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BY: I. S. Brokhin, I. S. Zolotarev, et. al.

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Introduction

The disilicide of molybdenum has been known since 1907 (8), however, only in the most recent years has it acquired technical interest as a material possessing an exceptionally high blister-resistance at high temperatures (up to 1700°).

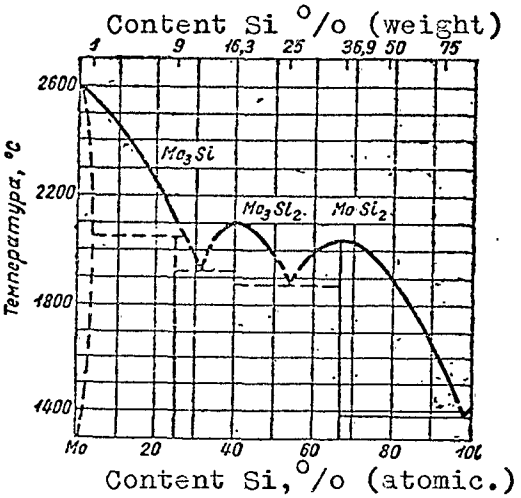

Fig. 1. Diagram of the condition of the system molybdenum-silicon (according to Keefer and Kervenka)

At the present time are widely explored the methods of protection from oxidation of metallic molybdenum and its alloys by thermodiffusion silicate, and attempts were even made to directly apply a disilicide of molybdenum as heat-resisting material and, in particular, as heating elements of electro-resistance furnaces.

The existence of three chemical compounds of molybdenum with silicon was established, answering to the formulas: Mo_3Si, Mo_3Si_2, and $MoSi_2$.

In figure 1, is presented a structural diagram of the system molybdenum -silicon according to the data of Keefer and Kervenka (2). The dissolubility of silicon into molybdenum at 1200° is 0.15% and at 1400° is 0.8 % Si.

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In table 1, are presented the known, physical properties of the silicides of molybdenum.

Table 1

The physical properties of the silicides of molybdenum

Compound	Type of crystal lattice	Density g/cm^3	Melting point ^{0}C	Micro-hardness (load 100g)
Mo_3Si	Cubic	8.7	2050	1310
Mo_5Si_3	Not estab.	7.4	2100	1170
$MoSi_2$	Tetragonal a=3.200; c=7.871	6.24	2030	1260

The disilicide of molybdenum possesses metallic conductivity (electro-resistance 21 microhm/cm.)

Blister-resistance in the system under consideration is high - in a volume range from 20 to 40% Si, during which the compound $MoSi_2$ is characterized by maximun blister-resistance.

Crystals of the oxide stage appear between 700 and 1000^0, and then dissolve into the forming quartz glass.

The high blister-resistence of the disilicide is based on the formation of a dense and lasting vitreous layer of SiO_2, the best protective properties are obtained by oxidation at a temperature above 1350-1400^0. The thickness of the protective layer is from 0.03 to 0.1 mm. Therefore, for the receipt of a stable, protective layer, it is expedient, first of all, to roast the specimens of the disilicide at 1400^0 and higher, Higher than 1700^0, the layer of SiO_2 melts, gathers into droplets and looses its protective properties.

The oxidation movement of the disilicide of molybdenum

sharply changes during relatively high temperatures (450-600°), during which it undergoes a high intercrystalline, corrosive destruction (3).

In accord with literary data,[3] the disilicide, which withstands several thousand hours of intense heat at 1200-1500° without noticeable increase or decrease in weight, after 30-50 hours of oxidation at 500°, it crumbles into powder (this phenomenon is not observed in the protective atmosphere).

From the mechanical properties of the disilicide of molybdenum, it is expedient, first, to record its frangibility at medium hardness. The extent of durability during condensation at room temperature is 70 kg/mm^2 (4). The extent of durability on bending at 1200° is 37 kg/mm^2 (5). Prolonged (100-hour) durability at 1100° is equal to 6.3 kg/mm^2 (6).

