

Evidence for self-sustained MoSi₂ formation during room-temperature high-energy ball milling of elemental powders

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We present evidence indicating that rapid, self-sustained, high-temperature reactions play an important role in the formation of tetragonal MoSi₂ during room-temperature high-energy ball milling of elemental powders. Such reactions appear to be ignited by mechanical impact in an intimate, fine-grained, Mo–Si physical mixture formed after an initial milling period. Under certain conditions, limited propagation of self-sustained reactions in these uncompacted powder mixtures renders the compound formation seemingly gradual in bulk-averaged analysis. It is suggested that this type of reaction is an important mechanism in the mechanical alloying of highly exothermic systems. Results are discussed in comparison with similar reactions we observed in ball-milled Al–Ni powders, with self-sustained combustion synthesis previously reported for Mo–Si powders, and with interfacial diffusional reactions in Mo–Si powders or thin-film diffusion couples.

I. INTRODUCTION

The refractory molybdenum disilicide is currently of considerable interest because of its importance and potential in industrial applications.¹ The combination of high melting point (2050 °C), low density (6.24 g/cm³), and very high stability in oxidizing and corrosive environments makes MoSi₂ an excellent high-temperature structural material. This is demonstrated, for example, by the increasing use of MoSi₂ for heating elements in furnaces that operate in air at temperatures up to 1700 °C. MoSi₂ has been synthesized using various methods such as arc-melting and casting, or powder reactions involving sintering and hot-pressing.^{2–4} There are at least two drawbacks to these traditional techniques. First, most processes require very high temperatures and industrial furnaces. Second, contaminants are usually incorporated into the material during processing and affect its properties. For example, oxygen, when reacting to form SiO₂ particles inside the MoSi₂ matrix, degrades its high-temperature mechanical properties.

Combustion synthesis, often termed self-propagating high-temperature synthesis (SHS), has also been used to produce MoSi₂.^{5,6} This type of reaction makes use of the high heat of formation of MoSi₂ from the constituent elements ($\Delta H_f = 31$ kcal/mole MoSi₂⁵). The reaction to form MoSi₂ is induced in the surface layer of a compacted Mo–Si powder mixture pellet by radiative heat from an ignition coil placed close to the pellet surface. The strong exothermic reaction at the surface liberates sufficient heat to raise the temperature of adjacent regions of reactants and the reaction becomes

self-sustained. The reaction front propagates at a speed on the order of 10 cm/min, without additional external heating.^{5,6} It has also been reported that SHS volatilizes impurities, and that its products can be sintered at lower temperatures compared with commercial powders.⁵

Very recently, high-energy ball milling, a mechanical alloying technique, has been applied to synthesize MoSi₂ from elemental Mo and Si.⁷ This technique has several advantages. First, ball milling can lead to atomic-level alloying at room temperature even for refractory metals. Second, it can produce alloys with a very low level of oxygen contamination. Third, it offers the flexibility of controlling solute or second-phase additions as well as grain/particle sizes of the product, with beneficial effects on subsequent processing and properties.⁷ In this paper, we address the mechanism of MoSi₂ formation by high-energy ball milling. We show evidence that a self-sustained exothermic reaction is a key mechanism in this process. The results will be compared with those obtained recently in another system, Al–Ni, in which self-sustained exothermic reactions have been observed and monitored *in situ*.^{8,9}

II. EXPERIMENTAL

Commercially available Mo (purity 99.95%, –100 mesh, <150 μm) and Si (purity 99.5%, –325 mesh, <44 μm) powders were blended into mixtures with overall compositions, 1Mo:2Si, 2Mo:3Si, and 3Mo:1Si, in atomic fractions. Ball milling was conducted using a SPEX 8000 laboratory shaker mill. For each milling run, 6 g of powder mixture were loaded into a hardened stainless steel vial, together with three 8-g and eight 1-g hardened stainless steel balls, at a ball-to-powder weight ratio of about 5 to 1. During milling,

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these balls typically carry kinetic energy on the order of 0.01 J, and the upper bound can be as high as 0.5 J for an 8-g ball.¹⁰ The powders were stir-mixed in the vial, which was subsequently sealed in Ar atmosphere. Milling was performed at room temperature with durations ranging from 1 h to 20 h. The durations cited are all for uninterrupted runs with a sealed vial. The temperature of the vial was about 65 °C during typical milling runs.

For phase identification of the milling product, about 0.1 to 0.2 g samples of the milled powders were examined by x-ray diffraction in the θ - 2θ geometry using Cu K α radiation at a power of 0.9 kW. A Rigaku diffractometer equipped with a rotating anode source operating at 6.5 kW and a graphite monochromator were also used in some cases for improved intensity and reduced background. The silicide phases were identified by comparing diffraction patterns with published JCPDS files.¹¹

