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Effect of Chromium Content on Formation of $(Mo_{1-x}-Cr_x)Si_2$ Nanocomposite Powders via Mechanical Alloying

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ABSTRACT

$(Mo_{1-x}-Cr_x)Si_2$ composite powders were successfully synthesized by ball milling of Mo, Cr and Si elemental powders. Effects of the Cr content, milling time and annealing temperature were investigated. X-ray diffraction (XRD) was used to characterize the milled and annealed powders. The morphological and microstructural evolutions were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Results showed that this composite formed after 20 h of milling. Increasing Cr content from 0.1 to 0.25 or 0.4 at.% changed the polymorph of synthesized $MoSi_2$ from α to β as well as the formation reaction mechanism from mechanically induced self sustaining reaction (MSR) to gradual. Annealing of the milled powders led to the formation of α-$MoSi_2$ in all Cr contents. An average grain size of less than 40 nm was obtained for all Cr contents at the end of milling. In spite of grain growth and strain release during annealing, these nanocomposites remained in their nanocrystalline nature.

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1. INTRODUCTION

$MoSi_2$ is a promising material for high temperature applications. Due to its high melting temperature, good oxidation resistance combined with low density, good electrical and thermal conductivity, this material may tolerate higher service temperatures in the field of energy machines, gas turbine parts, heat shields and tiles. Significant progress has been made in the last years in both the scientific and technological development of this intermetallic alloy [1,2]. Nevertheless, some of the properties still have to be improved to establish silicides for structural components, e.g. fracture toughness at room temperature and strength at high temperature. Reinforcement of $MoSi_2$ by hard ceramic particles, such as SiC, Si_3N_4, ZrO_2 and $CrSi_2$ is an effective approach to improve the mechanical behavior [2]. Oxidation resistance of $MoSi_2$ at high temperatures is due to the formation of a viscous SiO_2 scale. However, at 400-600°C, $MoSi_2$ suffers from catastrophic oxidation sometimes referred to as pesting [3]. Alloying additions to $MoSi_2$ is believed to improve its oxidation properties at low temperatures. Alloying studies so far have focused on additions of Ti, V, Cr, Zr, Nb, Ta, W, Cr, Re, and A1[4-7]. Elements that have stronger affinity to oxygen than Si can prevent $MoSi_2$ from pesting. They decrease the oxygen flux toward the oxide-intermetallic interface and increase the plasticity of the amorphous oxide formed along cracks [8].

Ideally, the added chromium in the form of $CrSi_2$ must be well dispersed in the matrix ($MoSi_2$) of composite as well as having small grain size (nanostructure). Mechanical alloying (MA) [9] has been considered as a powerful and practical process for fabrication of several advanced materials with unique properties [10], in particular, for those that are difficult to obtain by the traditional methods of liquid metallurgy. During ball milling, the diffusion couples are formed through a dynamic process of deforming, fracturing and cold-welding of the powders. After a certain milling time, each powder consists of a large number of diffusion couples formed by sequential stacking of elemental nano-sized thin elemental layers, or by agglomeration of equiaxed elemental particles ;the reaction occurs at low temperature [11].

$MoSi_2$ [12,13] and $CrSi_2$ [14,15] were separately synthesized by mechanical alloying. In our previous works, $MoSi_2$-$CrSi_2$ nanocomposite powders have been

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synthesized. In that research, effect of milling speed, milling time and annealing temperature were investigated [16-17]. The aim of this work is to synthesize $MoSi_2$-$CrSi_2$ nanocomposite powder by milling of Mo, Cr and Si elemental powders at nominal room temperature. Effect of Cr content, milling time and annealing temperature is to be investigated.

