Microalloying of molybdenum disilicide with magnesium through mechanical and field activation

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Utilizing a two-step method of mechanical and field activation, the heretofore-unachieved goal of incorporating Mg on the Si sub-lattice of $MoSi_2$ was successfully demonstrated. Mechanical activation was done through high-energy ball milling and field activation was achieved through the use of the spark plasma sintering (SPS) method. The incorporation of Mg was verified by a variety of techniques including XRD, SEM, and EDS. © *2004 Kluwer Academic Publishers*

1. Introduction

Interest in transition metal silicides is motivated primarily by potential and current applications as electronic materials (contacts and interconnects) [1] and as high temperature structural materials [2]. For the latter category of application in an oxidizing environment, these silicides and the silicon-based structural ceramics (e.g. Si_3N_4 and SiC) are the primary materials of interest. Both of these classes of ceramics possess attractive properties (high melting temperature, oxidation resistance, and adequate high-temperature mechanical properties) [3]. But both suffer from low ductility at low temperatures. This low temperature behavior is a consequence of the bonding nature of these materials, which for the structural ceramics is covalent and/or ionic. In contrast, bonding in refractory silicides (such as $MoSi_2$) has a hybrid metallic and covalent character [4]. The presence of a metallic character in the bonding of these silicides provides an opportunity to modify their properties through alloying [5].

Attempts to improve the fracture toughness of $MoSi_2$ have included several approaches, foremost among which is the addition of a second phase to form composites. Considerable success was reported with the addition of SiC (in both whisker and particulate forms), carbon (to form SiC), and ZrO_2 particles [6–9].

While the composite approach for the increase in fracture toughness of $MoSi_2$ has been generally successful, the synthesis and processing of such materials are experimentally challenging [3]. As an alternative to this approach, the use of alloying elements has been proposed as a promising method to overcome the shortcomings in the mechanical behavior of $MoSi_2$.

A systematic theoretical study on the effect of microalloying on the ductile brittle transition temperature (DBT) was made recently by Waghmare *et al.* [5, 10]. They formulated a model to predict the effect of selected elements substituted either for molybdenum or for silicon on DBT. They proposed a "disembrittlement" parameter, D, (defined as the ratio of the surface energy to the unstable stacking fault energy) and concluded that the element with the strongest effect on DBT is magnesium. Attempts to incorporate Mg into $MoSi_2$ by conventional methods (typically arc melting) have not been successful, primarily because of the high vapor pressure of Mg. In a recent short communication [11] we reported on our success in incorporating Mg, using a new experimental approach which combines mechanical and field activation [12, 13]. In this paper we describe in more detail the results of incorporating Mg into $MoSi_2$ with emphasis on the role of activation in the process.

2. Experimental materials and methods

The starting materials were pure elemental powders of silicon, molybdenum, and magnesium (Alfa Aesar Ward Hill Massachusetts). All powders had a sieve classification of −325 mesh. The Si and Mo powders were 99.999% pure and the Mg powders were 99.8% pure.

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The powders were mixed to give a nominal Mo/Si ratio of 1/2 but adjusted by the addition of Mg which is to be substitutionally incorporated into the Si sub-lattice. The level of addition was varied but a typical value is 5.00 at.% based on Si. Thus 5 at.% means the product would be Mo $(Si_{1.9}Mg_{0.1})$.

