

Features of the Solid Solution ($\text{Mo}_{0.9}\text{Cr}_{0.1}$) Si_2 Formation Depending on the State of Initial Mixture

I. Kud, L. Ieremenko, L. Likhoded, I. Uvarova, D. Zyatkevich*

Department for technology of refractory compounds and nanostructured composite coatings, Frantsevich Institute for Problems of Materials Science of NAS of Ukraine, Kyiv, 03142, Ukraine

Abstract The regularities of solid state synthesis of the solid solution ($\text{Mo}_{0.9}\text{Cr}_{0.1}$) Si_2 in vacuum have been investigated in the temperature range 400-1200°C depending on the dispersity and energetic state of the initial powders, namely molybdenum, chromium and silicon. The energetic state of the initial mixture was established to be a determining factor which affects the principal features of solid state interaction whereas an increase in dispersity only influences the temperature of the interaction start. When non-activated initial mixtures and ones mechanically activated in a planetary mill with low number of drum revolutions were used, the solid solution formation proceeded owing to diffusion of silicon into metals through successive formation of lower and higher molybdenum-based silicide phases followed by their interaction. Mechanical activation in a planetary mill with high number of drum revolutions was accompanied by not only decrease in particle size but also changes in the energetic state of the reaction mixture, which resulted in changing the regularities of the solid solution formation. Herein solid solutions on the basis of two higher molybdenum silicide phases, tetra- and hexagonal modifications, were formed with further polymorphic transition of the unstable high temperature hexagonal β - MoSi_2 phase into the low temperature tetragonal α - MoSi_2 phase. It has been established that temperature of the beginning of interaction decreases by 100°C as compared with non-activated initial mixtures and temperature of the end of the process depends on the amount of accumulated energy: under low energy mechanical activation the process is complete at 1200°C, while a high energy activation decreases this temperature by 200-400°C depending on the duration of activation.

Keywords Silicide, Solid State Reaction, Milling, Nanomaterial

1. Introduction

The transition metal silicides refer to refractory compounds with melting temperature close to that of borides and carbides. Their high thermal and chemical stabilities remain up to high temperatures, which makes them promising as materials for refractory coatings, various parts for aircraft and space engineering as well as for metallurgical and chemical industry[1-5]. Among all of the silicides, MoSi_2 based materials are most known for high temperature application. They typically have good mechanical properties and high heat and oxidation resistance at high (above 900°C) temperatures. However, a number of shortcomings at lower temperatures block their commercial application. A key shortcoming is drastic oxidation and disintegration at 800-900°C. Some positive results concerning the avoidance of the effect of the low temperature oxidation have been achieved lately. In particular, composite materials with ceramic additives from ZrO_2 , Al_2O_3 , SiC , etc. have been created. Also, a promising

solution of this problem consists in using solid solutions of molybdenum silicides added with chromium, niobium, titanium, tungsten and other refractory elements. The use of chromium as a basic additive to MoSi_2 increases the oxidation resistance of this material in the temperature range 600-900°C [6-9].

Investigations into the structure and physicochemical properties in complex silicide systems such as Cr-Me-Si, where Me stands for Ti, Ta, Re, and Mn[10-12], have shown that solid solutions on the basis of silicides exhibit better physicochemical properties compared to the related individual silicides. The broad region of the existence of solid solutions, within which the crystalline and electron structures are the same, guarantees a high reproducibility of the operation parameters. Herein solid solutions on the basis of higher silicide phases have the most stable properties.

The use of nanosized powders of solid solutions of silicides as materials for coatings and volumetric heaters markedly increases their high temperature resistance due to the formation of fine-grained protective film of scale. In spite of good enough clarification of mechanical alloying in various systems[13-15] as well as the regularities of formation of nanosized individual silicides, in particular silicides of molybdenum and titanium, via high energy mechanical treatment[16-22], the available information on

* Corresponding author:

dpz@ipms.kiev.ua (D. Zyatkevich)

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production of nanopowders of solid solutions of refractory compounds, especially silicides, is poor.

This work is devoted to investigation into the regularities of the solid solution $(\text{Mo}_{0.9}, \text{Cr}_{0.1})\text{Si}_2$ formation through a solid state synthesis depending on the dispersity and energetic state of the initial mixture after milling.

2. Experimental

In this study, the following microsized powders were used as initial components: silicon (99.998 % Si, $S_{sp}=2.2 \text{ m}^2/\text{g}$ produced by the Svitlovodsk Plant of Hard Alloys, Ukraine); molybdenum PM 99.95 (99.95 % Mo, $S_{sp}=0.5 \text{ m}^2/\text{g}$, Firm "Polema", Russia), and electrolytic chromium PERCr-1/280 (98.7% Cr, $S_{sp} = 0.2 \text{ m}^2/\text{g}$, "Polema", Russia).

According to the literature [10], the region of the solid solution $(\text{Mo}_{0.9}, \text{Cr}_{0.1})\text{Si}_2$ existence spreads up to 46 mol% CrSi₂. In this work, therefore, the initial mixture was calculated in view of production of the solid solution $(\text{Mo}_{0.9}, \text{Cr}_{0.1})\text{Si}_2$, namely (mass%): 58.45 Mo; 3.52 Cr, and 38.03 Si. Besides, some extra silicon was added, whose amount was selected tentatively to compensate losses of silicon during the mill discharge as the lightest and most inclined to oxidation element among the other components. A homogeneous component distribution was reached via milling in the steel drum of planetary mill «Pulverizette-6» in an ethanol medium. The powder particle size did not exceed 10 μm .