2. MATERIALS AND METHODS

MA was performed in a planetary ball mill at nominal room temperature and at a vial rotation speed (cup speed) of 640 rpm. Pure Merck Mo (99.7 %, 40 μm), Si (99.0%, 150 μm) and Cr (99.3 %, 40 μm) were mixed to give the desired $(Mo_{1-x}$-$Cr_x)Si_2$ composition with 0.1, 0.25 and 0.4 at.% Cr. The ball to powder weight ratio (BPR) was 10:1. For preventing excess agglomeration 0.8% (weight percent) Stearic acid was used as process controlling agent (PCA). The mixture of powders with the stainless steel balls was charged into a stainless steel cup (250 ml) in Ar atmosphere. Samples for analysis were removed in a glove box under argon atmosphere by interrupting the ball mill at various intervals.

XRD profiles were recorded on a Philips diffractometer (30 kV and 25 mA) with Cu $K\alpha_1$ radiation (λ = 1.5404 A°). All XRD experiments were done with the step size of 0.02° and a time per step of 1 s. The recorded XRD patterns were used for calculation of crystallite size and strain. Prior to calculations from the diffraction peaks, the background was automatically removed and the $K\alpha_2$ radiation was stripped (stripping ratio $K\alpha_2$/ $K\alpha_1$=0.5) from the scans using the computer software X-pert High Score developed by PANalytical B. V. Company (Netherlands).

Structural observations of milled powder were carried out with a Philips CM200 FEG TEM operating at 60 kV. Ultrasonic method was used for dispersing the powder in the methanol suspension. One drop of this suspension on a copper grid was used for the TEM observation. The morphology and particle size of the mechanically alloyed powder samples were examined by a Cambridge scanning electron microscope (SEM) operating at 25 kV. Heat treatment of the as-milled powders was conducted in a tube furnace in Ar atmosphere (2.2 l/min). The heating rate was 10°C/min and holding time at maximum temperature was 2h.

3. RESULTS AND DISCUSSION

3.1. Formation Reactions Formation of $MoSi_2$ and $CrSi_2$ were simultaneously investigated by ball milling of the elemental powders with $(Mo_{0.9}$-$Cr_{0.1})Si_2$ composition. Figure 1 shows the XRD results of the as received and the milled powders. As received powder reflections can still be seen after 15 h of milling, indicating that no reaction has yet occurred. Broadening of peaks and decreasing of intensity took place in the first stage of milling (Figure 1-A). By increasing milling time to 20 h (Figure 1-B), all of the starting powder reflections disappeared. On the other hand, $MoSi_2$ and $CrSi_2$ were formed at this stage of milling. $MoSi_2$ has two polymorphs: the α-$MoSi_2$ (low temperature polymorph) (LTP) with tetragonal structure and the β -$MoSi_2$ (high temperature polymorph) (HTP) with hexagonal structure [12]. In the 20 h milled sample the α-$MoSi_2$ was the major phase with some minor amount of β-$MoSi_2$. By further milling, up to 50 h, all of the β -$MoSi_2$ was transformed to α-$MoSi_2$ due to the instability of β-$MoSi_2$ at room temperature.

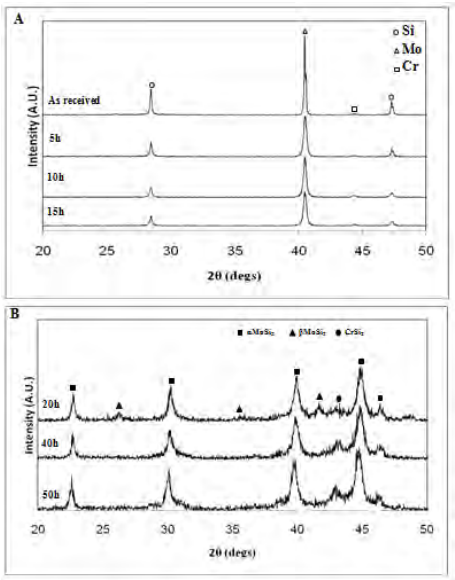

Fig. 1. XRD patterns of the as milled powders with 0.1 at.% Cr at the cup speed of 640 rpm.