During high temperatures, the disilicide yields a plastic deformation. It is expedient to consider its resistance to spreading at temperatures above 1000° unsatisfactory.

The possibility of using disilicide of molybdenum as a heat-stabilizing material, for example, for minute gas-driven turbine engines basically depends on the research for suitable cementing materials which could increase the toughness and density of the metallo-ceramic composition on its base. However, as it appears from the literary data, numerous combinations of $MoSi_2$ with different metals, obtained by methods of powder metallurgy, did not give positive results.

The combinations of disilicide with other carbides, borides and sulfides were studies by Novotny and Keefer and others (7); the system Mo-Si-C is particularly of interest. However, such

compositions are also highly frangible.

Application of the disilicide in combination with refractory acids, for example, SiO_2, Al_2O_3 (for the purpose of increasing electro-resistance), is perspective as a material for electric heating furnaces (3).

During the combination of $MoSi_2$ with acids, it is expedient to take into account that the reaction capacity of silicon in $MoSi_2$ is almost analogous to that of pure silicon.

Obtaining a disilicide of Molybdenum[a]

As the initial materials for obtaining a disilicide of molybdenum in the given experiment, they employed:

a) powdered molybdenum, reduced by hydrogen, of the structure: 0.005% Fe, 0.002% Ni, 0.03% O_2, the rest molybdenum, with the dimensions of the bulk of granules at 3 μ.

b) crystalline silicon of the type KrO (99% Si), exposed to continous pulverization in a pebble mill lined with a hard alloy. Obtaining a thin powder of silicon with the size of the bulk of granules at 2 μ after additional chemical purification (acid treatment), included the ingredients: 0.08% Al, 0.03% Ca, 0.015% Mg, 015% Fe.

The granules obtained, taken in a stoichiometric correlation (63.14% Mo, and 36.8% Si), were carefully stirred in alcohol for 48 hours. From the mixture, prepared in such a way by a method of hot compression (of caking under pressure), at the temperature 1100-1200° with 3-5 min. exposure, they produced cylindrical forms of disilicide measuring 50X25 mm. Hot compression was produced on a special press in a graphitic press-mold, under specific pressure

150 kg/cm^2. Heating was accomplished by direct passing of current through the walls of the press-molds. They measure the temperature by a visual pyrometer and simultaneously by a radiation pyrometer combined with a potentiometer.

The reaction of the formation of $MoSi_2$ takes place quickly and completely, producing compact specimens having , on a cross-section view, a steel-grey color with metallic luster. On the surface of the specimens, after the hot-compression in the graphitic press-mold, is formed a thin carbide crust which is removed on the polishing wheel.

In table 2 is cited a chemical analysis of the material of the obtained intermediate products.

Table 2

The chemical composition of the intermediate product

No. of spec.	Content, %		
	Mo	Si	C
1	65.35	37.08	none
2	63.52	36.05	0.2
3	63.0	36.9	0.1

As seen from the given table 2, the chemical composition of the intermediate product closely corresponds to the composition of a disilicide with the formula $MoSi_2$[b].

Preparing specimens and testing the physico-mechanical properties

The intermediate products of disilicide were ground in a hard-alloy pebble mill into fine powder (the bulk of the granules at 2 μ), which was exposed to repeated hot compression (caking).

They produced caking at the temperature 1500-1550° in the above specified conditions. They prepared specimens in the form of rectangular moldings, measuring 6X6X60 mm. for subsequent mechanical and corrosive tests.

The density of the specimens was increased after continous hot compression, at the expense of a decrease of porosity; the weight by volume of the specimens equalled 6.11 ÷ 6.13 g/cm^3.

In table 3 is cited the chemical composition by analysis of the repeatedly baked disilicide specimens.