The width of x-ray diffraction Bragg peaks, w (in 2θ), was monitored as a function of milling duration for various powders. The first two low-angle t -MoSi₂ diffraction peaks, (002) and (101), were chosen in these experiments because of their relatively high intensity and insignificant overlap with other peaks. w was obtained by subtracting the instrumental and K α_1 /K α_2 contributions to the peak width, w_i , from the directly measured peak width, w_{FWHM} , taken as the full width at half maximum (FWHM), using the relationship,

$$W^2 = W_{\text{FWHM}}^2 - W_i^2. \quad (1)$$

Using high-purity single crystal Si and sapphire as standards, the resolution limit, $w_i = 0.15^\circ$, was established for our diffraction setup. This limit was dominated by K α_1 /K α_2 broadening, since the two wavelengths were not resolved at low angles. Detailed experiments were carried out to observe the ball-milling effect on w for t -MoSi₂ powders obtained from commercial sources, and for 2Mo:3Si powders after 2 h of milling. In the former case, 10 g of commercial t -MoSi₂ powders (purity 98.9%, -325 mesh, <44 μm) were milled in the same manner as elemental powders. The ball-to-powder weight ratio was kept constant (5:1) throughout the experiment to simulate the milling conditions used for elemental powders. About 0.15 g of powder were removed from the vial after each milling interval and examined by x-ray diffraction for the determination of w using Eq. (1). For 2Mo:3Si powders after 2 h of milling, a 3 g load was milled for additional times after removing some of the powder for other analysis. The ball-to-powder weight ratio was thus 10:1. To compare with results obtained for other powders, linear scaling was assumed such that 5 min at a weight ratio of 10:1 are equivalent to 10 min at a ratio of 5:1.

Selected powder samples were examined in a Hitachi S-570 scanning electron microscope (SEM)

equipped with energy dispersive x-ray (EDX) analysis. Contamination from milling tools was found to be below the detection limit of our EDX analysis (about 1 at. %) for 1Mo:2Si powders milled to 5 h. Fe and Cr impurities were detected at a level of 2 at. % and 1 at. %, respectively, after 10 h of milling, and about 5 at. % and 2 at. %, respectively, after 20 h of milling. Thermal analysis was performed in a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) under flowing Ar at heating rates of 5–40 K/min. For each DSC run, 20–30 mg of powders were hermetically sealed in a gold pan to allow a temperature excursion to 730 °C.

III. RESULTS AND DISCUSSION

A. Silicide formation during ball milling

We first describe the results for the powders with the overall atomic composition of 1Mo:2Si. For milling durations <2 h, only Mo and Si peaks were present in the x-ray diffraction pattern. As expected for cold-work induced strain buildup and grain size reduction, the observed diffraction peaks were broadened compared with those of unmilled powder mixture.¹² A rapid decrease in integrated intensity was noticed for Si peaks. Similar behavior has been reported in Ref. 7 as well as for milling of other Si-containing powder mixtures.^{13,14} This reduction can be attributed to x-ray absorption effects,¹⁵ and possibly to dissolution of Si in Mo or at grain boundaries, and defects in the Si phase. No new diffraction peaks were observed at this stage. Tetragonal MoSi₂ (t -MoSi₂, JCPDS 41-612) appeared in trace amounts after milling to about 2 h and increased only slightly upon further milling up to <3 h. As an example, we show in Fig. 1(a) the x-ray diffraction pattern for a sample milled for 155 min. Only very low-intensity t -MoSi₂ peaks can be seen at this stage. SEM examination of this sample revealed a rather uniform particle size distribution, with a typical diameter of 30 μm . No discrete Mo and Si regions could be resolved under SEM or using EDX, suggesting absence of compositional heterogeneities on a scale greater than or equal to 1 μm .

A rapid increase in the amount of t -MoSi₂ was observed for milling duration ≥ 3 h. This is demonstrated in the diffraction pattern of Fig. 1(b) for powders after a 3 h milling run. The t -MoSi₂ phase dominates, with only a small amount of Mo visible in the diffraction pattern. The positions and relative intensities of the t -MoSi₂ Bragg peaks are similar to those observed for other t -MoSi₂ powders, either formed by ball milling,⁷ by SHS,⁵ or as-received from commercial sources, and also in good agreement with those given in JCPDS 41-612 (intensities differ somewhat from an older standard pattern, JCPDS 6-681). An SEM micrograph of the sample corresponding to Fig. 1(b) is shown in Fig. 2. The

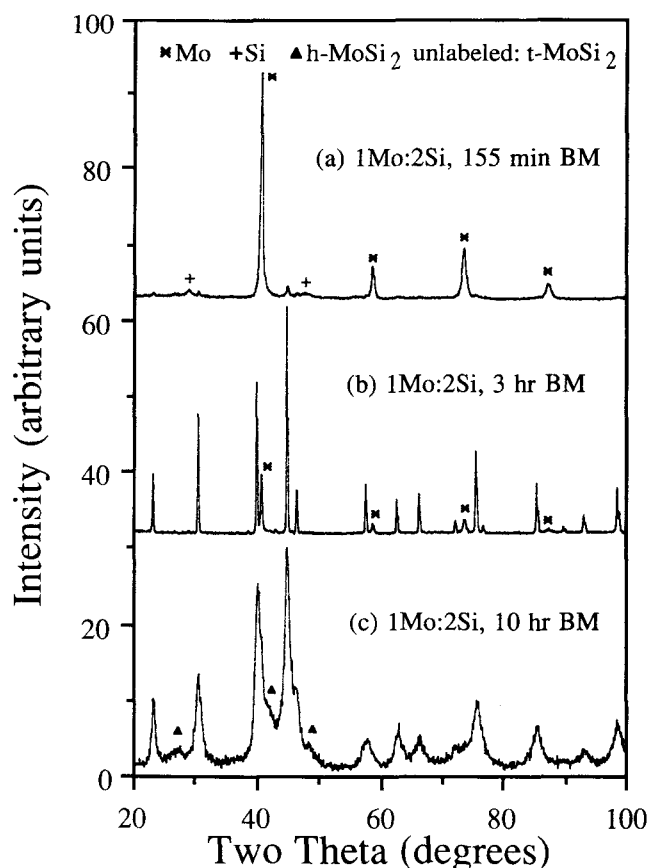


FIG. 1. X-ray diffraction pattern (CuK α) for 1Mo:2Si powder (a) ball-milled for 2 h and 35 min (155 min), showing the presence of only a trace amount of *t*-MoSi₂, (b) after a 3 h ball-milling run, showing the dominant presence of *t*-MoSi₂, with extremely sharp diffraction peaks, and (c) ball-milled for 10 h, showing full consumption of the elements to form *t*-MoSi₂ plus a trace amount of *h*-MoSi₂, and the obvious broadening of diffraction peaks.

powder particles had a size distribution ranging from 1 μm to a few hundred μm , but the diameter of the majority of the particles was still on the order of 30 μm . Again, no compositional heterogeneity was detectable using EDX.

