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Short Communication

Some Considerations Regarding $MoSi_2$ Synthesis

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Abstract: This paper presents some conditions of molybdenum disilicide synthesis. The references are made regarding the main factors that rule the synthesis process of this intermetallic compound with the refractory properties: the nature and fineness conditions of raw materials (reactant elements), synthesis temperature and reaction medium, etc. References are also made regarding the possibility of the appearance of other compounds whose formation in the Mo–Si system is also possible. The physical and compositional properties of the synthesis product obtained in various conditions are simultaneously shown in the present paper. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Molybdenum disilicide is one of the best known metallic silicides, and because of its specific properties it can be used in the top fields of worldwide techniques.

Previous works present a lot of methods regarding molybdenum disilicide synthesis, depending on various influential parameters.[1–7]

The study presents some of our determinations regarding $MoSi_2$ synthesis.

2 TESTING CONDITIONS AND METHODS

As reactant elements, molybdenum (obtained both by metallic powder method and smelt-chip) and silicon were used. Their chemical compositions are shown in Table 1. The reactant mixture that was obtained in the specific manner and dosed approximately to molybdenum disilicide stoichiometric formula, was heated (like pressed bricks) at various temperatures in the range of 1100–1550°C, under argon protection (at 0·3 atm. pressure) in an electric furnace. The increase of treatment temperature is rapid, with a 30 min maintenance period at the maximum temperature for each sample. Roentgenographic and chemical analysis, as well as the specific density, were determined by the usual methods, on the syntheses obtained in this procedure.

The qualitative consideration of the burned bricks was made, taking into account the characteristic roentgenographical lines of the silicides of type $MoSi_2$, Mo_5Si_3 and $MoSi_{0.65}$, as well as of the reactant elements (molybdenum and silicon). The quantitative estimation of the synthesised products was made, taking into account the intensities of the main line of the present silicides: $MoSi_2$ (d=0·2020 nm), Mo_5Si_3 (d=0·1986 nm) and $MoSi_{0.65}$ (d=0·2100 nm) — expressed in number of impulses per second, corresponding to each sample.

3 INTERPRETATION OF TEST RESULTS

The roentgenographic analysis of the dependence of the $MoSi_2$ developing process on temperature (Table 2) showed that the process takes place at 1300°C, with the same conditions as mentioned above. At the same time, the presence of two distinct reactants is no longer seen. At that temperature, $MoSi_2$ of average intensity forms, together with Mo_5Si_3 and $MoSi_{0.65}$, but these two silicides have a lower intensity. Molybdenum and silicon, the reactant elements that were introduced into the system at the beginning, have not been roentgenographically identified at that temperature, in the same context as that in which the presence of some crystalline molybdenum silicides were identified. This failure to identify, by roentgenographical means, the reactants (molybdenum and silicon) could be explained by the fact that the forming reaction of the intermetallic compounds in the Mo–Si system is at its beginning, and therefore intense reorganising processes take place, where the percentage of new microcrystalline formations is very high. At 1400°C, $MoSi_2$ is produced with very high intensity, together with the intense

Table 1. Raw materials used in molybdenum disilicide synthesis

Reactant elements	Chemical composition (%)										Grinding fineness
	Mo	Si	S	Fe	C	Mg	Ca	Mn	Cu	Al	
Molybdnenum powder	96.5	traces	0.75	0.16	0.09	0.75	1.85	0.53	<0.05	—	<70 μm
Powder obtained from molybdenum chip grinding	98.3	<0.02	0.01	0.12	0.26	<0.05	nd[a]	<0.03	<0.01	<0.03	0–0.09 mm
Silicon	—	96.36	—	1.51	—	traces	traces	—	—	1.28	<70 μm

[a]nd=not detected.

Table 2. Roentgenographic identified phases and their lattice parameters

Heat treatment temperature (°C)	Impulses/second for main line				
	Mo a=0.3147 nm b=0.3147 nm c=0.3147 nm	Si a=0.54301 nm b=0.54301 nm c=0.54301 nm	$MoSi_2$ a=0.320 nm b=0.245 nm c=0.785 nm	Mo_5Si_3 a=0.965 nm b=0.965 nm c=0.492 nm	$MoSi_{0.65}$ a=0.1546 nm b=0.1546 nm c=0.1546 nm
1100	7851.2	5555.9	nd[a]	nd[a]	nd[a]
1300	nd[a]	nd[a]	1856.3	249.7	107.5
1400	nd[a]	nd[a]	6045.6	1025.1	295.1
1500	nd[a]	nd[a]	7636.1	nd[a]	nd[a]
1550	nd[a]	nd[a]	8238.0	nd[a]	nd[a]

[a]nd=not detected.

forming of Mo_5Si_3; the presence of $MoSi_{0.65}$ is rather weak.

The forming of Mo_5Si_3 and $MoSi_{0.65}$ in different proportions on those terms can be explained as the fact that these silicides are modifications of the stable Mo_3Si_2 phase at low temperatures in the presence of carbon.[8] It was determined that only $MoSi_2$ with very high intensity was produced when the reactant mixture temperature was increased to 1500°C. Other types of molybdenum silicides have not been noticed with the roentgenographic analysis. The intense forming process of $MoSi_2$ is also maintained at temperatures higher than 1500°C (i.e. 1550°C), when only $MoSi_2$ can be found.