The elemental powders were mixed for 1 h in a Turbula mill (mechanical shaker mixer) in glass vials with alumina balls. X-ray diffraction of the mixture in the unmilled condition was preformed. The mixed powders were subsequently milled in a Fritsch planetary mill (Pulversette 4). The powders were loaded into ceria stabilized zirconia milling jars with approximately 150 g of ceria-stabilized zirconia 10 mm (diameter) milling balls. The milling bowls were then loaded into a glove box which contained an argon atmosphere, the bowls were sealed and placed into the planetary mill for the milling run. A charge ratio, CR, (also referred to as the ball to powder mass ratio, B/P) of 14 and a rotational speed of 250 RPM were utilized in this work. Choice of the CR was based on previous work in which it was shown that under a condition of CR = 14, Mo and Si react to form $MoSi_2$ after 10 h of milling [14]. However, X-ray diffraction phase analysis revealed that after 10 h of milling the powders had partially reacted to form the alpha, C_{11b} phase and the beta, C40, hexagonal high temperature phase. Unreacted molybdenum was also present. In this work our goal was to have as complete a conversion to $MoSi_2$ as possible during the ball milling process. After preliminary experiments, the milling cycle adopted was 24 h total time, with the cycle being 5 min on 10 min off, providing a total actual milling time of 8 h. X-ray diffraction patterns of powders milled under these conditions revealed that only unreacted molybdenum and beta phase $MoSi_2$ are present.

The starting unmilled and post-milled powders were analyzed in a Scintag XDS-2000 diffractometer using Cu K_α radiation ($\lambda = 1.5405$ Å). The powders (unmilled and milled) were then densified (and or reacted) in a Spark Plasma Sintering (SPS) apparatus

(Sumitomo, model 1050). The SPS apparatus consists of a water-cooled 100 kN press combined with a 15 V, 5000 A pulsed DC power supply [14]. Eight grams of milled powder from selected experimental runs (both milled and unmilled powders) were loaded into graphite dies and reacted and/or densified in the SPS apparatus.

The dense samples were analyzed for evidence of Mg incorporation using X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

3. Results and discussion

X-ray diffraction analyses of powder mixtures that were mixed for one hour in a Turbula mill (but were not subjected to high energy milling) showed the presence of molybdenum, silicon, and magnesium. X-ray diffraction analyses of the mixtures (Mo + 1.8 Si + 0.2 Mg), milled under the conditions described above but which were not densified in the SPS, revealed that nearly complete conversion to beta (C40) phase $MoSi_2$ had taken place (Fig. 1). No evidence for the presence of free Mg is seen in this figure, (the main peak for Mg is at a 2θ value of $36.620°$). In addition to the β phase, the sample also contained unreacted Mo. The peaks of both the product and Mo show broadening due to grain size reduction and lattice strain.