$MoSi_2$ forms during the following reaction [18]:

$0.9Mo+1.8Si=0.9MoSi_2$

$(\Delta H^\circ = -118.6kJ \qquad \Delta G^\circ = -136kJ)$

The exothermicity of a reaction is often characterized by the ratio of the heat of formation to the room-temperature heat capacity ($\Delta H/C$). Typically, $\Delta H/C$>2000K is required for MSR [19]. The reaction between Mo and Si is close to this limit, $\Delta H/C$= 2060 K. Consequently, the propagation of the reaction in different parts of the powder may possibly depend on the local composition, heat transfer and the degree of mixing and activation. This reaction may have taken place with MSR mode because of the above reason and short time of reaction (between 15 and 20h). For determination of the exact reaction mode, the temperature of the vial must be recorded during milling, which was not performed in this study.

Figure 2 shows the XRD patterns of the as received and milled powders with $(Mo_{0.75}\text{-}Cr_{0.25})Si_2$ composition. By increasing the Cr content to 0.25at.%, no change was observed in the early stages of milling (Figure 2-A) compared with the previous composition (0.1 at.% Cr). With further milling to 20 h the HTP of $MoSi_2$ was formed. This indicates that the formation of β-$MoSi_2$ is kinetically favorable to α-$MoSi_2$ because of its similar crystal system with $CrSi_2$ [20]. Hexagonal crystal system of $CrSi_2$ at higher contents promotes the formation of β-$MoSi_2$. As discussed before, the formation of $MoSi_2$ (reaction 1) may take place in the MSR mode. At the end of milling, some of the β-$MoSi_2$ was transformed to the α-$MoSi_2$ due to its instability at room temperature.

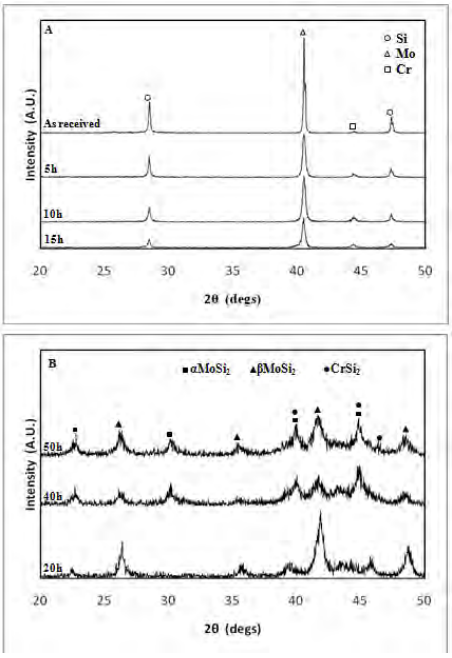

Fig. 2. XRD patterns of the as milled powders with 0.25at.% Cr at the cup speed of 640 rpm.

As can be seen in Figure 3-A, there is no difference in the structural evolution of the samples with 0.4 at.% Cr in the early stages of milling (up to 15h). But, in the 20 h milled sample, beside β-$MoSi_2$ and $CrSi_2$, un-reacted Mo reflection can be seen which indicates the gradual formation of $MoSi_2$ (reaction 1). This reaction propagates at longer milling time (40 h) and all of the starting materials disappear. Same as before, some of the β-$MoSi_2$ was transformed to the α-$MoSi_2$ at the end of milling. It can be concluded that Cr in higher content acts as a diluent and changes the reaction ($MoSi_2$ formation) mechanism from MSR to gradual.