Table 3

The chemical composition of the repeatedly baked specimens

No. of Specimen	Content, %		
	Mo	Si	C
1	62.0	37.0	none
2	62.14	37.6	"
3	62.42	36.07	0.01

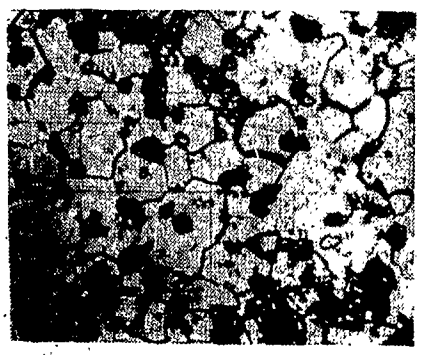

Fig. 2. Microstructure of hot-compressed $MoSi_2$

By an X-ray analysis of the original and of the repeatedly baked specimens, the presence was determined of only one phase with a tetragonal lattice and with parameters: a = 3.2A° and s = 7.86 Å, suitable for molybdenum disilicide $MoSi_2$. The presence of other phases was not detected by X-ray examination.

In figure 2 is presented the microstructure of a hot compressed specimen of $MoSi_2$, and in figure 3 - the repeatedly baked specimen, exposed to continous 100 hr. annealing at 1200°. The polyhedral, clear granules represent $MoSi_2$; the dark particles - the porosity.

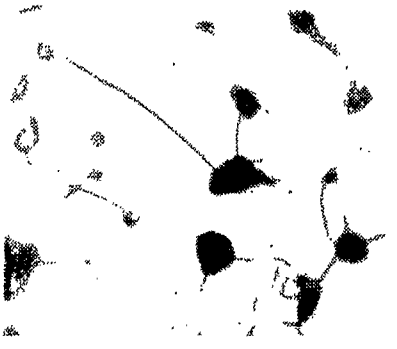

Fig. 3 Microstructure of a repeatedly baked and annealed (100 hr.) specimen of $MoSi_2$. X 600

Fig. 4 Impressions of a diamond pyramid during a test for microhardness on the molybdenum disilicide granules. X 1500

An increase of the granules of $MoSi_2$ was noted in the repeatedly baked specimens.

The microhardness of the disilicide granules, measured on the PMT-3 apparatus, during a load of 100g. forms 1200-1300 kg/mm^2. In all cases, there are ramified cracks in the carbon impressions, indicative of the brittleness of the material (fig 4). In figure 5 are presented the consequences of heat stability of the disilicide of molybdenum during heating to 1000°, measured on the apparatus VIM-1M by a diamond pyramid with a load of 1 kg (on the polished surface of the specimens). The stability decreases directly with the temperature from 1300 H_v at 20° to 350 H_v at 1000°, whereupon the direct slope indicates a relatively fast weakening of $MoSi_2$ during heating.

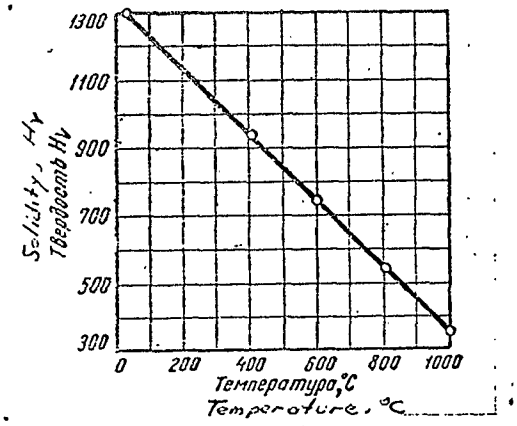

Fig. 5 Relation of stability of $MoSi_2$ to temperature

Corrosion tests of the specimens (moldings) were conducted at 1200° in air. The specimens, placed in corundum crucibles, were roasted in a muffled, globular electro-furnace with precise automatic regulation of temperature. The weight increase of the specimens consisted, in all, of 0.03 g/m^2. hour, the external appearance , for all practical purposes, did not change after the test.

The heat conductivity of the heat compressed specimens at room temperature was approximately determined on a special

calorimetric device (8); the heat-conductivity equalled 0.070-0.075 cal/cm.sec·°C.