X-ray diffraction patterns of the unmilled powders that had been reacted in the SPS are shown in Fig. 2a. The patterns show the presence of free magnesium, as well as, alpha $MoSi_2$, Mo_5Si_3, and unreacted Mo. Since the main peak of Mg ($36.620°$) is very close to one for Mo_5Si_3 ($36.542°$) the conclusion that free Mg was present was based on a careful, slow scan in the 2θ range 36.5 to $36.7°$. The resulting pattern shows clearly that Mg (as well as Mo_5Si_3) is present (Fig. 2b). In contrast, the X-ray diffraction pattern of the powder which was milled and subsequently treated in the SPS shows that no free magnesium is present (Fig. 3). The phases present in this sample are alpha $MoSi_2$ and Mo_5Si_3. As was discussed for the unmilled sample, because of the near overlap of the main Mg peak with
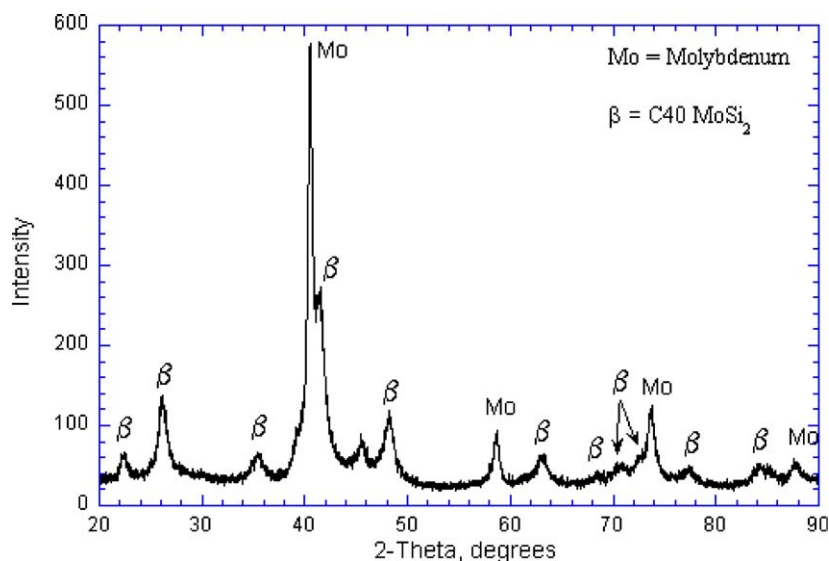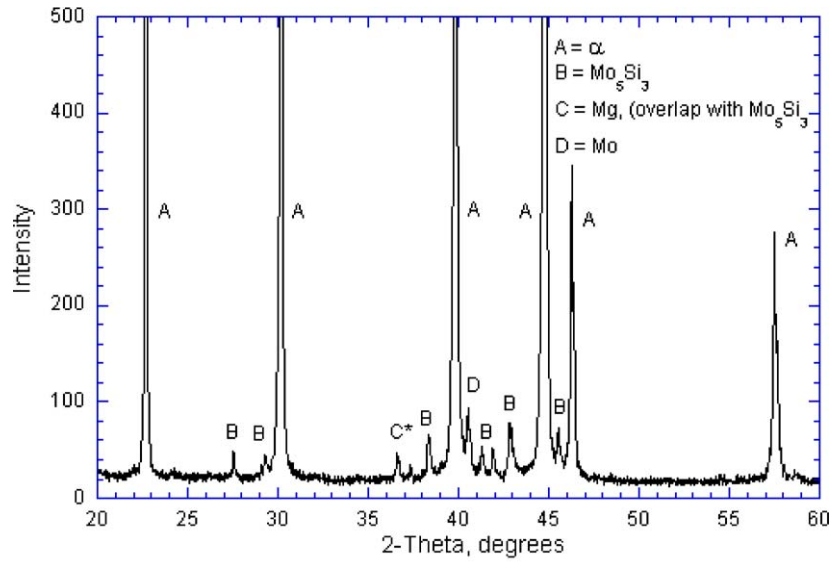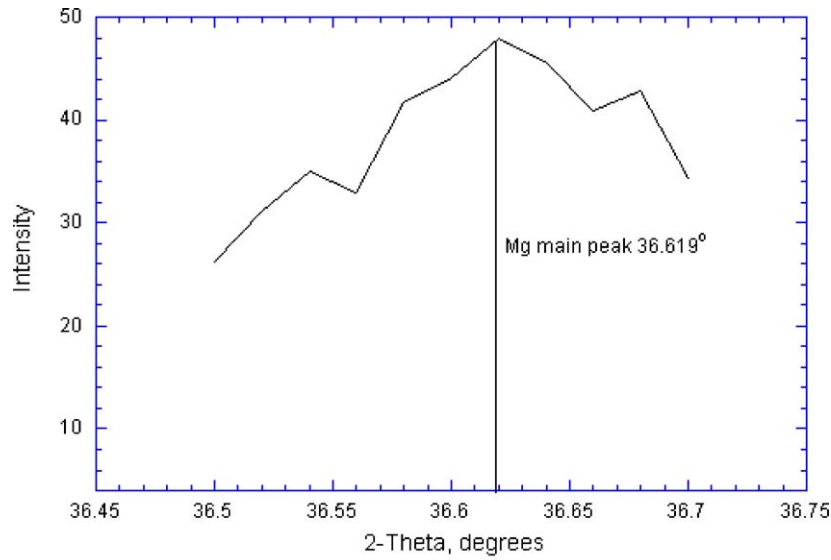

Figure 1 X-ray diffraction pattern of milled Mo + 1.8 Si + 0.2 Mg powders.