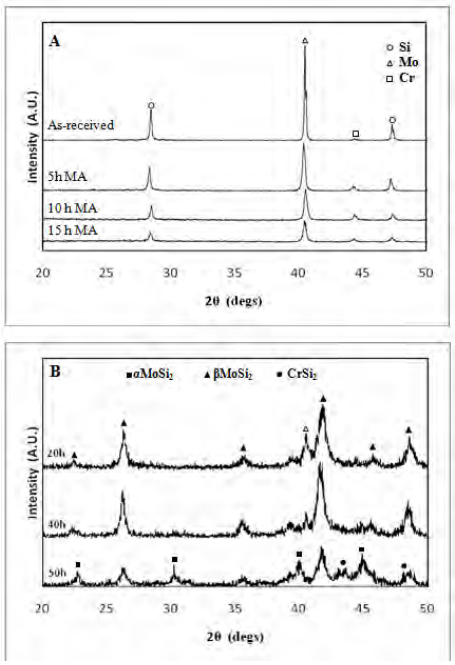

Fig. 3. XRD pattern of the as milled powders with 0.4at.% Cr at the cup speed of 640 rpm.

Phase transformation and thermal stability of the synthesized phases were investigated by annealing the milled powders at three temperatures of 700, 850 and 1000°C. Figure 4 shows the XRD patterns of the milled and annealed powders with 0.25 at.% Cr. The as milled powder (50h) includes both polymorphs of $MoSi_2$. Annealing at 700°C had no considerable effect, except for the peak sharpening due to the microstructure refinement. Increasing annealing temperature to 850 and 1000°C led to the transformation of all β-$MoSi_2$ to α-$MoSi_2$ (thermodynamically stable phase at room temperature). There is no difference in the annealing product of the 50 h milled powder with 0.4 at.% Cr compared with the previous ones. As seen in Figure 5, the annealed powder at 1000°C includes α-$MoSi_2$ and $CrSi_2$.

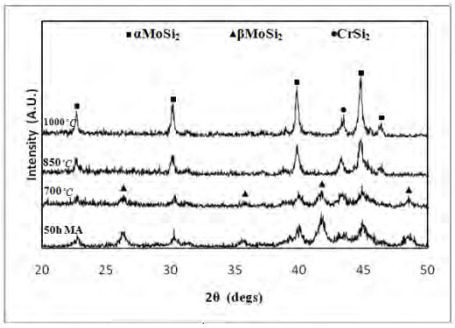

Fig. 4. Effect of the annealing on the structure of the 50 h milled powder with 0.25 at.% Cr at the cup speed of 640 rpm.

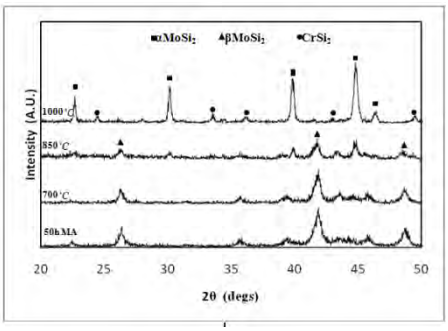

Fig. 5. XRD patterns of the annealed powders that 50 h milled with 0.4 Cr at the cup speed of 640 rpm.

3.2. Microstructure and Morphology Mean grain size (G.S.) and lattice strain of the $MoSi_2$ and Mo were calculated by peak profile analysis. The reference powders were the Mo and $MoSi_2$ powders that annealed at 1000 and 1400℃ for 6 h, respectively. The well-known Williamson-Hall method was used for calculation of mean grain size and lattice strain [21].

Effect of the milling time on the mean grain size and lattice strain is shown in Table 1.

TABLE 1. Mean grain size and micro-strain of the milled powders with different Cr content at the vial speed of 640 rpm.

Phases		Mo		Si		α $MoSi_2$		β $MoSi_2$	
X_{Cr} At.%	milling time (h)	G.S. (nm)	Strain %	G.S. (nm)	Strain %	G.S. (nm)	Strain %	G.S. (nm)	Strain %
0.1	5	39	0.18	68	0.13	----	----	----	----
	10	27	0.27	45	0.19	----	----	----	----
	15	24	0.3	36	0.24	----	----	----	----
	20	----	----	----	----	115	0.71	----	----
	40	----	----	----	----	86	0.87	----	----
	50	----	----	----	----	81	0.96	----	----
0.25	5	173	0.31	137	0.21	----	----	----	----
	10	138	0.33	92	0.22	----	----	----	----
	15	107	0.37	87	0.23	----	----	----	----
	20	----	----	----	----	----	----	198	0.5
	40	----	----	----	----	----	----	138	0.64
	50	----	----	----	----	37	0.85	36	0.9
0.4	5	99	0.21	277	0.16	----	----	----	----
	10	82	0.23	107	0.19	----	----	----	----
	15	73	0.24	82	0.21	----	----	----	----
	20	48	0.4	----	----	----	----	64	0.68
	40	----	----	----	----	----	----	40	0.84
	50	----	----	----	----	19	0.62	35	1.25