To investigate the effect of the dispersity and the energetic state of the initial mixtures on the solid solution $(\text{Mo}_{0.9}, \text{Cr}_{0.1})\text{Si}_2$ formation, different conditions of mechanical activation were selected which were provided by different types of planetary mills used. In particular, mechanical activation was performed in a high-energy planetary mill «AIR-0.015» («Gidrotsvetmet», Russia) in an argon medium at a planetary disk revolution number of 548 rpm with an acceleration of 25 g as well as in a planetary mill «Pulverizette-6» at a disk revolution number of 200 rpm. The mass powder/balls ratio was 1:10. Milling in «Pulverizette-6» was performed under the conditions, which provided a decrease in the particle size of the initial powder with no change in its composition. Milling in «AIR-0.015» was conducted using an impulse regime, which made it possible to avoid an uncontrolled SHS (self-propagating high temperature synthesis) reaction. The amount of the initial mixture was the same in all experiments and equal to 50 g. The steel drums and 10 mm milling balls were prior charged with silicon to prevent contamination of the products with the reactor material. The energy transferred to the powder under milling was estimated on the basis of the specific energy, that is, the energy acquired by 1 g powder after one ball collision [23-24], taking into account the time of milling. A criterion for choice of the milling time was minimal change in the phase composition of initial mixture.

Solid state synthesis of both non-activated and previously mechanically activated reaction mixtures (3 g samples

pressed under 0.5 MPa) was conducted in a vacuum furnace SNV-1.3,1/20-II at $\sim 1 \cdot 10^{-3} \text{ Pa}$ in the temperature range 400-1200°C and 2 h isothermal holding. The average rate of temperature rise to the isothermal holding was 10 K/min.

The synthesis products were examined by an XRD analysis using a diffractometer DRON-3 under filtered Co radiation. The angles were determined with an error of $\pm 0.05 \text{ deg}$. The size of crystallites was calculated using the Sherrer formula. The phases were identified following the powder diffraction database file ICDD-JCPDS PDF-2. The error of the lattice parameter calculation was $\pm 0.001 \text{ nm}$. The specific surface area was determined using thermal desorption of nitrogen with an error of 5-10 %.

The particle size and elemental composition of the powders produced by a low temperature synthesis were determined with help of a transmission electron microscope JEM 2100 S (Japan).

Standard techniques of chemical analysis were used for determination of the elemental composition of the final product and estimation of the amount of iron milled into it.

3. Results and Discussion

3.1. High Temperature Interaction of Non-activated Powders of Molybdenum, Chromium and Silicon in Vacuum

The regularities of the $(\text{Mo}_{0.9}, \text{Cr}_{0.1})\text{Si}_2$ formation in the course of solid state interaction of the initial components in the temperature range 400-1200°C were investigated at an isothermal holding of 2 h. The corresponding XRD findings for the synthesis products are listed in Table 1.

These data evidence that the solid state interaction of the initial components begins at 700°C, when the lower molybdenum silicide appears, whose reflection intensities change extremely with a maximum at 800°C. The interaction is accompanied with reduction in the molybdenum lattice parameter, which may be assigned to diffusion processes and dissolution of chromium in molybdenum (atomic radius of chromium is smaller than that of molybdenum by 10 %). Below 700°C no phase transition is fixed and the reflection intensity is unchanged.

The further temperature rise is accompanied with the beginning of formation at 800°C of the tetragonal phase Mo_5Si_3 , which is present in the interaction products up to 1100°C. At 1000°C the higher molybdenum silicide of the tetragonal modification, $\alpha\text{-MoSi}_2$, is formed. Thus, in the temperature range 1000-1100°C the basic products are Mo_5Si_3 and $\alpha\text{-MoSi}_2$ along with traces of Si, whereas at 1200°C only $\alpha\text{-MoSi}_2$ is identified. The change in the $\alpha\text{-MoSi}_2$ lattice parameters (a decreases and c markedly increases) indicates the formation of the interstitial solid solution $(\text{Mo}_x\text{Cr}_y)\text{Si}_2$. The data of chemical analysis demonstrate high reproducibility of the elemental composition (58.5 Mo; 3.74 Cr; 37.6 Si, mass%), which practically corresponds to the calculated formula $(\text{Mo}_{0.9}, \text{Cr}_{0.1})\text{Si}_2$; contamination with iron does not exceed 0.1

mass%. The absence of chromium silicide phases in the temperature range studied draws a conclusion that the solid state interaction proceeds through successive formation of interstitial solid solutions on the basis of molybdenum silicide phases owing to the dissolution of chromium. This is well consistent with the equilibrium diagrams of the Mo-Cr-Si system[10], according to which the isostructural silicides Cr₃Si-Mo₃Si and Cr₅Si₃-Mo₅Si₃ form a continuous series of solid solutions.

3.2. Low Temperature Interaction of Previously Mechanically Activated Powders of Molybdenum, Chromium and Silicon

The effect of the dispersity of the initial mixture and the energy acquired by it on the regularities of the solid solution (Mo_xCr_y)Si₂ formation was studied using an XRD and TEM analyses. Table 2 lists the XRD data and the results of determination of the specific surface energy upon milling.

As seen, a high-energy milling leads to the powder refining, which is accompanied by change in the diffraction peaks and the phase composition of reaction mixture.