(a)

(b)

Figure 2 (a) X-ray diffraction pattern of unmilled powders reacted in the SPS. (b) X-ray diffraction pattern showing the presence of Mg and Mo_5Si_3 in results of Fig. 2a.
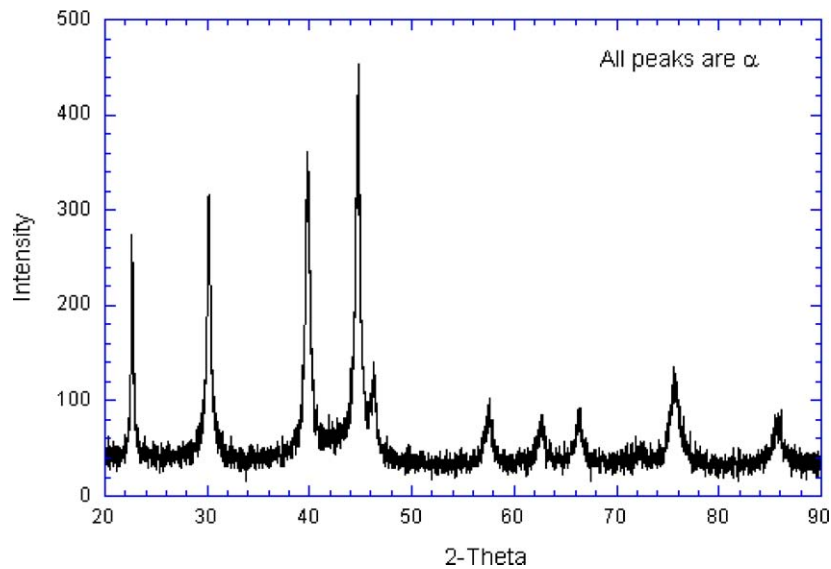

Figure 3 X-ray diffraction pattern of milled and subsequently reacted powders in the SPS.

a high-intensity Mo_5Si_3 peak, additional analysis was carried out. In order to determine if indeed there is free Mg present in the milled densified SPS samples, an extremely sensitive XRD scan was performed on the sample of the milled and reacted (in the SPS). The sample was scanned from 36.04 to 37.04°, with a step of 0.005° and an extended count time of 20 s. The curve was fitted without stripping the k-alpha 2 component of the Cu radiation, and the result reveals a good match for Mo_5Si_3. While this procedure still leaves some uncertainty, subsequent EDS and EELS analyses show that there is indeed free Mg present in the unmilled SPS samples, while the milled SPS samples show no free Mg.

Figs 4 and 5 show X-ray dot maps of the unmilled and milled samples, respectively. In the former, which shows the presence of unreacted Mo, magnesium-rich regions are clearly evident. In the latter magnesium is evenly distributed in the sample. The Mg-rich regions in the unmilled samples are associated with residual porosity.

Further analyses on the regions in Figs 4 and 5 were made using energy dispersive spectroscopy (EDS). The analysis showed the presence of three phases in the
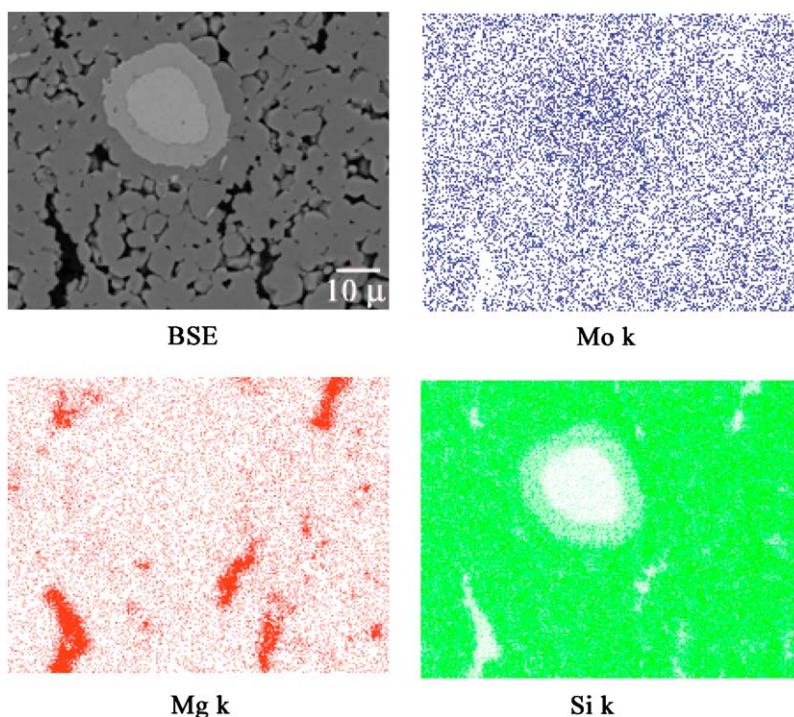