Alloys of $MoSi_2$ with an excess of silicon

A series of alloys were prepared with an excess of silicon in the mixture: +3; +5; and +10% Si, for the study of the properties of molybdenum disilicide with an excess content of silicon against a stoichiometric composition.

They prepared specimens by the method of hot compression of the pulverulent disilicide with a suitable admixture of a calculated quantity of powdered silicon.

First of all, the carefully prepared mixture of powder was compressed at a temperature of 1400-1450° for 3-4 min. under 150 kg/cm^2 pressure. The choice of a given temperature range of compression (caking) is conditioned by the fact that during higher temperatures the extrusion of melting silicon was observed, during lower temperatures the specimens turned out porous.

The minimum temperature is applied for specimens with the maximum surplus of free silicon in the mixture (10%) and vice versa.

The composition of experimental alloys is cited in table 4.

Table 4

The chemical composition of experimental alloys

No. of The specimen	Alloys	Chemical composition, %			
		by calculation		by analysis	
		Mo	Si	Mo	Si
1	$MoSi_2$+ 3%Si	61.3	38.7	61.2	38.8
2	$MoSi_2$+ 5%Si	60.0	40.0	60.4	39.2
3	$MoSi_2$+10%Si	57.4	42.6	57.1	42.3

The caking of specimens with a 5% excess of silicon in the blend gave good results according to density and other properties, the micro-structure of the specimens with the excess of silicon up to 5% is analogous to that presented in figure 3.

The weight by volume of specimens No 1, 2, and 3 (+3; +5 and +10% Si) respectively. formed 6.0; 5.9 and 5.7 g/cm^3.

On specimens of the alloy with 5% excess silicon, the mechanical properties were defined at room and high temperatures, and even are blister-proof.

The solidity of the specimens was 87-88 R_A and 1000-1100 kg/mm^2 H_V.

The breaking point on bending was established at 20, 1000, and 1200° (on the specimens-moldings, measuring 6X6X60 mm).

The specimens were shattered by a concentrated load in the testing machine R-5 in the space between the supports 30mm according to the method accepted for testing metallo-ceramic hard alloys.

Tests for bending at high temperatures were conducted on the R-5 machine in a special apparatus with a Silit heating device and with fulcrums of baked aluminum oxide.

The mean values of the breaking point (no less than five specimens were tested at a time) compiled: at 20° $\sigma_{bend.}$ = 47 kg/mm^2, at 1000° - 44 kg/mm^2, at 1200° - 39 kg/mm^2.

During the 100 hr. corrosion tests, the weight increase of alloy No. 2 specimens insignificantly differs from the weight increase of the specimens from pure disilicide: 0.03 ± 0.04 $g/m^2 \cdot$ hour; for alloy No. 3 with 10% surplus of silicon, the weight increases to 0.2 $g/m^2 \cdot$hour.

The test for prolonged bending

Because of the extreme brittleness of the disilicide of molybdenum at room temperature and the difficulty of preparing from it breaking specimens for an approximate determination of prolonged heat-endurance, a test was used for protracted bending, which was carried out on the same prismatic specimens, 6X6X60 mm.

The test allowed for setting up the dimensions of the plastic deformation at high temperatures along the depth of camber of the specimens, under the influence of a constant load.

The specimens of pure disilicide and also those obtained from a mixture with 5 % excess silicon, were exposed to the test at 1200°.

A special setting was prepared (fig. 6) for the indicated tests. The specimens were placed on fulcrums of baked aluminum oxide of 30 mm intervals between the supports. The load was transmitted onto the specimen with the aid of a switch of a second kind of surface supports, passing through an opening in the roof of the furnace. The relation of the lever arms is 1:3.

The bending of the specimen is registered by a micronic indicator for the duration of the whole test.