It appears that the majority of the reaction to form *t*-MoSi₂ occurred shortly after the powder mixture had been milled for about 3 h. We have repeated the experiment with about fifteen uninterrupted milling runs of length between 2 and 4 h. The fraction of powder consumed in the reaction to form *t*-MoSi₂, determined from the reduction in intensity of the Mo (110) diffraction peak, is plotted versus milling duration in Fig. 3. The volume fractions transformed are observed to be either less than 17% or greater than 68%, with no intermediate values. This indicates an abrupt *t*-MoSi₂ formation reaction, which occurred at milling durations that varied between 3 and 3.25 h. For all the milling runs we performed, a dominant portion of the powder, similar to the case in Fig. 1(b), had transformed to *t*-MoSi₂ after no

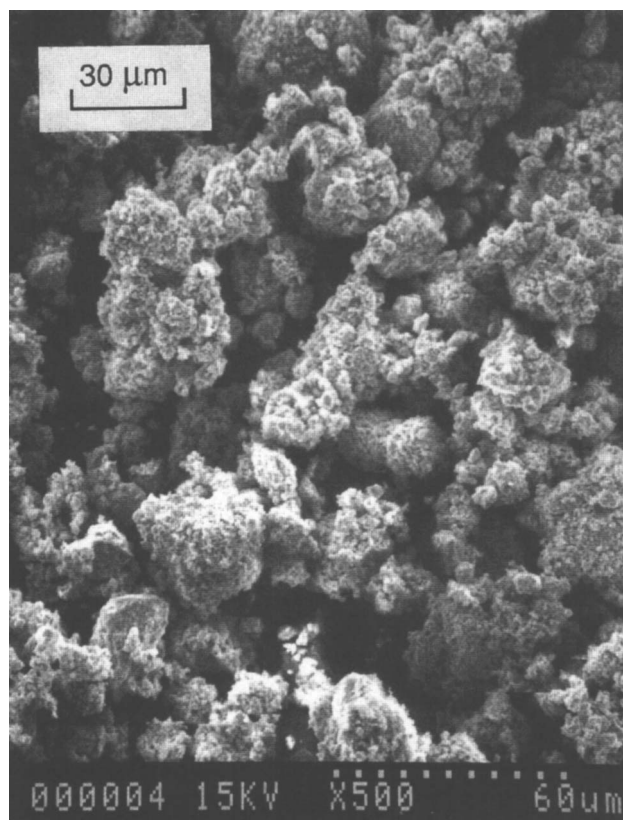


FIG. 2. Scanning electron micrograph of 1Mo:2Si powder milled 3 h [same sample as that used in Fig. 1(b)].

later than 3.5 h of milling. The majority of the reaction appears to have taken place within a fraction of this 0.5 h period. Further milling for several hours after this stage led to only a slow increase of the amount of *t*-MoSi₂, accompanied by increased broadening of all diffraction peaks, with the remaining Mo being consumed gradually.

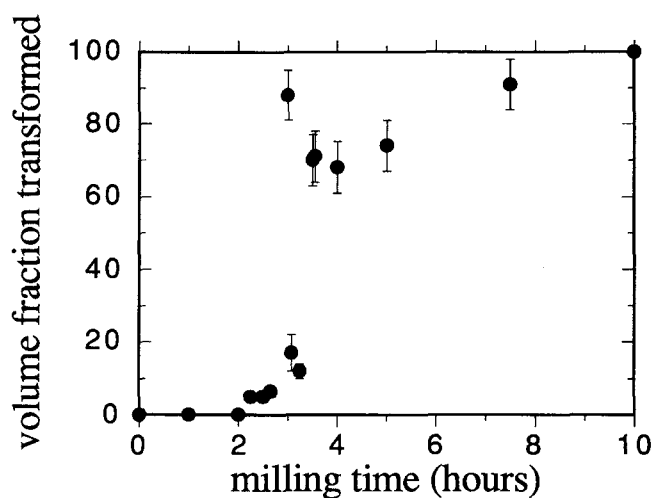


FIG. 3. Volume fraction transformed versus milling duration, showing the majority of the silicidation occurring between 3 and 3.5 h of milling. Each data point was obtained for a separate, uninterrupted run.