For mixtures 1-3 subjected to mechanical activation in the mill «Pulverizette-6», prolongation of milling from 600 to

3000 min results in changing the peak intensity and broadening the peaks for all of the components used. First of all, this may be connected with powder refining: the specific surface area monotonously increases from 3.7 m²/g (600 min milling) to 4.5 m²/g (3000 min milling).

The dynamics of changing in the XRD patterns from the reaction mixtures subjected to milling in the planetary mill «AIR-0.015» demonstrates the significant influence of the acquired energy on the reactivity (Fig. 1).

The 30 min milling does not cause any change in the phase composition of reaction mixture; only some distortion of the diffraction peaks is observed, which is particularly characteristic for silicon, which is more brittle compared to molybdenum and chromium and is therefore affected by mechanical processing to a greater extent. Its energetic state is more strained owing to refining and disordering of the crystalline lattice.

Prolongation of milling to 45 min leads to change in the phase composition. The molybdenum peaks markedly broaden, and reflections from silicon and chromium are absent. In addition, nuclei of molybdenum disilicide of two modifications, namely low temperature α -MoSi₂ and high temperature β -MoSi₂, appear practically in equal quantity.

Table 1. Phase Composition of the Product of Solid State Interaction of Molybdenum, Chromium and Silicon

Temperature of interaction, °C	Data of XRD analysis					
	Phase composition	Lattice parameters, nm				
		Mo	Mo ₅ Si ₃		MoSi ₂	
		<i>a</i>	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
400	Mo, Si, Cr,	0.315	–	–	–	–
500	Mo, Si, Cr,	0.315	–	–	–	–
600	Mo, Si, Cr,	0.315	–	–	–	–
700	Mo, Si, Cr, Mo ₃ Si	0.314	–	–	–	–
800	Mo, Mo ₃ Si, Mo ₅ Si ₃ , Si	0.314	0.965	0.491	–	–
900	Mo, Mo ₅ Si ₃ , Mo ₃ Si, Si	0.314	0.964	0.489	–	–
1000	Mo ₅ Si ₃ , α -MoSi ₂ , Mo, Si, Mo ₃ Si*	–	0.963	0.490	0.320	0.786
1100	α -MoSi ₂ , Mo ₅ Si ₃ *, Si*	–	–	–	0.319	0.788
1200	α -MoSi ₂	–	–	–	0.319	0.787

* traces

Table 2. Specification of Reaction Mixtures Under Different Conditions of Milling

Mixture	Type of mill	Conditions of milling		Phase composition	Specific surface area, m ² /g
		Number of revolutions, rpm	Time, min		
1	«Pulverizette-6»	200	600	Mo, Cr, Si	3.7
2			1800	Mo, Cr, Si	3.9
3			3000	Mo, Cr, Si	4.5
4	«AIR-0.015»	548	30	Mo, Cr, Si	3.6
5			45	Mo, β -MoSi ₂ , α -MoSi ₂	4.3
6			60	Mo, α -MoSi ₂	3.0
7			90	Mo, α -MoSi ₂	4.2

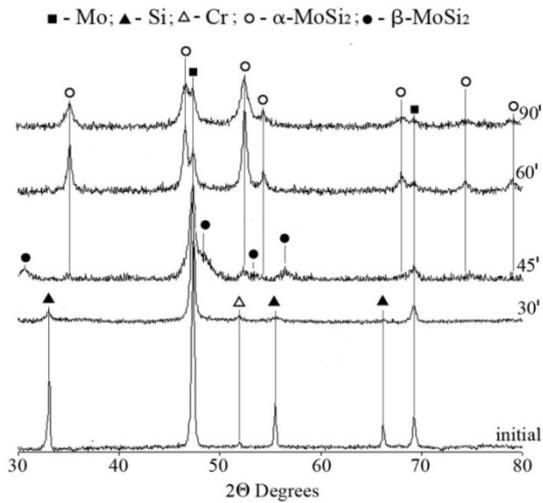


Figure 1. XRD patterns from the reaction mixture before (initial) and after milling for 30, 45, 60, and 90 min in the planetary mill «AIR-0.015»

The absence of silicon peaks may be related to silicon amorphousness relative to XRD examination caused by the refinement in particle size and deformation of the crystalline lattice during milling. In order to clarify this point, the particles that formed a small cloud at the moment of powder discharge were specially examined.

Fig. 2 illustrates the TEM spectra from the light phase separated from air during the mill discharge: it contains mostly silicon particles as they are the lightest of the initial components (specific density: Si – 2.33; Cr – 7.16; Mo – 10.22 g/cm³).

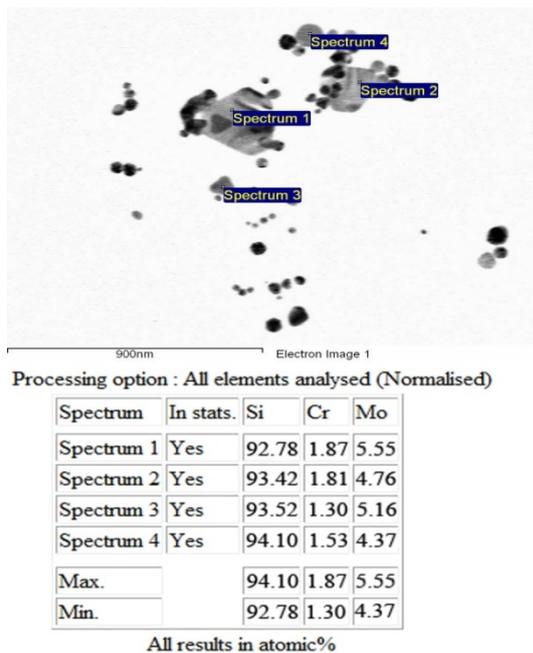


Figure 2. Elemental composition of the light phase separated from air during discharge of the planetary mill «AIR-0.015»

