Metastable phase transitions in Mo-Si and V-Si systems activated by high energy ball milling [①]

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[Abstract] Mechanical alloying of Mo-Si ($Mo_{33}Si_{67}$) and V-Si ($V_{75}Si_{25}$) powder mixtures was activated by high energy ball milling at ambient temperature. The metastable phase transitions in both systems during milling were investigated by X-ray diffraction, scanning and transmission electron microscopy. It is found that the alloying processes are closely related to the milling conditions. As far as the Mo-Si system is concerned, ball milling leads to the formation of both α-$MoSi_2$ (room temperature phase) and β-$MoSi_2$(high temperature phase), but lower energy milling favors the formation of β phase, while higher energy milling promotes the formation of α phase. In addition, if the milling energy is high enough, the Mo/Si reaction is governed by a self-propagating high temperature process. On the other hand, two different pathways of phase transition in the V-Si system were also identified depending on the milling intensity, i. e. weak milling leads to amorphous transition, whereas intensive milling causes the formation of V_3Si and V_5Si_3 intermetallic compounds. Finally, the thermodynamics and kinetics related to the different phase transitions in the two systems were discussed.

[Key words] mechanical alloying; phase transitions; energy transfer; Mo-Si; V-Si

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1 INTRODUCTION

Refractory metal silicides have attracted an increasing attention in recent decades because of their unique combination of mechanical, physical and chemical properties. However, synthesis of these materials is usually difficult because of their extremely high melting temperatures. Recently, mechanical alloying (MA) has shown to be a promising technique for materials synthesis, especially for those with high melting temperatures, such as refractory metal silicides and carbides[1, 2]. Mechanical alloying is basically a solid-state process activated by high-energy ball milling at room temperature[3], so the high temperature process usually involved in the conventional metallurgy can be totally avoided. Developed from the synthesis of oxide-disperse-strengthening (ODS) superalloys in 1970s[4], MA has been extensively used to prepare a variety of non-equilibrium phases or alloys. These include amorphous phases, supersaturated solid solutions, metastable crystalline and quasicrystalline intermediate phases as well as nanostructured materials[3, 5]. In this work, MA was used to prepare Mo- and V-silicides starting from elemental powders, as both of them are most promising materials in high temperature applications. To the best of our knowledge, little work has been done on V-Si system, but there have been a few works on the preparation of $MoSi_2$ and $MoSi_2$-based composites by means of mechanical alloying[6~8]. It has been re-

ported that both α-$MoSi_2$ and β-$MoSi_2$ are usually formed simultaneously during mechanical alloying. However, some investigators indicated that β-$MoSi_2$ is the dominant phase obtained[6], while other authors reported that α-$MoSi_2$ is the phase mainly formed[7, 8]. The aim of the present study is to try to clarify these discrepancies and to investigate the correlation between energy transfer and the phase transitions in both Mo-Si and V-Si systems.

2 EXPERIMENTAL

Mo-Si and V-Si powder mixtures with nominal composition of $Mo_{33}Si_{67}$ and $V_{75}Si_{25}$ were prepared using pure Mo, V and Si powders (purity> 99. 5%, size< 75 μm). Mechanical alloying was carried out in both planetary (Fritsch P5) and shaker (Spex 8000) ball mill under Ar protection. Different balls and plate rotation speeds were selected in order to vary the milling intensity. The process parameters used in this work are summarized in Table 1. Based on Magini's model[9, 10], the energy input per collision (ΔE) for planetary mill can be quantified through the following equation:

$$\Delta E = 4. 31 \times 10^{-2} R_p^{1.2} \cdot \rho^{0.6} \cdot d_b \cdot$$
$$\omega_p^{1.2} / \sigma \cdot (\frac{1}{E_1} + \frac{1}{E_2})^{0.4} \tag{1}$$

where R_p is the radius of plate of the mill, ρ and d are the density and the diameter of ball ($\rho_{ss}= 7. 64 \times 10^3$ kg/ m^3, $\rho_{wc} = 15. 82 \times 10^3$ kg/ m^3), respectively;