The Mo diffraction peaks completely disappeared after 10 h of milling, as shown in the diffraction pattern of Fig. 1(c). The phase present was almost solely *t*-MoSi₂, with a trace amount of hexagonal MoSi₂ (*h*-MoSi₂, JCPDS 17-917). This *h*-MoSi₂ phase has been reported to be the equilibrium phase above 1900 °C.¹⁶ It also appears during annealing of elemental diffusion couples below 800 °C,^{17–21} probably as a metastable phase^{21,22} when the formation of the equilibrium *t*-MoSi₂ is prevented by kinetic constraints. Additional ball milling up to 20 h caused the amount of *h*-MoSi₂ to increase, which appears to result from a transformation of *t*-MoSi₂ to *h*-MoSi₂ during milling. This transformation is not surprising, since ball milling is known to induce phase transformations into high-temperature phases due to stored cold-work energy.²³ The coexistence of *t*-MoSi₂ and *h*-MoSi₂ has been observed before for 20 h ball-milled Mo–Si powder mixture.⁷ For powders milled to various durations, EDX confirmed the overall compositions to be close to 1Mo:2Si with variations less than 5%.

The observations above indicate that, although full consumption of Mo and Si may require several hours of milling, a dominant portion of the powders always reacted to form *t*-MoSi₂ within a short milling period. The exact length of this period is difficult to determine since the point in time at which the sudden reaction occurs varies from run to run (Fig. 3) and is thus difficult to pinpoint. Periodic sampling requires opening and resealing the vial, which is found to lead only to a gradual reaction over several hours. However, a key observation suggests that the reaction duration can be shorter than a few minutes; when milling runs were terminated at the appropriate time, the Bragg diffraction peaks for the dominant *t*-MoSi₂ phase were exceedingly narrow, $w = 0.07$ for the (002) *t*-MoSi₂ peak. These narrow peaks can be seen in Fig. 1(b). They are in fact narrower than for many pure elemental materials [e.g., as-received Mo, Si, and commercial *t*-MoSi₂ powders (Fig. 4), or annealed Ag sheet] examined with our x-ray diffractometer. Further milling of the same powder for an additional 5 to 30 min led to appreciable broadening of all *t*-MoSi₂ diffraction peaks [w increased to about 0.30° after 30 min for the (002) *t*-MoSi₂ peak]. For comparison, we have carried out a systematic measurement of the Bragg peak broadening for commercial *t*-MoSi₂ powders as a function of milling time. The w values measured for the (002) and (101) peaks are represented by filled circles in Figs. 4(a) and 4(b), respectively. We can conclude from Fig. 4 that milling of MoSi₂ for short durations will lead to significant broadening, which can be readily detected for powders milled for times as short as 5 min. More pronounced broadening was observed for the (101) peak than for (002). This dependence of the peak width, ΔK , on the magnitude

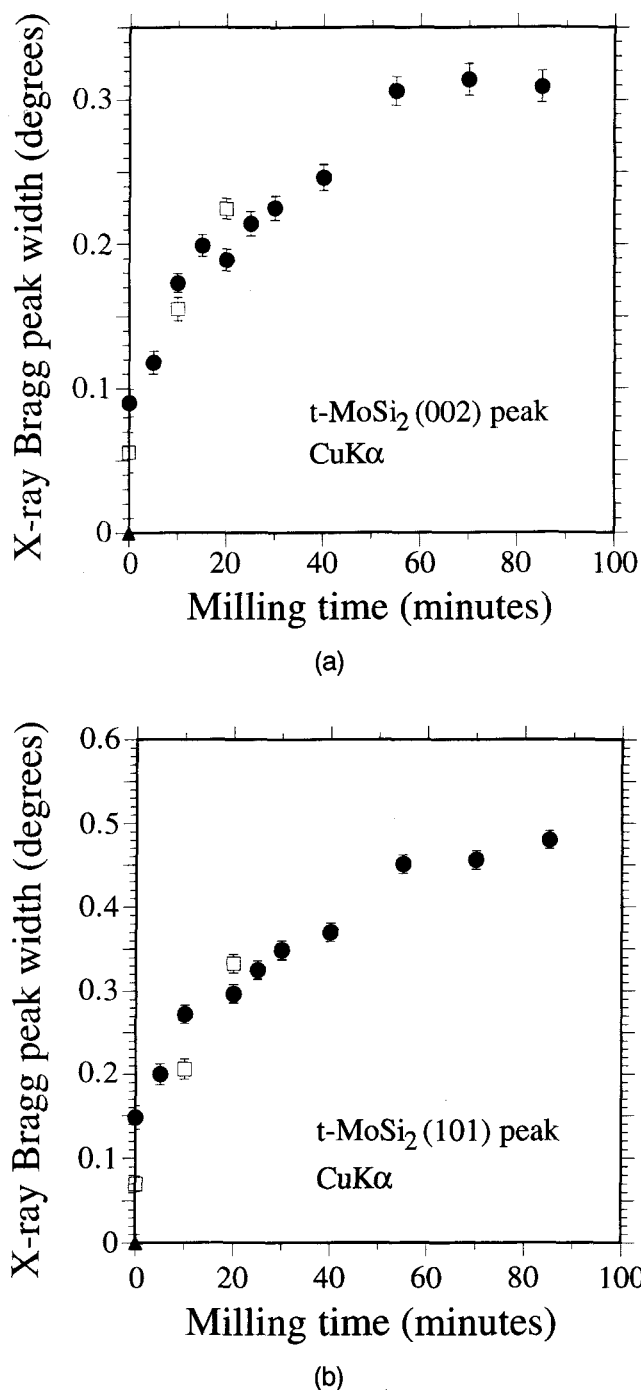


FIG. 4. X-ray diffraction Bragg peak width, determined using Eq. (1), of *t*-MoSi₂ x-ray diffraction peaks: (a) (002) peak and (b) (101) peak, as a function of additional ball-milling time, showing the broadening effect upon milling. Two different types of samples are included: commercial *t*-MoSi₂ powders (●) and 2 h milled 2Mo:3Si powders after near-complete reaction (□). In addition, peak-width below the detection limit for 1Mo:2Si or 2Mo:3Si powders formed by flame-induced SHS and no milling (▲) is shown for comparison.

of the scattering vector, K , is consistent with broadening due to strains.²⁴ This experiment suggests that the powders have undergone an abrupt reaction and subsequently experienced milling for a few minutes at most.