As shown, silicon particles are polycrystals sizing from 15 to 100 μm. The elemental analysis reveals the presence of small amount of molybdenum and chromium on free silicon particles. The formation of molybdenum disilicide nuclei

indicates that 45 min milling (mixture 5) provides the reaction mixture with the energy required for partial mechanosynthesis. The increase in the energy acquired by mixtures 6 and 7 thanks to prolongation of milling to 60 and 90 min, respectively, provides the necessary conditions for intensification up to the completeness of solid state interaction, which is confirmed by the XRD patterns. The content of molybdenum in the synthesis products monotonously reduces, whereas that of the α-MoSi₂ phase increases. The change in the α-MoSi₂ lattice parameters (*a*=0.321; *c*=0.783 nm) evidences to the formation of the solid solution (Mo_xCr_y)Si₂. The calculation of crystallite sizes using the Sherrer formula (15 nm for α-MoSi₂ and 55 nm for Mo) confirms a nanostructural state of the initial mixture. The specific surface area of the latter is 3.05 m²/g.

The TEM micrographs from mixture activated for 90 min (mixture 7) manifest a homogeneous distribution of the initial elements (Fig. 3).

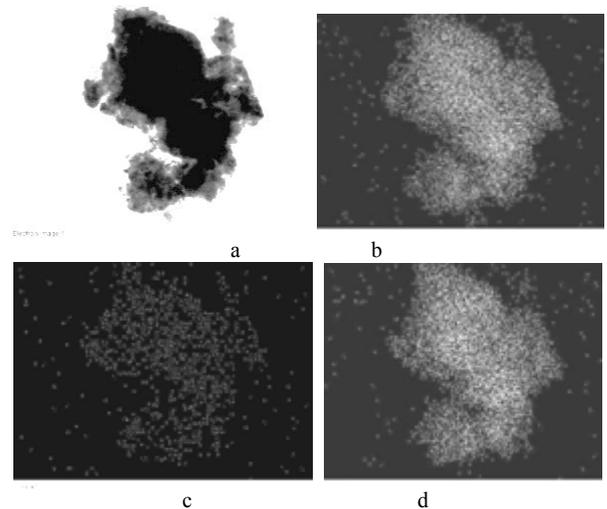


Figure 3. The surface of agglomerate (a) and maps of distribution of silicon (b), chromium (c) and molybdenum (d) over it for the reaction mixture mechanically activated for 90 min

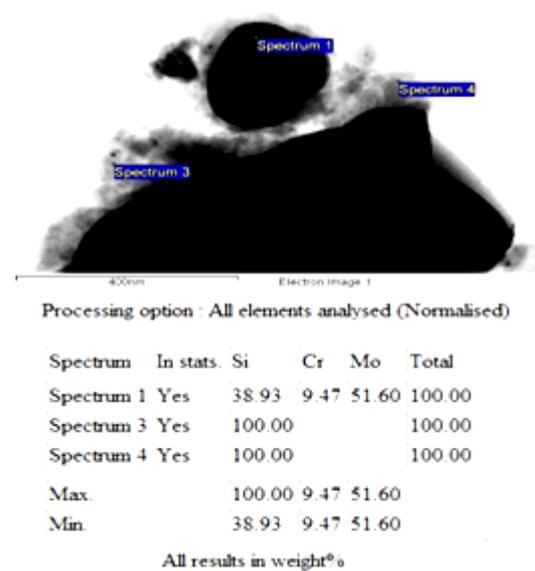


Figure 4. Elemental composition of the activated reaction mixture

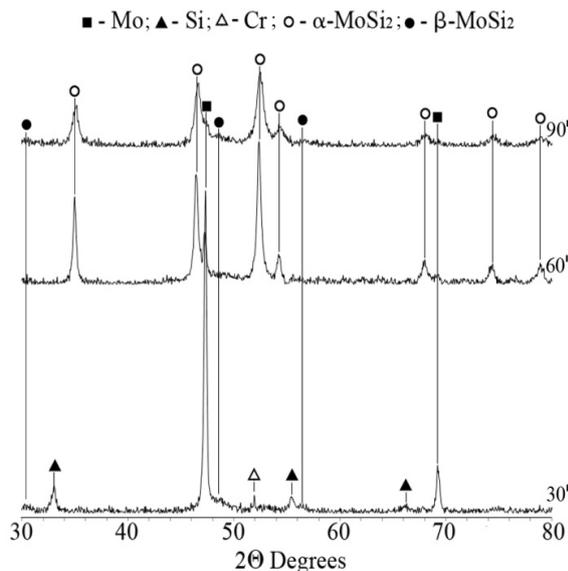
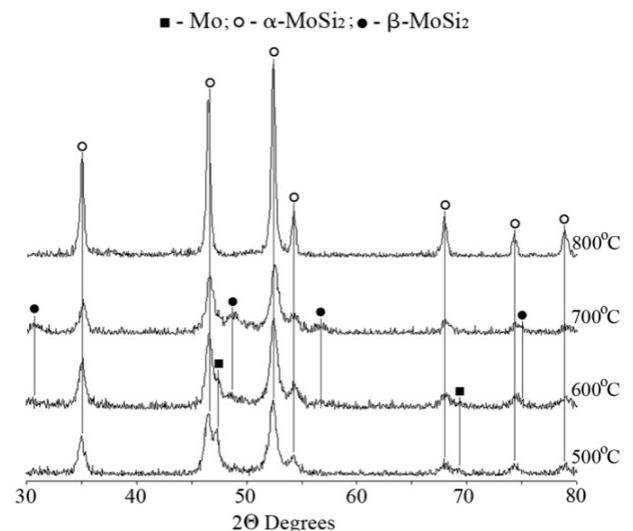
Table 3. XRD Data for the Products of Two-hour Solid State Interaction of Mechanically Activated Reaction Mixtures in Vacuum