Table 1 Energy input per collision under different milling conditions

System	Code	Ball mill	Rotation speed /(r·min⁻¹)	Ball /size	Energy input per collision ΔE /(J·g⁻¹)
	A	Fritsch P5	150	ss/d 3 mm	26
	B	Fritsch P5	280	ss/d 4 mm	55
	C	Fritsch P5	280	ss/d 6 mm	85
Mo-Si	D	Fritsch P5	280	ss/d 10 mm	170
	E	Fritsch P5	320	ss/d 15 mm	375
	F	Spex 8000	–	wc/d 8 mm	610
V-Si	G	Fritsch P5	280	ss/d 10 mm	120
	H	Fritsch P5	280	wc/d 10 mm	240

ss —stainless steel ball; wc —WC ball, stainless steel vials are used in all the milling conditions

ω_p is the rotation speed of the supporting plate and σ is the adhering powder surface density, which can be estimated by measuring the mass of the powder coating the balls; E_1 and E_2 are the Young's modulus of the ball and vial used (E_{ss}= 2. 11 × 10¹¹ N/m², E_{wc} = 7. 2 × 10¹¹ N/m₂), respectively. The energy inputs derived from the above equation for different milling conditions (A ~ H) are shown in the last column of Table 1. To be noted that the energy input given by Spex mill (condition F) is indirectly attained according to the empirical correlation between Spex mill and planetary mill[9].

Samples for analysis were taken out by interrupting milling at selected times. X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM) were employed to monitor the structure change of milled powders. XRD patterns were recorded by a Seifert diffractometer (PAD VI) using MoK$_\alpha$ radiation. SEM and TEM observations were performed under Amary-1000B scanning electron microscope and Joel-200CX transmission electron microscope, respectively.

3 RESULTS

The XRD patterns of Mo-Si mixture after 60 h of milling in the planetary mill under conditions A ~ E are shown in Fig. 1. The XRD spectrum at the lowest energy input (condition A in Table 1) shows that no reaction at all has occurred, as indicated by the presence of the sharp peaks of the starting components. The Mo/Si reaction takes place with the formation of some α-MoSi₂(room temperature phase) and β-MoSi₂ (high temperature phase) when the milling energy reaches the level corresponding to condition B. Further increasing milling energy then causes more Mo and Si to transform into the two Mo-disilicides until

complete depletion of the starting components in condition D. It is worthy to note that the lower energy milling favors the formation of β-MoSi₂, while the higher energy milling promotes the formation of α-MoSi₂. The relative change in the amount of α and β phase (in the form of the ratio of the integral intensity of α(111) and β(111) reflections) with energy input is shown in Fig. 2. It is clearly demonstrated that the amount of α-MoSi₂ monotonously increases with milling energy.
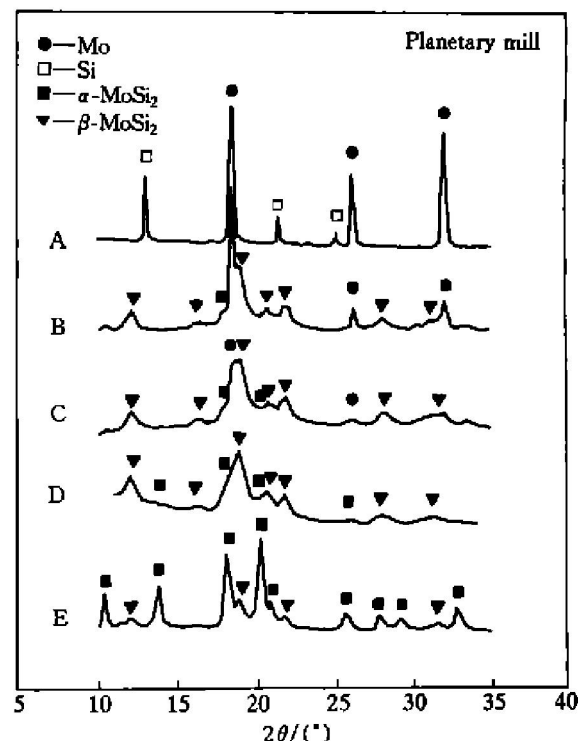