Had these *t*-MoSi₂ powders formed gradually, e.g., over a time period on the order of 10 min, they would not have exhibited sharp diffraction peaks virtually free of deformation-induced broadening [Fig. 1(b)]. We will return to this point again below in the discussion of the results for the 2Mo:3Si powders.

Abrupt *t*-MoSi₂ formation throughout a large portion of the powder mixture is difficult to explain using conventional arguments for interfacial, gradual, diffusional reactions during ball milling.^{10,25} During milling, mechanical collisions in laboratory mills cannot produce temperatures higher than a few hundred degrees^{10,25,26} unless heat is liberated by rapid chemical reactions. Isothermal diffusional reactions at such temperatures are slow for systems like Mo–Si. As will be discussed later (Sec. III. B), thermal annealing of premilled powders to 730 °C at 5–40 K/min would not result in a single silicide phase, *t*-MoSi₂, nor in a reacted fraction as high as that seen in Fig. 1(b). Research in our group, as well as reported in literature, e.g., Ref. 10, indicates that, for most alloy systems, significant intermetallic phase formation through a gradual, diffusional process in a SPEX ball mill requires milling durations on the order of 10–20 h. The resultant products, if crystalline, have small grain size and large strain, as evidenced by pronounced broadening of x-ray diffraction peaks.

The observed abrupt reactions require rapid equilibration involving a large portion of the powder mixture. This can obviously be achieved through a self-sustained reaction, similar to that described in Sec. I for SHS. Temperatures as high as 1900 K,^{5,6} a value close to the melting point of the MoSi₂ intermetallic compound, 2293 K, have been reported for SHS. Such rapid, high-temperature, and large-scale reactions can therefore explain the observed rapid *t*-MoSi₂ formation and the absence of deformation-induced peak broadening in the x-ray diffraction pattern obtained for *t*-MoSi₂ product shortly after its formation [Fig. 1(b)]. We believe that mechanical impact serves here as the ignition mechanism. The collisions between the milling balls and the vial walls may trigger reactions at some local “hot spots”.²⁷ The reaction to form *t*-MoSi₂ in a small local volume releases the heat of formation of the compound within a very short time. As long as the rate of heat generation far exceeds that of the heat dissipation, the excess heat causes reaction in neighboring regions, and the reaction becomes self-propagating. Once ignited, the reaction may propagate through most or a sizable fraction of a sample. It is conceivable that propagation in our uncompact powders may not be as easy as in compacted powders. However, as our vial containing 11 balls vibrates at a frequency of 20 Hz, a few minutes of milling can provide numerous collisions, and hence numerous potential ignition events, if the probability of ignition is sufficiently high. In such a case, a significant

portion of the powder mixture would still react within several minutes of milling, even if the propagation distance is limited for each ignition event. We observed a small amount of 0.1–0.5 mm large aggregates of powder particles (Fig. 2) that were not present before silicide formation. A large amount of such aggregates, suggesting melting and long-range propagation, was found in ball-milled Al–Ni powders after the entire sample had reacted within less than a second and the run was terminated immediately after the abrupt reaction^{8,9} (see Sec. III. C).

Our data indicate that the initiation of self-sustained rapid silicidation requires an initial period of milling (hereafter referred to as prereaction milling, or for simplicity, premilling), on the order of 2–3 h. This may be explained as follows: the ignition, as well as propagation, requires a sufficiently high heat generation rate, which increases with decreasing elemental domain size when there is sufficient contact between the reactant phases. For compacted powder pellets, in fact, it has been reported⁵ that propagation of SHS was easy when the particle size was small, but became difficult and eventually impossible as the particle size increased. This effect was demonstrated in detail for varying Si particle sizes. It was explained to result from melting of Si which was suggested to be a rate-limiting process in the self-sustained reaction.⁵ Thus, we suggest the existence of a critical particle size for our powders, which accounts for the absence of silicidation during the initial 2 h of milling. Experiments to be discussed later in Sec. III. B lend further support to this explanation. We note here that the stored enthalpy due to cold work (several kJ/mol¹²) is small compared with the heat of reaction, and does not significantly affect the thermodynamics of alloying.

Due to the statistical nature of the milling process, a fraction of the powders may become “ready” for ignition locally earlier than the majority. This is likely to be responsible for the slow appearance of *t*-MoSi₂ for milling between 2 and 3 h. In this period, ignition is rare and propagation very limited. Thus, the self-sustained reactions occur only on a small scale, e.g., on a particle-by-particle basis, so that compound formation appears to be gradual when analyzed using bulk-averaged techniques such as x-ray diffraction. The majority of the powder mixture becomes ready for ignition at a later time within a short time interval, during which rapid ignition and propagation occurs, resulting in a massive, abrupt reaction. The abruptness of the reaction therefore depends on the distribution of the elemental domain sizes as milling proceeds. A small fraction of the powder at the high end of the size distribution may not be ready for ignition/propagation until a later time. A complete consumption of the reactants may thus be difficult to achieve. Also, it is known that poor particle-particle contact in low-density compacts would cause the reaction

front to propagate in an irregular fashion and significant unreacted regions would remain after propagation.⁵ In our uncompact Mo–Si powders, the propagation of self-sustained reactions may conceivably encounter more difficulties and may sometimes be limited to the regions immediately adjacent to an ignition event. It is therefore not surprising that unreacted elemental domains remained after the majority of the powder had reacted [Fig. 1(b)].