Temperature of interaction, °C	Phase composition				
	Time of mechanical activation in «Pulverizette-6» mill, min		Time of mechanical activation in «AIR-0.015» mill, min		
	1800 (mixture 2)	3000 (mixture 3)	30 (mixture 4)	60 (mixture 6)	90 (mixture 7)
Reaction mixture	Mo, Si, Cr	Mo, Si, Cr	Mo, Si, Cr	Mo, α-MoSi ₂	Mo, α-MoSi ₂
400	Mo, Si, Cr	Mo, Si, Cr	Mo, Si, Cr	Mo, α-MoSi ₂	Mo, α-MoSi ₂
500	Mo, Si, Cr	Mo, Si, Cr	Mo, Si, Cr	Mo, α-MoSi ₂	Mo, α-MoSi ₂
600	Mo, Si, Cr, Mo ₃ Si, Mo ₅ Si ₃	Mo, Si, Cr, Mo ₃ Si, Mo ₅ Si ₃	Mo, Si, Cr, β-MoSi ₂ *	Mo, α-MoSi ₂ , β-MoSi ₂ *	α-MoSi ₂ , β-MoSi ₂ , Mo*
700	Mo, Si, Cr, Mo ₃ Si, Mo ₅ Si ₃	Mo, Si, Cr, Mo ₃ Si, Mo ₅ Si ₃	Mo, Si, α-MoSi ₂ , β-MoSi ₂	Mo, α-MoSi ₂ , β-MoSi ₂	α-MoSi ₂ , β-MoSi ₂
800	Mo, Si, Cr, Mo ₃ Si, Mo ₅ Si ₃	Mo, Si, Cr, Mo ₃ Si, Mo ₅ Si ₃	Mo, Si, α-MoSi ₂ , β-MoSi ₂	α-MoSi ₂ , β-MoSi ₂	α-MoSi ₂
900	Mo, Si, Mo ₃ Si, Mo ₅ Si ₃ , α-MoSi ₂	Mo, Si, Mo ₃ Si, Mo ₅ Si ₃ , α-MoSi ₂	α-MoSi ₂ , β-MoSi ₂ *	α-MoSi ₂	-
1000	Mo ₃ Si, Mo ₅ Si ₃ , α-MoSi ₂ , Mo*, Si*	Mo ₃ Si, Mo ₅ Si ₃ , α-MoSi ₂ , Mo*, Si*	α-MoSi ₂	-	-
1100	α-MoSi ₂ , Mo ₅ Si ₃ , Si*	α-MoSi ₂ , Mo ₅ Si ₃ , Si*	-	-	-
1200	α-MoSi ₂	α-MoSi ₂	-	-	-

* traces

TEM micrographs of the reaction mixture (Fig. 4) confirms its nanostructural state and demonstrates that it is composed of agglomerates of polycrystals. The data of micro-XRD analysis revealed the presence of free silicon (light-grey zone), which is amorphous towards XRD examination: the XRD patterns contain no silicon reflections beginning from a milling time of 45 min (Table 2).

The formation of the solid solution (Mo_{0.9}Cr_{0.1})Si₂ through solid state interaction of mechanically activated reaction mixtures in vacuum was investigated in the temperature range 400-1200°C. The phase composition of the synthesis products was determined using an XRD method (Table 3, Figs. 5 and 6).

**Figure 5.** XRD patterns from the products of solid state interaction at 600°C of mixtures mechanically activated for 30, 60 and 90 min**Figure 6.** XRD patterns from the products of solid state interaction at different temperatures of the reaction mixture mechanically activated for 90 min

The findings for the reaction mixtures that underwent a long milling (1800 and 3000 min) in the planetary mill «Pulverizette-6» suggest that the main features of the solid solution (Mo_{0.9}Cr_{0.1})Si₂ formation do not depend on the time of mechanical activation. The beginning of solid state interaction is fixed at 600°C, that is, 100°C lower than that for non-activated powders (700°C, Table 1). Then the interaction runs through successive formation of lower silicide phases based on molybdenum, namely Mo₃Si and Mo₅Si₃. At 900°C, there appears a molybdenum disilicide based phase, α-MoSi₂, and at 1000°C the interaction products are a mixture of the all above phases and the initial components. Finally, temperature rise to 1200°C provides the formation of an

α -MoSi₂ based solid solution. All this makes it possible to draw a conclusion that mechanical activation of reaction mixture in the planetary mill «Pulverizette-6» is accompanied by refining the initial components, which is confirmed by the increase in the specific surface area of the reaction mixture from 2.0 (initial mixture) to 3.9 (upon 1800 min milling) and 4.5 m²/g (upon 3000 min milling). The energy acquired thanks to the formation of new surfaces and the change in the crystalline lattice of the initial components due to formation of various defects of structure (dislocations, vacancies, etc.) leads to lowering the temperature of the beginning of interaction with no change in the main features of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ formation. Herein the process of interaction proceeds by a diffusion mechanism similar to non-activated initial mixtures. As for milling in the «AIR-0.015» mill, at any phase composition of mechanically activated reaction mixture, which depends on the energy acquired during milling, the appearance of the dissipative β -MoSi₂ phase is registered at 600°C. Prolongation of milling results in the acquired energy increasing, which, in its turn, increases the mixture reactivity and the amount of the β -MoSi₂ phase (Fig. 5).