Figure 1, which represents a graphic correlation between the temperature and number of impulses per second that corresponds to the $MoSi_2$ main line, d=0·2020 nm (reflecting the interaction rate with $MoSi_2$ forming), shows a strong rising evolution up to 1500°C. At temperatures higher than 1500°C, the $MoSi_2$ graphic also has an increasing evolution, however it is much slower than the former period. Graphic analysis regarding the correlation between temperature and number of impulses per second, that is specific for $MoSi_2$, suggests a constant but rapid increasing rate of $MoSi_2$ production in the temperature range of 1300–1500°C. At temperatures above 1500°C this increasing rate is decelerating.

The analysis of the data presented in Table 3 shows that the specific density increases with the synthesis temperature. This increase can be explained by the fact that the forming process of the intermetallic compounds from the analysed system is a continuous evolution, having as a final effect the exclusive synthesis of $MoSi_2$. Thus, the increase of the specific density from 6·16 g/cm^3,

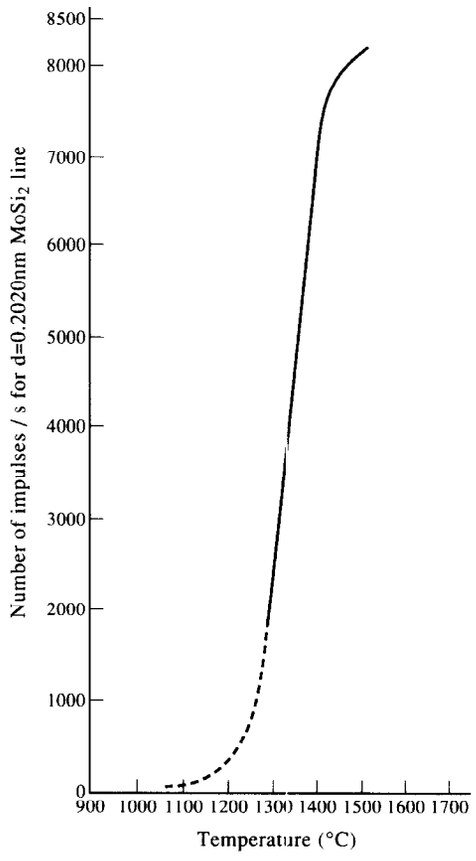

Fig. 1. Dependence of $MoSi_2$ processing kinetics on temperature.

Table 3. Physical and chemical properties of the reactant mixture at various heat treatment temperatures

Heat treatment temperature (°C)	Specific density (g/cm^3)	Chemical composition (%)										
		Mo	Si	Fe	Mg	Ca	Mn	Cu	Al	S	C	Free Si and SiO_2
1100	4.69–4.71	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]	nd[a]
1300	5.97	61.92	31.08	3.82	0.14	1.69	1.69	0.05	0.47	0.012	0.24	traces
1400	6.22	59.82	29.84	2.78	0.16	1.51	1.51	0.06	0.66	0.010	0.22	traces
1500	6.16	63.61	31.22	1.93	0.13	0.97	0.97	0.07	0.13	—	—	—
1550	6.26	64.01	33.10	1.39	0.17	1.03	1.03	0.06	0.69	0.009	0.29	traces

[a]nd=not detected.

Table 4. Roentgenographic analysis of the synthesised products having molybdenum from different sources as reactants

Characteristic line (nm)	Intensity (Impulses/s)		Identified phase
	Molybdenum powder	Molybdenum chipping	
0.3920 (45)	1956.2	2397.0	$MoSi_2$
0.2960 (95)	4796.5	2823.0	$MoSi_2$
0.2260 (70)	2633.1	1885.5	$MoSi_2$
0.2020 (100)	6045.6	3954.9	$MoSi_2$
0.1960 (40)	2471.1	1162.4	$MoSi_2$
0.1600 (30)	1440.3	1116.7	$MoSi_2$
0.1480 (20)	1478.5	913.6	$MoSi_2$
0.1410 (25)	1091.2	1294.0	$MoSi_2$

determined from the sinter obtained at 1500°C, to 6·26 g/cm^3, which corresponds to the heat treated product at 1550°C, is an eloquent example. Even the synthesis obtained at 1300°C has a specific density of 5·97 g/cm^3, a value that is within the lower limit of the range (5·90–6·24 g/cm^3) shown by Budnicov[9] or Huffadine[10] for $MoSi_2$.

The influence of raw material nature on the $MoSi_2$ forming process can be seen by analysing the data in Table 4. As compared to molybdenum powder, it can be seen that ground molybdenum resulted from chipping, with a grain size below 0·09 mm, has a lower reactivity rate. Hence, the forming of $MoSi_2$ by using this last compound represents 65·42% of the $MoSi_2$ amount formed at 1400°C when molybdenum powder was used for the same purpose. The reduced quantitative presence of $MoSi_2$ when molybdenum from chipping is used as the raw material is first of all due to its lower reactivity rate compared to that of the molybdenum powder with a grinding fineness below 70 μm.

4 CONCLUSIONS

After carrying out the above presented work, the following results can be confirmed:

- The $MoSi_2$ forming process starts at temperatures in the range of 1100–1300°C.
- At low synthesis temperatures, the $MoSi_2$ forming process takes place at the same time as that of Mo_5Si_3 and $MoSi_{0.65}$. These last two are found in smaller quantities compared to the first silicide.
- As the synthesis temperature increases, $MoSi_2$ concentration also increases, while the presence of Mo_5Si_3 and $MoSi_{0.65}$ is not detected above 1400°C.
- It is supposed that the $MoSi_2$ forming process takes place in the first stage with a high but constant value, and in the second stage the process has a decelerated rate.
- The smaller the grain size of the reactant powder, the greater the $MoSi_2$ forming rate is.

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