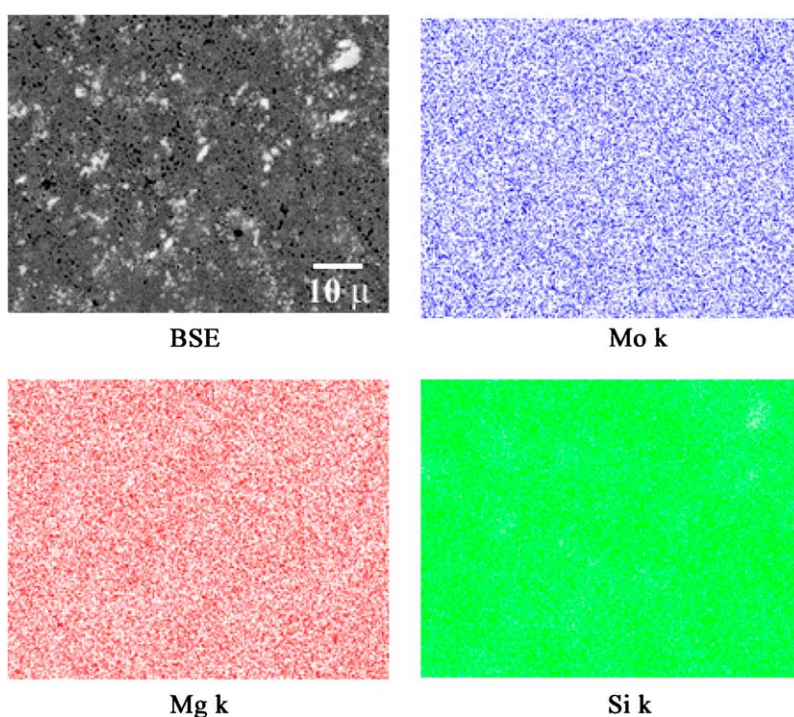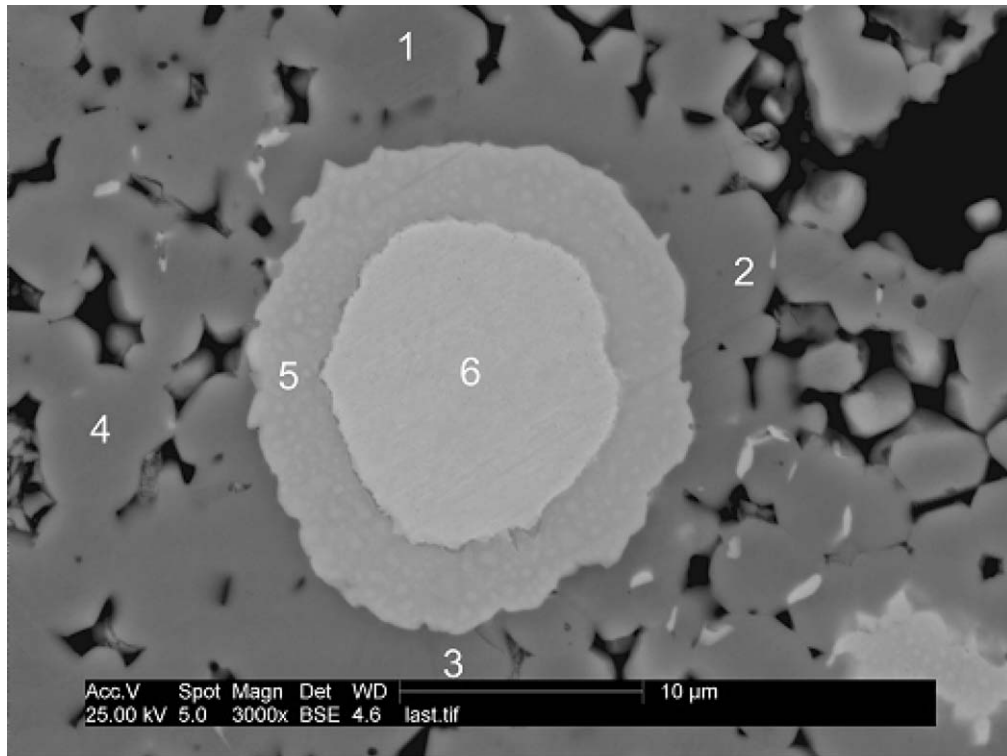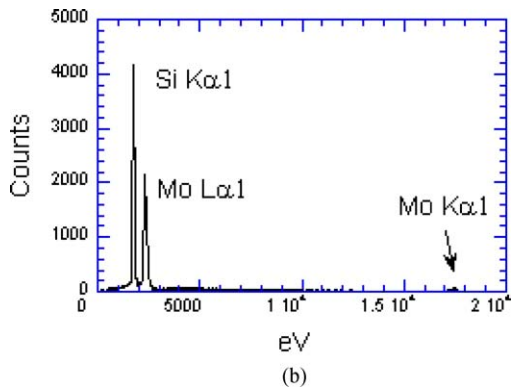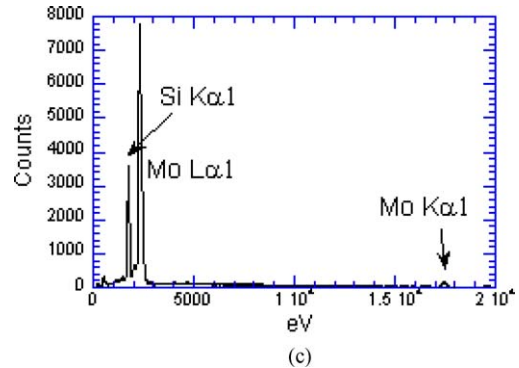*Figure 4* X-ray dot maps of unmilled and reacted powders.