According to the XRD patterns from the products of interaction at 600°C of reaction mixture 4, they contain all the initial components, that is Mo, Si and Cr, plus β -MoSi₂ nuclei. In the temperature range 700-800°C, chromium peaks disappear and an α -MoSi₂ based phase is formed, the amount of which gradually increases. At 900°C the interaction yields the solid solution (Mo_x,Cr_y)Si₂ on the basis of the both (α and β) modifications of molybdenum disilicide, and at 1000°C the $\beta \rightarrow \alpha$ polymorphic transition occurs.

The solid state interaction of reaction mixtures activated in the planetary mill «AIR-0.015» for 60 and 90 min (mixtures 6 and 7) is different from that for mixture 4, which is due to a higher acquired energy and different composition of mechanically activated reaction mixtures containing α -MoSi₂ nuclei, molybdenum and XRD-amorphous silicon (Fig. 6). As formation of silicides through a solid state synthesis is determined by silicon-in-metal diffusion [25], the availability of much silicon in an XRD-amorphous state ensures its higher reactivity compared to crystalline silicon and leads to the formation of solid solution on the basis of molybdenum disilicide of both modifications at 700 (mixture 7) and 800°C (mixture 6) depending on the milling duration. The size of polycrystals calculated using the Sherrer formula is 20 nm for α -MoSi₂ and 15 nm for β -MoSi₂. The rise in synthesis temperature by 100°C stimulates the polymorphic $\beta \rightarrow \alpha$ transition (mixture 7).

The product of synthesis at 800°C of the reaction mixture 7 milled for 90 min was a brittle briquette easy to disintegrate. An SHS reaction was not observed even in the case of big initial mixture (to 50 g), which may be associated with phenomenon of "blocking": high-active particles of the initial components become separated with big enough amount of the α -MoSi₂ formed. The size of the powder particles, polycrystals, calculated using the Sherrer formula did not exceed 45-50 nm. The chemical analysis showed

reproducibility of the elemental composition, mass%: 58.1 Mo; 3.3 Cr; 36.7 Si; 1.6 Fe, which corresponds to the formula (Mo_{0.9},Cr_{0.1})Si₂. The presence of iron is due to contamination of the powder with the mill material during mechanical activation.

The powder of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ produced under the selected conditions was examined using a TEM microscope. The micrographs are presented in Figs. 7 and 8.

The (Mo_{0.9},Cr_{0.1})Si₂ powder produced from mechanically activated reaction mixture was composed of polycrystal agglomerates sizing to 100 nm whose crystallites did not exceed 20 nm.

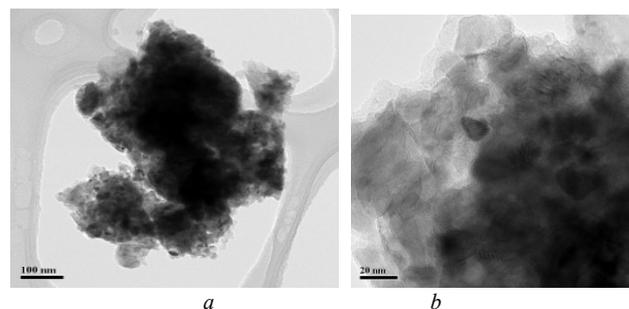


Figure 7. TEM micrographs of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ particles produced at 800°C

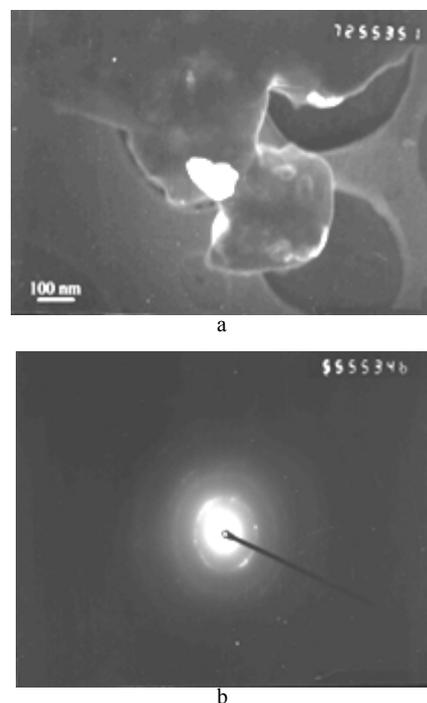


Figure 8. TEM micrographs of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ powder produced at 800°C (a) and electron-diffraction pattern of a particle (b)

The carried out investigation into synthesis of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ depending on the energetic state of the reaction mixtures made it possible to establish a number of features of the solid state interaction between the initial components which determine the difference in phase transitions and, as a result, in runs of the process and its products.

In the case of non-activated powders, the solid solution

formation proceeds by a diffusion mechanism through successive formation of solid solutions on the basis of lower silicides, (Mo,Cr)₃Si and (Mo,Cr)₅Si₃ (within 800-900°C) and the higher molybdenum silicide phase α -(Mo,Cr)Si₂ (at 1000°C) followed by their interaction/homogenization in the temperature range 1100-1200°C (Table 1).