As seen, higher milling time led to smaller grain size and larger lattice strain. The mean grain size of β-$MoSi_2$ with 50 h of milling and 0.4 at.% Cr is less than 40 nm on the basis of peak profile analysis. The TEM image of this sample is presented in Figure 6. Very small grains with the size less than 40 nm can be seen in this figure that is in consistent with XRD results. In general, it can be concluded that $MoSi_2$-$CrSi_2$ nanocomposites with the grain size less than 100 nm were obtained at the end of milling in all compositions. High impact between ball-ball and ball-wall during milling leads to heavy plastic deformation of the powders and increasing of lattice defects such as dislocations. Fracturing and rearrangement of the dislocations leads to the microstructure refinement as well as grain size reduction. Diffusion in smaller grain size can be performed at higher speed in grain boundaries during annealing. Grain boundary diffusion promotes the recovery mechanism during annealing and leads to the grain growth as well as lattice strain release. The results of mean grain size and lattice strain measurement of the annealed phase confirm this.

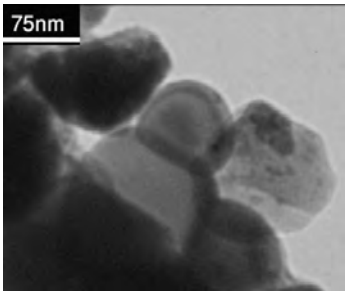

Fig. 6. Bright field image of the 50 h milled powder with 0.1at.% Cr.

As seen in Table 2, the mean grain size of both polymorph of $MoSi_2$ increases at high temperature. In spite of this grain growth, both phases maintain their nanocrystalline nature after annealing. As discussed above, strain release is the other consequence of annealing. The lattice strain of β-$MoSi_2$ is normally higher than that of α-$MoSi_2$ (in same condition) which explains the instability of β-$MoSi_2$ at room temperature. On the other hand, the lattice of β-$MoSi_2$ must endure larger strain to be stable in room temperature.

TABLE 2. Mean grain size and micro-strain of the annealed powders with different Cr content at the vial speed of 640 rpm.

Phases		α $MoSi_2$		β $MoSi_2$	
X_{Cr} At. %	Annealing Temperature ˚C	G.S. (nm)	Strain %	G.S. (nm)	Strain %
0.25	As milled (50 h)	37	0.85	36	0.9
	700	39	0.6	39	0.67
	850	51	0.24	----	----
	1000	63	0.16	----	----
0.4	As milled (50 h)	19	0.62	35	1.25
	700	21	0.57	42	0.83
	850	31	0.41	58	0.71
	1000	53	0.4	----	----

Cold welding, fracturing and re-welding processing are frequently performed during milling. Particle size and morphology of the end product will be determined by the interaction between cold welding and fracturing. Effect of the Cr content on the morphology and particle size of the 50 h milled powders is shown in Figure 7. There is a distribution of very small particles and medium (less than 20μm) agglomerates in the powder

with 0.1 at.% Cr after 50 h of milling (Figures 7-A and 7-B). As seen in Figures 7-C and 7-D, the amount of agglomeration increased due to the cold welding of the small particles at the higher Cr content (0.25 at.%). At the sample with 0.4 at.% Cr, more fracturing led to the smaller particles and agglomerates (Figures 7-E and 7-F). It can be concluded that the mean particle size in all Cr content is less than 20 µm.