Fig. 1 XRD patterns of Mo₃₃Si₆₇ mixture milled for 60 h in planetary mill under different milling conditions
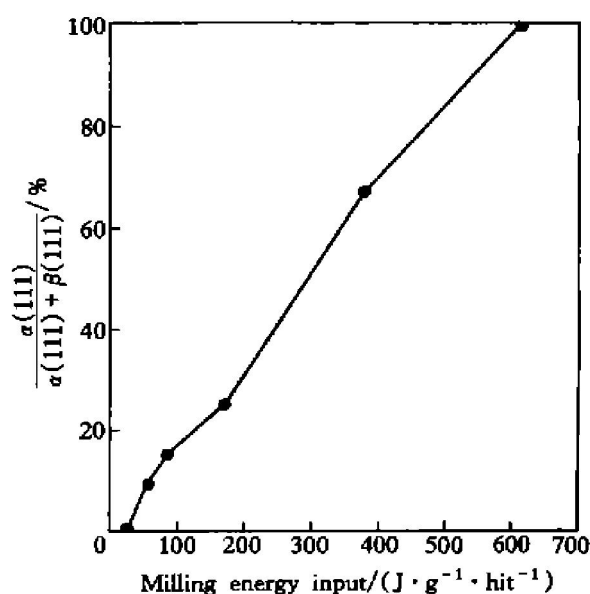

Fig. 2 Change in amount ratio of α-MoSi₂/ β-MoSi₂ with energy input

Regarding the phase transitions occurring in the Spex shaker mill, which provides the highest energy input of the present investigation. The XRD results of Mo-Si mixture after various milling times in this case are shown in Fig. 3. For milling duration less than 2 h (not shown), no Mo/Si reaction occurs except broadening and decrease of Mo and Si peaks. After 2 h of milling, a trace amount of α-MoSi$_2$ can be noticed. Based on the linewidth of reflections and Scherrer formula, the mean crystallite size of Mo and Si is estimated to be 14 nm and 9 nm, respectively. This demonstrates that the intimate mixing of starting powders at nano scale is achieved by milling. After 3 h of milling, a rapid reaction with a sharp increase in α phase is observed. Further processing then leads to considerable broadening of the formed α-MoSi$_2$ peaks while the remaining Mo peaks gradually drop down. After 10 h of milling, Mo peaks totally vanish, α-MoSi$_2$ peaks dominate, and small peaks corresponding to β-MoSi$_2$ appear. The latter increases when extending the milling time up to 20 h. This indicates that α-MoSi$_2 \longrightarrow$ β-MoSi$_2$ transition is occurring at the latest stage of milling. Fig. 4 shows the SEM photographs of Mo-Si samples milled for 2 h and 3 h. A rather uniform particle size distribution, with typical diameter of about 5 μm, was observed just before the rapid Mo/Si reaction (Fig. 4(a)). However, after 3 h of milling, SEM shows extensive agglomerates with the size of a majority of particles ranging from 10 ~ 30 μm, some particles even overpass 100 μm and the trace of melting can be frequently
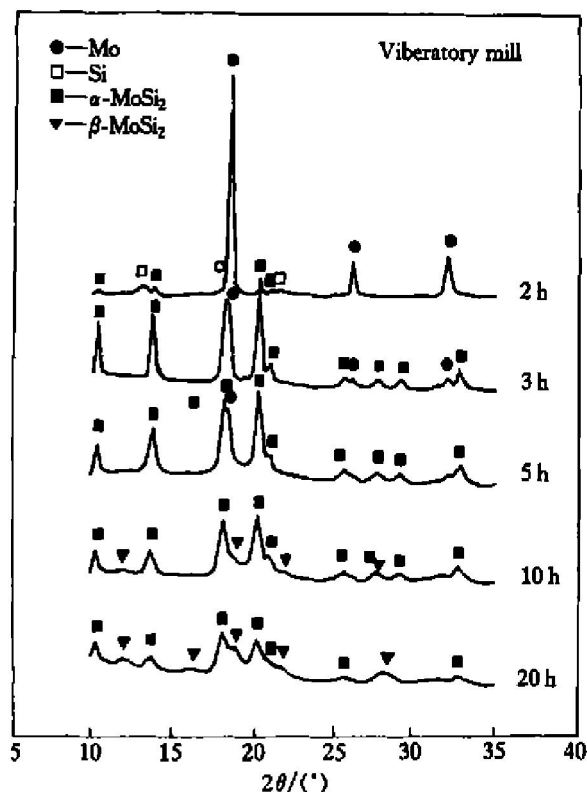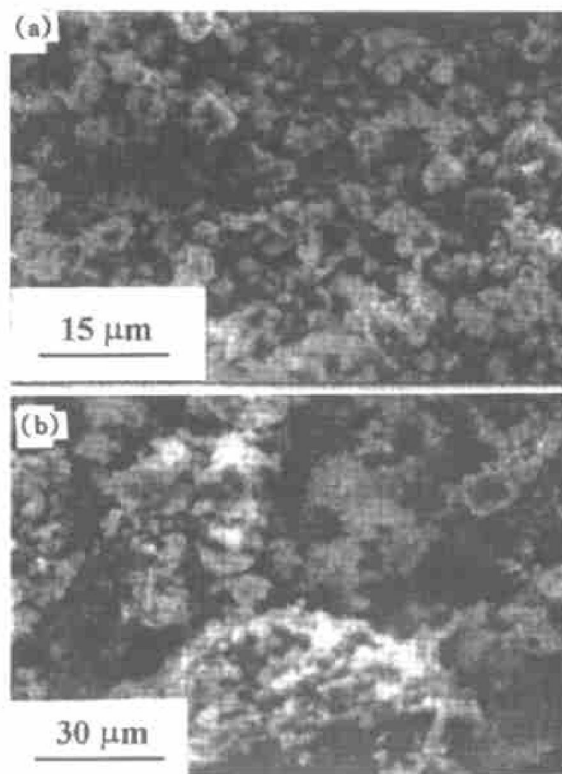