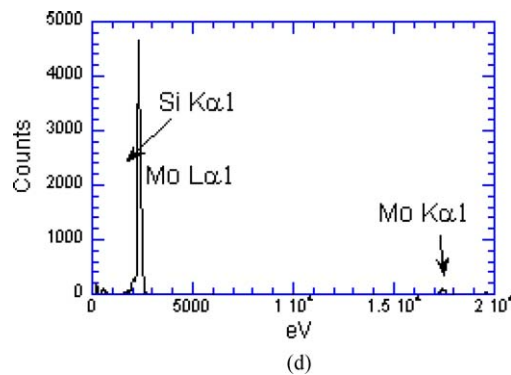*Figure 5* X-ray dot maps of milled and reacted powders.

(a)

(b)

(c)

(d)

Figure 6 (a) Back-scattered electron (BSE) image of reacted unmilled powders. (b) Energy dispersive spectroscopy (EDS) analysis for region 1 in Fig. 6a. (c) EDS spectra for region 5 in Fig. 6a. (d) EDS spectra for region 6 in Fig. 6a.

unmilled samples. Referring to Fig. 6a, which represents a portion of the BSE image from Fig. 4, the regions identified by the numbers 1 through 4 give spectra typified by Fig. 6b which is for region 1. Spectra for regions 5 and 6 in Fig. 6a are shown in Fig. 6c and d, respectively. A quantitative chemical composition of all the regions is shown in Table I. These results show that regions 1 through 4 are $MoSi_2$, region 5 is Mo_5Si_3,

and region 6 is unreacted molybdenum. The amounts of Mg are insignificant and likely represent the background level. EDS analysis of the milled samples was made on the regions identified in Fig. 7a, which is a portion of the BSE image of Fig. 5. The spectra from regions 1 and 2 are nearly identical and are typified by Fig. 7b, which is for region 2. The spectrum for region 3 is shown in Fig. 7c. In both spectra, the small peak
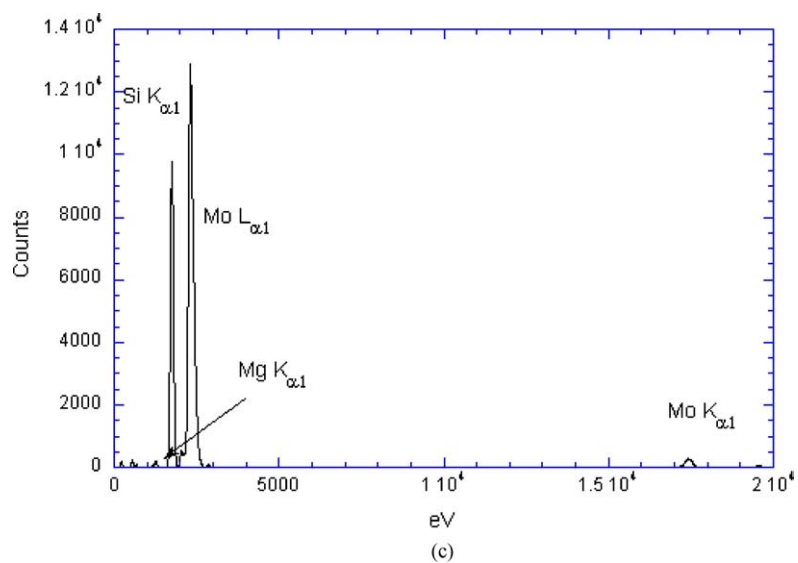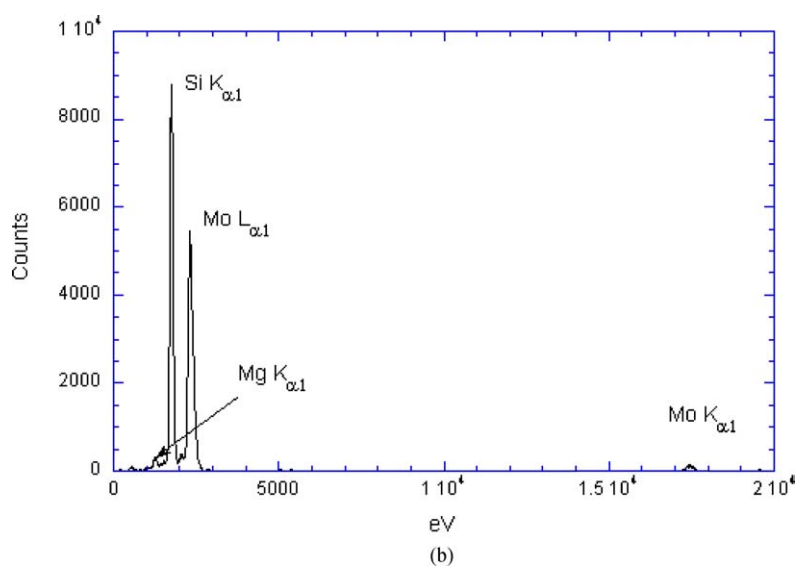
(a)

(b)