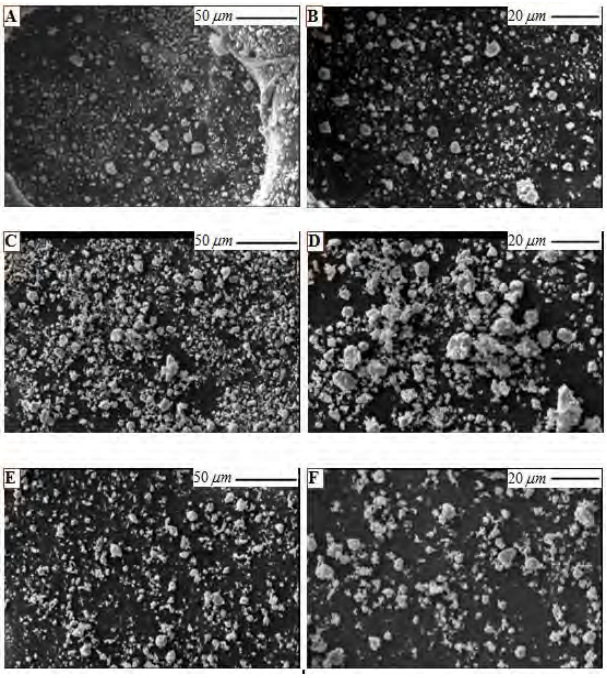

Fig. 7. SEM images of the 50 h milled powders at the cup speed of 640 rpm with different Cr content: A) 0.1at.%, B) 0.1at.% at higher magnification (HM), C) 0.25at.%, D) 0.25at.% (HM), E) 0.4at.% and F) 0.4at.% (HM)

4. CONCLUSION

$MoSi_2$-$CrSi_2$ nanocomposite powders were successfully synthesized by ball milling of Mo, Si and Cr elemental powders at nominal room temperature. These composites were formed after 20 h of milling. Increasing Cr content from 0.1 at.% to 0.25 or 0.4 at.% changed the polymorph of synthesized $MoSi_2$ from α(LT) to β(HT) as well as the formation reaction (1) mechanism from MSR to gradual. Annealing of the milled powders led to the formation of α(LT) polymorph in all Cr contents. $MoSi_2$-$CrSi_2$ nanocomposite powders with the mean grain size less than 40 nm were obtained on the basis of peak profile analysis that is in consistent with TEM result. These nanocomposites maintain their nanocrystalline properties after annealing. The mean particle size less than 20µm was obtained for 50 h milled powders in all Cr content.

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چکیده

پودر کامپوزیتی $(Mo_{1-x}\text{-}Cr_x)Si_2$ با آسیاکاری پودرهای عنصری مولیبدن، کروم و سیلیسیم با موفقیت سنتز شد. تاثیر مقدار کروم، زمان آسیاکاری و دمای آنیل بررسی شد. پودرهای آسیا شده و آنیل شده با پراش پرتوایکس شناسایی شدند. تغییرات مورفولوژی و ریزساختار، به ترتیب با SEM و TEM مطالعه شد. نتایج نشان داد که این کامپوزیت پس از ۲۰ ساعت آسیاکاری تشکیل می شود. افزایش مقدار کروم از ۰/۱ به ۰/۲۵ و ۰/٤ درصد اتمی باعث تغییر ساختار $MoSi_2$ تشکیل شده از α به β و همچنین مکانیزم انجام واکنش از MSR به تدریجی شد. در تمامی مقادیر کروم، آنیل کردن پودرهای آسیا شده موجب تشکیل فاز α گردید. در پایان آسیاکاری در تمامی مقادیر کروم، اندازه متوسط دانه‌های کمتر از ٤۰ نانومتر به دست آمد. علی‌رغم رشد دانه و آزاد شدن کرنش در حین آنیل، این کامپوزیت در حالت نانوساختار باقی ماند.

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