Data analyses and additional experiments provide further evidence for the occurrence of self-sustained high-temperature reactions, as detailed in the remainder of this section. First, we note that *t*-MoSi₂ appeared as the sole silicide phase early in the reaction [Fig. 1(a)] and remained the only silicide phase up to the completion of the sudden, rapid, reactions [Fig. 1(b)]. If the silicidation occurs in a gradual, low-temperature (<800 °C), interfacial, diffusional reaction, one would expect to observe the hexagonal form of MoSi₂, *h*-MoSi₂, as the first phase, which may (600–800 °C), or may not (<600 °C), coexist with *t*-MoSi₂, as shown by various authors in diffusion-couple experiments.^{17–21} We have made similar observations for unreacted, premilled Mo–Si powders; upon heating to 730 °C, a small amount of *h*-MoSi₂ formed together with a comparable amount of *t*-MoSi₂ (see below in Sec. III. B). It has been repeatedly demonstrated that *t*-MoSi₂ forms as a single phase only at reaction temperatures in excess of about 800 °C.^{17,18,21} Also, the rather slow low-temperature diffusional reaction in our premilled powders (see Sec. III. B) is insufficient to account for the near-complete silicidation obtained through longer milling [Fig. 1(b)], again suggesting the presence of a different mechanism, namely, self-sustained reactions. These arguments obviously rely on the assumption that the ball-milling process does not significantly affect the nucleation and growth of new silicide phases in diffusion couple reactions. We now proceed with further arguments which do not rely on such an assumption.

In a self-sustained reaction, for which equilibrium is likely to be reached, the phase(s) formed should correspond to the equilibrium phase diagram and hence, depend on the overall composition of the mixture. On the other hand, in a slow, diffusional reaction, the first phase to appear depends on the thermodynamic and kinetic conditions at the interface, but not on the overall composition. To examine this point, we performed milling experiments for powder mixtures with an overall composition of 2Mo:3Si. The off-stoichiometric 2Mo:3Si composition is in the two-phase region (Mo₅Si₃ and MoSi₂) of the equilibrium phase diagram.¹⁶ Figure 5(a) shows the x-ray diffraction pattern for a 2 h milled 2Mo:3Si sample. It can be seen that the majority of the powder has reacted to form the equilibrium products, *t*-MoSi₂ and smaller amounts of Mo₅Si₃. In all

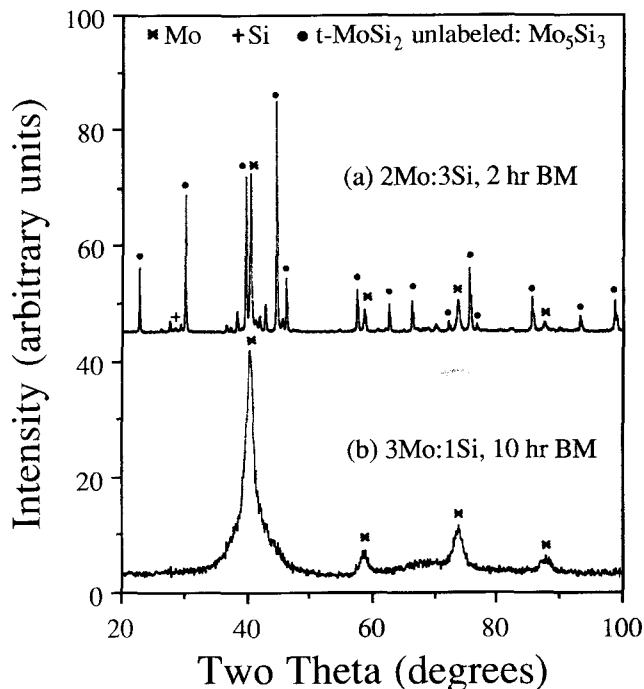


FIG. 5. X-ray diffraction pattern (Cu K α) for (a) 2Mo:3Si powder ball-milled for 2 h, showing the co-presence of *t*-MoSi₂ and Mo₅Si₃, with extremely sharp diffraction peaks, and (b) 3Mo:1Si powder ball-milled for 10 h, showing no silicide formation.

experiments at 2Mo:3Si, we observed that *t*-MoSi₂ and Mo₅Si₃ appeared together as the first reaction product, both present in small amounts after milling for durations greater or equal to 1.5 h. This is different from the stoichiometric 1Mo:2Si sample, in which only *t*-MoSi₂ was observed as the first phase. Thus, mechanical alloying is observed to lead to equilibration and *not* to a gradual interfacial reaction. The *t*-MoSi₂ diffraction peaks in Fig. 5(a) are again very narrow [for the (002) *t*-MoSi₂ peak, $w = 0.055$, squares in Fig. 4]. This w is only slightly higher than for *t*-MoSi₂ formed by a high-temperature SHS reaction (Sec. III. B), $w = 0$, triangle in Fig. 4) and lower than for the as-received MoSi₂ powder ($w = 0.09$, filled circles in Fig. 4). The results for the increase of w upon additional milling have been included in Fig. 4. As before, the narrow Bragg peaks indicate the abrupt nature of the reaction.