(c)
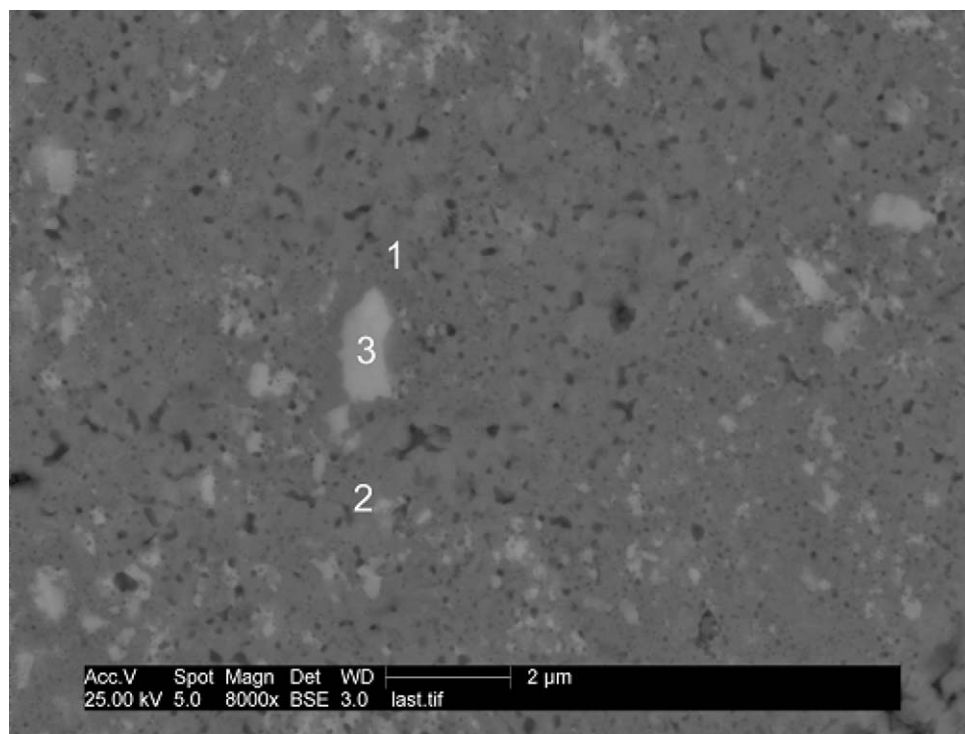
Figure 7 (a) Back-scattered electron (BSE) image of reacted milled powders. (b) EDS spectra for region 2 in Fig. 7a. (c) EDS spectra for region 3 in Fig. 7a.

TABLE I EDS chemical composition of labeled regions in Fig. 6a. Values in at.%

Element	Region 1	Region 2	Region 3	Region 4	Region 5	Region 6
MgK	0.08	0.12	0	0.03	0.32	0.84
SiK	63.83	60.24	64.56	63.71	37.55	1.97
MoK	36.08	39.64	35.44	36.26	62.13	97.19
Total	100	100	100	100	100	100

TABLE II EDS chemical composition of labeled regions in Fig. 7a. Values in at.%

Element	Region 1	Region 2	Region 3
MgK	4.32	5.96	1.63
SiK	59.4	55.38	45.7
MoK	36.28	38.66	52.67
Total	100	100	100

to left of the Si peak indicates the presence of Mg. The quantitative analyses of these regions, which are presented in Table II, show that regions 1 and 2 are $MoSi_2$ and region 3 is Mo_5Si_3. More importantly, the analyses show that the $MoSi_2$ phase, and to a lesser extent, the Mo_5Si_3 phase contain Mg. The latter result is consequence of the nature of SEM EDS. Since this technique samples from the bulk sample, it is indeed possible that a $Mo(Si_{2-x}Mg_x)_2$ grain lying beneath the Mo_5Si_3 grain is the origin of the Mg signal, hence the need for more exact TEM EDS analysis, which will be reported in a subsequent paper [15].

The results presented indicate that the incorporation of Mg into the $MoSi_2$ has been successfully accomplished. However, in order to further ascertain the validity of this conclusion, additional analytical techniques were used. These included transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Subsequent analyses using these techniques were made and the results confirmed the above conclusions [15].

4. Conclusions

Theoretical work has been reported showing that the incorporation of Mg into $MoSi_2$ would have the strongest effect on the reduction of the silicide's ductile-brittle transition temperature (DBT). Attempts to incorporate this element by conventional means have not been successful due to the high vapor pressure of this metal. In this work, the incorporation of Mg into the Si sublattice of $MoSi_2$ was successfully demonstrated through the use of two forms of activation: mechanical and field.

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