.

(b) The transformation into the high temperature β-MoSi$_2$ phase may proceed by plastic deformation owing to the redistribution of close-packed silicon–molybdenum layers in the α-MoSi$_2$ structure. Since the structural designs of the α and β phases of molybdenum disilicide are essentially identical and are a system of
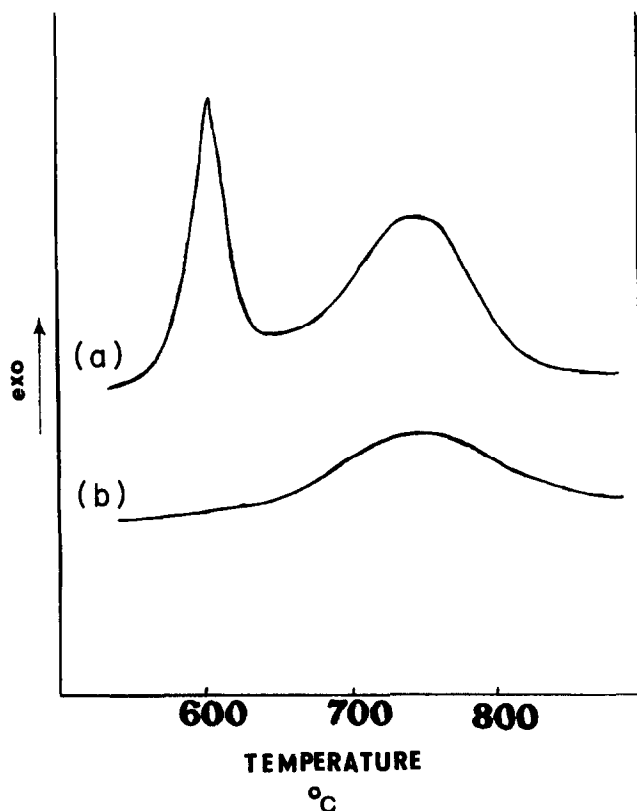

Fig. 8. DTA curves of Mo–66.6at.%Si powders milled for various times: curve a, 10 min; curve b, 30 min.
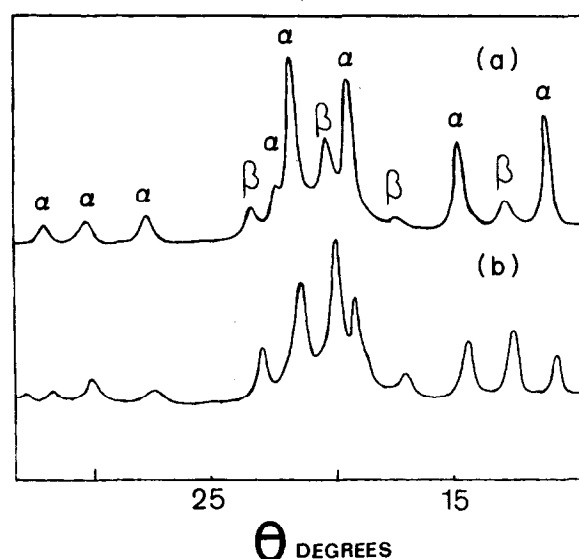

Fig. 9. X-ray diffraction patterns of MoSi$_2$ powders milled for 10 min (curve a) and 30 min (curve b).

close-packed silicon–molybdenum planes differing only in alternation (for α-MoSi$_2$ the layers alternate as ABAB, and the alternation as ABCABC is typical of β-MoSi$_2$), then during plastic deformation the redistribution of the alternation of the close-packed layers can possibly occur. This does occur in many close-packed oxide systems studied previously [12].

In order to establish the actual mechanism of transformation of stable α-MoSi$_2$ into high temperature β-MoSi$_2$, additional studies of the change in the morphology and structure of disilicide phases during mechanical treatment are needed.

4. Conclusion

The present investigation of MA in the Mo–Si system has shown that the formation of the silicide phases MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si shares a number of traits.

At the initial stage of the MA process with a different ratio of the components of the reaction mixture, an amorphous silicide of the approximate composition of molybdenum disilicide initially forms, and then amorphous silicides enriched with molybdenum do. Silicides of such compositions (from Mo$_{70}$Si$_{30}$ to Mo$_{60}$Si$_{40}$) are obtained using traditional methods of preparation of amorphous substances, namely the spinning of alloys, and joint spraying of substances on a support being cooled [10]. Therefore it is not surprising that amorphous silicides of the composition Mo$_5$Si$_3$ and Mo$_3$Si form during MA.

The formation of the amorphous silicide of the approximate composition of MoSi$_2$ at the initial stage of MA also has an analogy in the solid state synthesis of molybdenum silicides. In this case, for such systems a rule has been proposed for the determination of the first incipient phase at the planar metal–silicon interface [2]. This rule is based on the assumption that, as the metal is deposited at the interface between silicon and the metal, an amorphous phase forms, as in the case of rapid cooling of atoms of the metal on a surface. During annealing at the temperature of formation of silicides, a silicide of the approximate composition of the given amorphous phase is the first to form. The compositions of the amorphous phases approximate the high eutectic point in the phase diagram. The rule proposed in this work is that the silicide with the highest melting point near the deepest point of the eutectic in the binary phase diagram, i.e. the most stable silicide melting in a congruent manner is taken as the first

incipient phase. For the alloys of silicon and molybdenum, molybdenum disilicide (MoSi$_2$) is the first phase formed, as shown by the results in [2].

It is likely that during MA the formation of molybdenum silicides proceeds by a mechanism similar to the mechanism of solid state synthesis. At the initial stages of MA of molybdenum and silicon, the solid state diffusion of silicon into molybdenum proceeds under the action of plastic deformation. This character of the progress of the process allows the formation of amorphous silicide phases with different silicon contents in the silicide phase of molybdenum over a wide concentration range. In this case, for different Mo-to-Si ratios of the constituents of the reaction mixture the sequence of formation of amorphous phases is the same. The phase of composition MoSi$_2$ is the first amorphous phase formed and then the phase of approximate composition Mo$_5$Si$_3$ or Mo$_3$Si forms.

Despite the fact that it is at present not clear why the phase Mo$_3$Si does not form in the system under study, it can be suggested that the formation of an amorphous silicide of such composition as the end product is associated with the structure of the crystalline Mo$_3$Si phase (structure of the β-W type) which is an icosahedron inscribed in a cube. The presence of such structural elements in the crystalline structure determines largely the possibility of formation of the amorphous state.

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