The fact that the premilling period required for ignition was shorter (<2 h) for the 2Mo:3Si powders than for the 1Mo:2Si powders (3 h) is also consistent with the report that 2Mo:3Si is in the composition range most favorable for self-sustained reaction in the Mo–Si powder system.⁶ The reaction products are also the same as those reported in Ref. 6. Furthermore, according to Ref. 6, no self-sustained reaction could be achieved at the composition 3Mo:1Si, even when the powder compact was preheated to 500 °C. Indeed, we failed to observe silicidation at this composition after

extended ball milling up to 20 h. Figure 5(b) shows the x-ray diffraction pattern for 10 h ball-milled 3Mo:1Si powder. The phase obtained were terminal Mo and Si, and possibly some metastable amorphous phase. There is no evidence of any equilibrium Mo silicide. The phases remained unchanged for 20 h milled powders. Similarly, only a small amount of *t*-MoSi₂ was obtained in 1Mo:3Si powders after 5 h of milling. This again is consistent with Ref. 6 in that, for Si content higher than in MoSi₂, the reaction becomes difficult and requires preheating. To summarize these observations, massive silicidation in milled Mo–Si powders is observed only in a composition range similar to that favorable for SHS reactions. This similarity further supports our conclusion that the mechanism of mechanical alloying in Mo–Si is one of self-sustained reactions.

B. Silicide formation upon thermal treatment

It is useful to compare the above ball-milling results with those of conventional SHS reactions in the same powders, as-received or premilled. We prepared hand stir-mixed elemental powder mixtures of these compositions, and some powders premilled for times insufficient for significant silicidation to take place. These powders were compacted at room temperature under 3×10^4 kPa, using a hydraulic press, into disks, 13 mm in diameter and about 0.5 mm thick. The flame from a natural gas burner was used for ignition. For the compositions 1Mo:2Si and 2Mo:3Si, premilled powder compacts easily ignited when one end of the compact was placed in the flame. Upon ignition, the glowing reaction front propagated through the 13 mm disk within a fraction of a second. The corresponding propagation speed was similar to that reported in Ref. 5. On the other hand, no significant propagation of reaction was observed for a stir-mixed, unmilled, powder mixture compact for these two compositions. This result confirms that intimate mixing and/or elemental domain size reduction is a necessary condition for self-sustained reaction and supports our explanation of the premilling requirement discussed in Sec. III. A. For the composition 3Mo:1Si, even milled powder compacts failed to undergo SHS. Thus, our results corroborate those of Zhang and Munir⁶ who determined the composition range for which SHS can be obtained (also see end of Sec. III. A).

As stated earlier, the formation of Mo silicides by low-temperature diffusional reaction is sluggish and cannot account for the near-complete reaction observed in Fig. 1. The failure to synthesize any crystalline silicide by ball milling of 3Mo:1Si powders, in which also no self-sustained reaction has been achieved, is consistent with this conclusion, as are additional annealing experiments of 1Mo:2Si powder mixtures. Prior to annealing, powders were premilled for 2–3 h for mixing, resulting

in only trace amounts of *t*-MoSi₂. Heat evolution during subsequent annealing was monitored using DSC. Typical DSC traces for powders from a 3 h premilling run, after which only a small amount of *t*-MoSi₂ was observed, are shown in Fig. 6. Such a premilling is expected to prepare the powders in a condition close to that necessary for fast silicidation during milling (usually occurs between 3 and 3.5 h, see Sec. III. A). DSC and x-ray diffraction indicate that annealing to 520 °C at 5–40 K/min resulted in little phase change in the powders. This is consistent with the results of Holloway *et al.*²⁰ and Cheng *et al.*¹⁹ that annealing at temperatures below 520 °C for several minutes would lead only to *h*-MoSi₂ growth to a thickness of less than 20 nm at a Mo/Si interface. An exothermic signal begins above 520 °C and ends between 600 and 700 °C, depending on heating rates (Fig. 6). X-ray diffraction showed that some *h*-MoSi₂, and possibly also additional *t*-MoSi₂, formed during this period. These two phases are known to grow simultaneously at these temperatures.^{17,18,21} However, the fractions of these two phases are rather low, and the Mo diffraction peaks remained dominant. In fact, integration of the exothermic peak in Fig. 6 gives a heat of reaction of about 16 kJ/mol, which is only 12% of the expected heat of formation of *t*-MoSi₂, 131 kJ/mol.⁵ The relatively sharp trailing edge of the DSC peak is typical of consumption of the reactants.²⁸ We therefore suggest that after 3 h of premilling, there still exists a nonuniform elemental domain size distribution. The DSC peak results from the consumption of the smallest regions, following which the reaction rate drops sharply. The major portion of Mo and Si remains unreacted within the temperature range of the DSC instrument, since our premilling has not converted the entire powder mixture into a sufficiently fine layered structure such as that in previous thin-film interdiffusion experiments (a few hundred angstroms in thickness). Further analysis

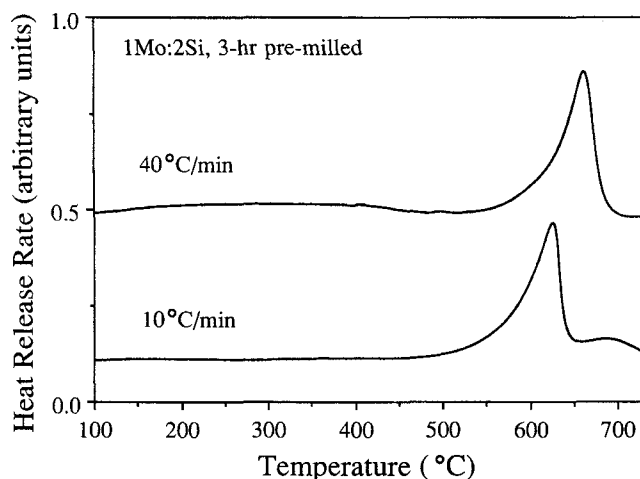


FIG. 6. Typical DSC traces, at 10 K/min and 40 K/min, for powders after a 3 h premilling run.