Fig. 4 SEM micrographs of Mo$_{33}$Si$_{67}$ mixture milled for 2 h (a) and 3 h (b) in Spex mill

found (Fig. 4(b)). Considering both XRD and SEM results, we believe that the rapid reaction of Mo+ Si $\longrightarrow$ α-MoSi$_2$ during 2~ 3 h in Spex mill is governed by a self-propagating high-temperature synthesis (SHS) process, similar to the previous findings of Ma[11] and Yan[12].

The XRD results of V-Si mixture milled for 3 h and 60 h under conditions G (lower energy) and H (higher energy) are shown in Fig. 5. Two different pathways of V/Si reaction are clearly identified, depending on milling intensity. Lower energy milling leads to an amorphous transition, whereas higher energy milling mainly causes the formation of intermetallic compounds, such as V$_3$Si and V$_5$Si$_3$. The TEM micrographs of the V-Si alloys milled for 60 h under the two milling conditions are shown in Fig. 6. The featureless structure in the bright field image and the diffused halo in the corresponding selected-area electron diffraction (SED) as seen in Fig. 6(a) further confirm the formation of an amorphous phase when low energy milling is carried out. On the contrary, the formation of nanocystalline phases with grain size of 10~ 30 nm is observed when high energy milling is employed (Fig. 6(b)). The corresponding SED patterns demonstrate that the phases formed are mainly composed of V$_3$Si and V$_5$Si$_3$. Results revealed by TEM are in agreement with XRD data.