The formation of the solid solution from reaction mixtures that were previously mechanically activated for 1800-3000 min in the planetary mill «Pulverizette-6» is characterized by the same regularities as for non-activated mixtures except for the shift (by 100°C) of the start of interaction towards lower temperatures due to the increase in the specific surface area and the structure defectiveness of the initial components. Despite the decrease in the interaction start temperature, the solid solution homogenization was complete in the same temperature interval, 1100-1200°C. This draws a conclusion that only increase in the specific surface area from 2.3 (non-activated powders) to 4.5 m²/g (3000 min milling) and the acquired energy are not sufficient for a change in the mechanism of solid state interaction.

The solid state interaction in the course of low temperature synthesis in vacuum of previously mechanically activated mixtures in the planetary mill «AIR-0.015» is quite different. In our opinion, the change in the regularities of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ formation may be related to the silicon structure peculiarities in mixtures 4-7, where, according to the XRD and TEM data, silicon is amorphous towards XRD analysis (mixtures 5-7) or partially amorphous (mixture 4). Upon 30 min milling, reaction mixtures contain all of the initial components, whereas upon 60 and 90 min milling, the α -MoSi₂ phase is fixed along with molybdenum, chromium and XRD amorphous silicon (Table 2), which indicates the fact that under the selected conditions of intense milling, the chemical reaction yielding molybdenum disilicide prevails over diffusion process as MoSi₂ is the most energetically preferable compound (heat of MoSi₂ formation is three times higher than that of lower silicide phases[25]).

It was established that at any phase composition of initial mixture activated in the mill «AIR-0.015», the β -MoSi₂ phase is fixed at 600°C (Table 3). Here the formation of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ occurs without formation of intermediate lower silicide phases. The acquired energy significantly affects the reactivity of the initial mixture, which, in its turn, determines the final temperature for phase transformations.

Having compared the processes running in planetary mills «Pulverizette-6» and «AIR-0.015», one can suggest that mechanical processing in «Pulverizette-6» accompanied with chaotic combination of collisions and abrasion proceeds mostly at the expense of abrasion, whereas in the mill «AIR-0.015», under the conditions of the impulse milling proposed by the authors, the action of collisions dominates, which leads to amorphization of free silicon. Herein the peculiarities of system defectiveness may be different.

To sum up, the investigation carried out has shown up that the formation of the solid solution (Mo_{0.9},Cr_{0.1})Si₂

predominantly depends on the reactivity of initial mixture, that is, on the energy acquired by the mixture owing to the milling and also on the phase composition and state of silicon. According to the calculations performed, the acquired energy is proportional to the number of revolutions of the mill drums. In this work, the number of drum revolutions in the «AIR-0.015» mill was greater than that in «Pulverizette-6» mill by three times. At practically the same specific surface area (4.5 m²/g for «Pulverizette-6» (3000 min milling) and 4.2 m²/g for «AIR-0.015» (90 min milling)), the regularities of the solid solution formation are quite different. Also, it should be noticing that the energy acquired owing to milling determines the formation of the dissipative phase β -MoSi₂ and α -MoSi₂ and their solid state interaction. The higher this energy, the sooner the final phase α -MoSi₂ is formed.

4. Conclusions

The energy acquired by the initial reaction mixture during mechanical activation was established to be a determining factor among the others affecting the process of solid state interaction, whereas the role of the dispersity exhibits itself only in the change in the interaction start temperature.

Formation of the solid solution (Mo_{0.9},Cr_{0.1})Si₂ through solid state interaction of non-activated initial powders occurs owing to diffusion processes via intermediate stages of formation of solid solutions based on lower and higher molybdenum silicide phases and their subsequent interaction.

Mechanical activation in a planetary mill «Pulverizette-6» is accompanied with refining the initial components; the energy acquired by them permits a decrease in the temperature of the interaction start by 100°C; herein the regularities of formation of dissipative intermediate phases and the final temperature of the solid solution formation, 1200°C, are the same as for non-activated powders.

Mechanical activation in a high-energy mill «AIR-0.015» allows one to produce high reactivity mixtures, which intensifies the solid state interaction. Under the following heat treatment, solid solutions on the basis of higher molybdenum silicide phases of two modifications, tetragonal α -MoSi₂ and hexagonal β -MoSi₂, are formed with further transformation of the unstable high temperature β -MoSi₂ phase into the low temperature α -MoSi₂ phase.