and discussion of the thermal annealing induced silicidation in Mo–Si powders will be presented elsewhere.¹⁵

C. Comparison with Al–Ni

In our recent related work, we have also observed rapid reactions during the ball milling of 1Al:1Ni powders.^{8,9} The milling conditions were similar to those in the Mo–Si case, except that air circulation was used to keep the vial close to room temperature. After premilling for 2 h, the milling run was interrupted, and the vial was kept sealed for 30 min under air circulation. A chromel–alumel thermocouple was then attached to the vial to monitor later reactions *in situ*. Thirty to 60 s after the resumption of milling, the temperature rose abruptly, within about 1 s. X-ray diffraction before and after this event confirmed that a rapid reaction had occurred, transforming the entire Al–Ni physical mixture into the AlNi compound. There are obvious similarities between the Al–Ni and Mo–Si cases. First, both alloy systems have a large negative heat of mixing. Second, the product equilibrium compounds, MoSi₂ and AlNi, are formed directly, bypassing the “first phase”, i.e., the compounds that form first during slow, diffusional reactions upon low-temperature annealing (in the Al–Ni case, it is Al₃Ni).^{8,9} More importantly, the first phase(s) to form correspond to the equilibrium phase diagram at the overall sample composition. Third, a period of initial milling (pre milling) is required to prepare the powders for ignition.

There are, however, also differences between the two cases. Most noticeably, the abrupt, extensive, self-sustained reaction in Al–Ni was observed when, and only when, a milling run, performed near room temperature (cooling fan used), was interrupted. Before interruption, the milling had prepared a well-mixed powder mixture with small elemental domain sizes. After interruption, cooling, and possibly some leak of oxygen into the vial that may have assisted the ignition, each particle reacted following the resumption of milling. An extremely abrupt reaction of all powders thus resulted, such that the entire powder mixture transformed into AlNi within less than 1 s. Such a scenario allowed *in situ* monitoring, as one can determine the onset of the reaction to within 1 s. In the Mo–Si case, however, interruption did not affect phase formation and was not needed to obtain abrupt reactions. Also, unlike for Al–Ni,^{8,9} no obvious difference was noted between milling runs with or without a cooling fan. Finally, the reaction in Mo–Si appeared less abrupt compared with the Al–Ni case (with interruption).

These differences probably arise from the fact that a Mo–Si powder mixture is easier to ignite by mechanical impacts, e.g., because of its brittle nature. Self-sustained reactions can be initiated, once the required premilling

is completed, without additional procedures such as cooling and interruption. Although the majority of the powders reach the “ready” state at approximately the same time, giving rise to a short period during which the rapid silicidation occurs, there are also particles that experience somewhat different premilling and, hence, reach the “ready” state at an earlier or later time. The silicidation thus appears somewhat gradual. We did not perform an *in situ* temperature monitoring experiment, because it is difficult to locate the right point in time at which the majority of the Mo–Si powder mixture is “ready”, especially since it varies somewhat from run to run (see Sec. III. A). There are also practical difficulties in performing thermocouple *in situ* monitoring for extended durations. The observation that reactions in 1Al:1Ni converted the entire powder sample into the compound AlNi within a second or less, while unreacted elements always remained in the Mo–Si case, seems to suggest easier propagation in the AlNi case. In Al–Ni, both Al and Ni, and possibly also AlNi, melted during the reaction, and as a result, the AlNi product consisted of 1 mm size aggregates.⁹ In Mo–Si, however, only Si is expected to melt during a self-sustained reaction.⁵ This difference may be, at least in part, the cause of the observed difference in the extent of the reaction.

Based on these two cases studied, Mo–Si and Al–Ni, we suggest that self-sustained reactions may be common in many alloy systems with large, negative heat of mixing when subjected to high-energy ball milling. This type of reaction therefore constitutes an important mechanism of mechanical alloying.²⁹ Such reactions may escape detection when only bulk-averaged analysis techniques are used, as these reactions may not necessarily propagate through the entire powder mixture. In fact, these reactions may occur locally at the ignition (collision) spot, such that the entire sample reacts gradually on a particle-by-particle basis.

IV. CONCLUSIONS

We have shown evidence indicating that Mo silicides form by rapid, self-sustained, high-temperature reactions during room temperature high-energy ball milling of elemental powders. The evidence can be summarized as follows: (1) The silicidation reaction occurred rather abruptly, as indicated by the discontinuity in the reacted fraction vs time, and the absence of significant diffraction peak broadening expected for gradual reaction; (2) The first silicide phase(s) formed differs from that in slow, diffusional reactions and corresponds to the equilibrium phase diagram at the overall sample composition; (3) A number of similarities exist between our observations and those for conventional SHS, and also those in another mechanically alloyed system, Al–Ni, for which such reactions have been studied in more detail. No

silicidation was observed outside the composition range favorable for SHS reactions. We suggest that the self-sustained reaction is an important mechanism during mechanical alloying of highly exothermic systems.

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