4 DISCUSSION

The experimental results demonstrate that me-

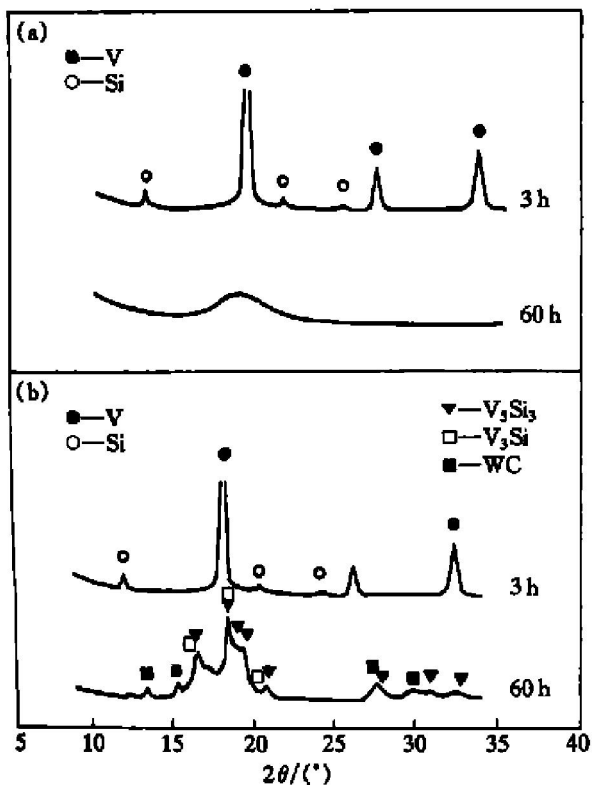**Fig. 3** XRD patterns of Mo$_{33}$Si$_{67}$ mixture milled for different time in Spex mill

Fig. 5 XRD patterns of $V_{75}Si_{25}$ mixture milled for 3 h and 60 h in planetary mill under condition G (a) and condition H (b)
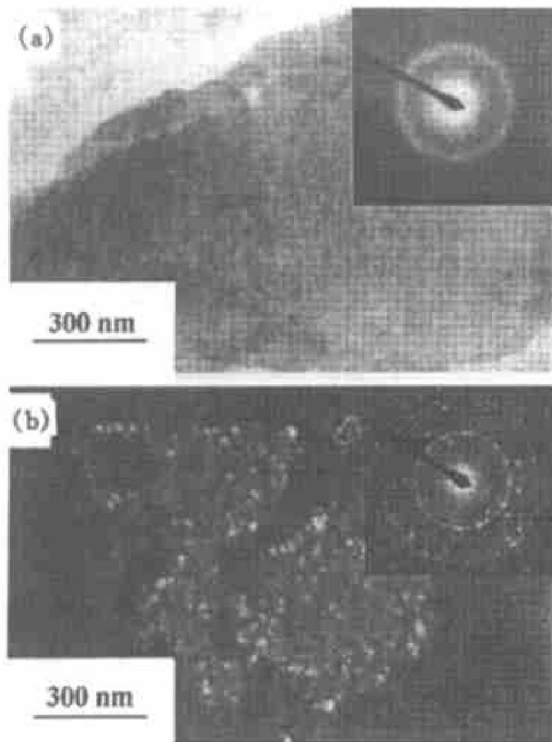

Fig. 6 TEM micrographs and corresponding selected electron diffraction patterns of $V_{75}Si_{25}$ mixture milled for 60 h under condition G (a) and condition H (b)