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REFERENCES

- [1] F. Baras, D. K. Kondepudi, and F. Bernard, "Combustion

- Synthesis of MoSi_2 and $\text{MoSi}_2\text{-Mo}_5\text{Si}_3$ Composites: Multilayer Modeling and Control of the Microstructure”, *Journal of Alloys and Compounds*, vol. 505, no. 1, pp. 43-53, Aug. 2010.
- [2] E. Bruneton, S. Martoia, and S. Schelz, “Ellipsometry and Transmission Electron Microscopy Study of MoSi_2 Coatings After Oxidation at High Temperature in Air”, *Thin Solid Films*, vol. 519, no. 2, pp. 605-613, 2010.
- [3] M. Zakeri, R. Yazdani-Rad, M. H. Enayati, and M. R. Rahimpour, “Synthesis of Nanocrystalline MoSi_2 by Mechanical Alloying”, *Journal of Alloys and Compounds*, vol. 403, no. 1-2, pp. 258-261, Nov. 2005.
- [4] K. Hellström, J. E. Tang, T. Jonsson, M. Halvarsson, R. Pompe, M. Sundberg, and J.-E. Svensson, “Oxidation Behaviour of a (Mo, W) Si_2 -based Composite in Dry and Wet Oxygen Atmospheres in the Temperature Range 350-950°C”, *Journal of the European Ceramic Society*, vol. 29, no. 10, pp. 2105-2118, Jul. 2009.
- [5] L. Ingemarsson, M. Halvarsson, K. Hellström, T. Jonsson, M. Sundberg, L.-G. Johansson, and J.-E. Svensson, “Oxidation Behavior at 300-1000°C of a (Mo,W) Si_2 -based Composite Containing Boride”, *Intermetallics*, vol. 18, no. 1, pp. 77-86, Jan. 2010.
- [6] I. Rosales; H. Martinez, D. Bahena, J. A. Ruiz, R. Guardian; J. Colin, “Oxidation performance of Mo_3Si with Al additions”, *Corros. Sci.*, vol. 51, pp. 534-538, 2009.
- [7] S. Ochiai, “Improvement of the oxidation-proof property and the scale structure of Mo_3Si intermetallic alloy through the addition of chromium and aluminum elements”, *Intermetallics*, vol. 14, pp. 1351-1357, 2006.
- [8] K. Yoshimi, S. Nakatani, T. Suda, S. Hanada, H. Habazaki, “Oxidation behavior of Mo_5SiB_2 -based alloy at elevated temperatures”, *Intermetallics*, vol. 10, pp. 407-414, 2002.
- [9] Jiang Xu, Shuyun Jiang, and Yue Wang, “Influence of Chromium Alloying on the Cyclic Oxidation Behavior of Nanocrystalline $(\text{Mo}_x\text{Cr}_{1-x})_5\text{Si}_3$ Films at 800 Degrees C in Air”, *Applied Materials & Interfaces*, vol. 2, no. 1, pp. 301-311, 2010.
- [10] H. J. Goldschmidt, “Interstitial alloys”, Butterworths, London, 1967.
- [11] Kud I.V., Lihoded L.S., Yeremenko L.I. “Formirovanie Faz na Osnove Disilicidov Reniya i Chroma v Troinoi Systeme Re-Cr-Si pri Tvedofaznom Vzaimodeistvii”, *Poroshkovaya metallurgia*, № 7/8, pp.92-97, 2004.
- [12] Bei H., Yahg Y., Viswanathan G. B., Rawn C. J., “Formation, Stability and Crystal Structure of the σ Phase in Mo-Re-Si Alloys”, *Acta Materialia*, no. 58, pp.6027-6034, 2010.
- [13] V.V. Boldyrev, C. Suryanarayana, E.Ivanov “The Science and Technology of Mechanical Alloying”, *Mater. Sci. Eng.*, vol. 304a, pp. 151-158, 2001.
- [14] Grigorieva T. F., Barinova A. V., Lyakhov N. Z., “Mechanosynthesis of Nanocomposites”, *J. of Nanoparticle Research.*, no. 5, pp. 439-453, 2003.
- [15] C. Suryanarayana, “Mechanical Alloying and Milling”, *Progress in Materials Science*, no. 46, pp. 1-184, 2001.
- [16] Liu Lin, “Metastable Phase Transitions in Mo-Si and V-Si Systems Activated by High Energy Ball Milling”, *J. Trans. Nonferrous Met. Soc., China*, vol. 12, no. 1, pp. 62-66, 2002.
- [17] Liu L., Padeliia F., Guo W. and Magini M. “Solid state reactions induced by mechanical alloying in metal-silicon (metal=Mo, Nb) systems”, *Acta Metall. Mater.*, vol. 43, no. 10, 3755-3761, 1995.
- [18] Gras Ch., Vrel D., Gaffet E., Bernard F., “Mechanical Activation Effect on the Self-sustaining Combustion Reaction in the Mo-Si System”, *J. Alloy Comp.* vol. 314, no. 1-2, pp. 240-250, 2001.
- [19] Peizhong Feng, Xuanhui Qu, Farid Akhtar, “Effect of the Composition of Starting Materials of Mo-Si on the Mechanically Induced Self-propagating Reaction”, *J of Alloys and Compounds*, no. 456, pp. 304-307, 2008.
- [20] Peizhong Feng, Akhtar Farid, Xiaohong Wang, “Mechanically Activated Reactive Synthesis of Refractory Molybdenum and Tungsten Silicides”, *Refract. Metals & Hard Mater.*, no. 26, pp. 173-178, 2008.
- [21] Zakeri M., Yazdani-Rad R., Enayati M.H., Rahimpour M.R., “Synthesis of Nanocrystalline MoSi_2 by Mechanical Alloying”, *J Alloy Compd.*, no. 403, pp. 258-261, 2005.
- [22] Ma Q., Wang C., Xue Q., “Structure Development During Mechanical Alloying of Mo and WSi Powders”, *Rare Metal Mater Eng.*, vol. 32, no. 3, pp.170-172, 2003.
- [23] Zhang H, Liu X., “Analysis of Milling Energy in Synthesis and Formation Mechanisms of Molybdenum Disilicide by Mechanical Alloying”, *Int J. Refract Met Hard Mater.*, vol. 19, pp. 203-208, 2001.
- [24] M. Magini, N. Burgio, A. Iasonna, “Analysis of Energy Transfer in the Mechanical Alloying Process in the Collision Region”, *J. Mater. Synt. Process.*, no. 1, pp. 135-140, 1993.
- [25] S. P. Murarka, “Silicides for VLSI applications”, Academic Press, New York London, 1983.