chanical alloying of Mo-Si and V-Si mixture can be realized by simple ball milling at ambient temperature. However, the milling condition plays a critical role in the alloying processes and the attainment of the end products. As far as Mo-Si system is concerned, increasing milling intensity not only speeds up the Mo/Si reaction to form Mo-disilicides, but also increases the amount ratio of α-$MoSi_2$/β-$MoSi_2$. It follows that lower energy milling favors β-$MoSi_2$ formation, while higher energy milling promotes α-$MoSi_2$ formation. These phenomena can not be explained solely on the basis of thermodynamic data. According to the Mo-Si phase diagram, the α phase (tetragonal) is stable at room temperature, while β phase (hexagonal) becomes stable only at the temperature higher than 1 900 ℃. In other words, α phase possesses a lower free energy than β phase at ambient temperature, formation of the latter, however, requires a smaller mechanical activation. To understand the present results, the kinetics associated with phase transition should be also taken into account. In general, a phase formation in any process requires a minimum energy to overcome the kinetic barrier for nucleation. In MA process, the kinetic energy is uniquely supplied by the ball collisions. Our previous work[13] has demonstrated that, when the premilled Mo-Si mixture is submitted to annealing, β-$MoSi_2$ is always formed prior to the formation of α-$MoSi_2$. Similar result has been also found by Doland and Nemanich[14] who studied the solid state reaction between Mo thin film and Si substrate. It is revealed that the preferential formation of β-$MoSi_2$ is due to the lower β-$MoSi_2$/Si interfacial energy, which results in a lower nucleation barrier (i. e. low activation energy). This kinetic constraint should also be the key factor controlling Mo/Si reaction in the process of mechanical alloying. Although α-$MoSi_2$ possesses a lower free energy, its formation is suppressed, when using lower energy milling, by supposing higher activation energy of nucleation of this phase.

Discussed above concerns only the phase transitions in the planetary mill. In such a case, the Mo/Si reaction follows a slow process, governed typically by the interdiffusion mechanism. However, if Mo-Si mixture is submitted to Spex mill (condition F), a rapid Mo/Si reaction process with the formation of single α-$MoSi_2$ is observed. Considering the phenomena of melting and heavy agglomeration of particles underlying the rapid process (see Fig. 4(b)), it is suggested that the phase transitions in Spex mill be dominated by a self-propagating high-temperature synthesis (SHS) process. Recent studies have shown that, for the systems with large negative heat of mixing, a sustained high temperature process could take place if a proper milling condition was adopted[15]. We believe that the high impact pressure at collision site in Spex mill ($6. 2 \times 10^9$ N/m^2, using WC ball and stainless steel vial[16]) and the nanostructure generated by milling are two critical parameters inducing the

SHS process in the present study. As the Mo/Si reaction to form α-MoSi$_2$ is highly exothermic, once the reaction is triggered in one particle or a small local volume, the heat released (− 132 kJ/mol) is sufficient to ignite the neighbor region, so the reaction can be self-sustained.

The thermodynamic and kinetic considerations can also be used to interpret the phase transitions in V-Si system, for which lower energy milling always led to amorphization, while higher energy milling resulted in the formation of V$_3$Si and V$_5$Si$_3$ intermetallic compounds. A few of works have demonstrated that the kinetic barrier for the formation of amorphous phase is generally lower than that for an intermetallic compound, because atomic rearrangement is usually involved in the latter case in order to meet the structural and compositional requirements for nucleation. Therefore, high energy milling is required for the formation of an intermetallic compound, although it has a lower free energy with respect to amorphous phase.

5 CONCLUSION

Mechanical alloying of Mo-Si and V-Si powder mixtures is activated by high-energy ball milling. However, the phase transitions in both systems are closely related to the energy input. As far as the Mo-Si system is concerned, higher energy milling favors the formation of the room temperature phase α-MoSi$_2$ while lower energy milling promotes the formation of metastable phase β-MoSi$_2$. This is likely due to a higher nucleation activation energy of α phase with respect to that of β phase. Moreover, if the energy input is high enough, Mo-Si reaction is governed by a self-propagating high-temperature synthesis (SHS) process. The high shock pressure and the nanostructure generated by milling act as the ignition of the reaction, and the large heat of formation of α-MoSi$_2$ is believe to catalyze the whole transformation of the phase itself. As for the V-Si system, two different pathways of phase transition have also been identified, depending on the milling intensity, i. e. lower energy milling leads to the formation of an amorphous phase, whereas higher energy milling results in the formation of V$_3$Si and V$_5$Si$_3$ intermetallic compounds. The difference in activation energy for the formation of amorphous phase and intermetallic compound is responsible for the different pathways of V-Si phase transitions.

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