Silit resistors were used for heaters. Measuring and regulation of temperature was carried out with the help of a thermocouple, the junction of which is directly adjacent to the specimen and by a second thermocouple, fastened to the upper support above the specimen. The thermocouples were connected with an electronic potentiometer for automatic regulation of the temperature by the controling potentiometer PP.

The preliminary tests showed that even with small loads and

comparatively little time for testing, the specimens of disilicide like the alloy $MoSi_2$ +5%Si, gave a noticeable bending. Proceeding from this, the tests were conducted for ten hours (with a somewhat increased load on the specimen).

The bending of the specimen was registered by the indicator every fifteen minutes.

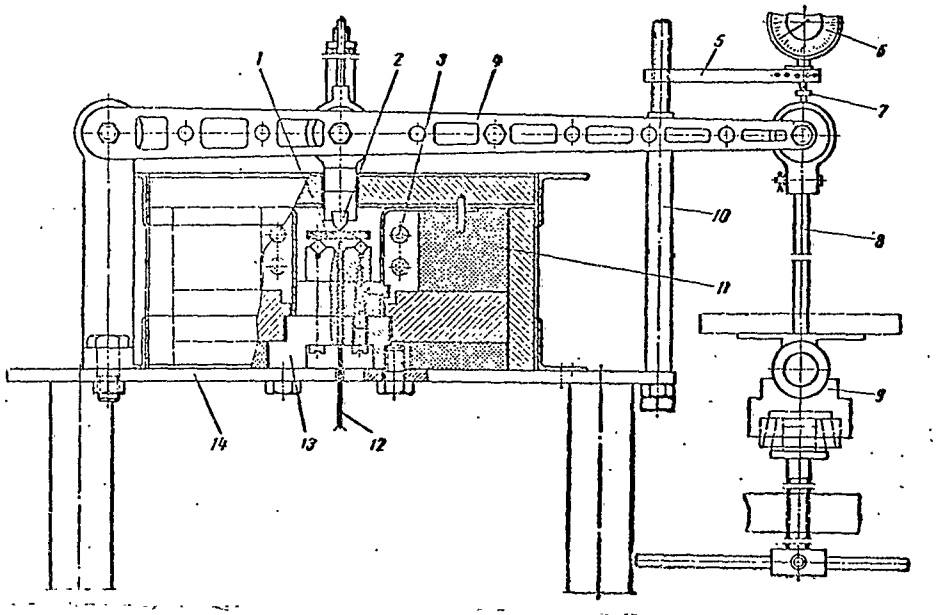

Fig. 6. Installation for the test on prolonged bending

1-specimen; 2-upper support; 3-heating Silit; 4-lever; 5-plank; 6-indicator; 7-adjusting screw; 8-suspension support; 9-shock-absorbing equipment; 10-support; 11-heat insulation; 12-platinirhodium-platinum thermoelectric couple; 13-compound lower support;14-the foundation plate

After the test, the final bending was also measured directly on the specimens. Tensions for specimens of pure disilicide varied from 3 to 20 kg/mm^2, for the specimens- from 3 to 10 kg/mm_2.

The bending is clearly seen on the specimens after the experiment at 1200° (fig. 7) during which the deformation is considerably more noticeable for the alloy and considerably less for the specimens

of pure disilicide. The results of the experiments are presented on the curves figure 8.

The curved deformation of the specimens in relation to the time shows that with small loads, the speed of deformation at the beginning of the test is considerably higher than in the later hours.

Thus, for a disilicide under tension of 3 and 10 kg/mm^2, within 5-6 hours, the speed of deformation is already significantly and smoothly decreased and becomes almost fixed; for the alloy , an analogous rate of curving is already reached at =1.5kg/mm^2.

An increase of load up to 12 kg/mm^2 for $MoSi_2$ and up to 5 kg/mm^2 for the alloy , steps up the speed of the deformation and leads to the appearance of inflextion on the curves. A further increase of load to 14-15 and 20 kg/mm^2 for pure disilicide increase the speed of deformation even more. After a bend on the curves, the speed of deformation sharply increases, right up to the breaking point of the specimens.

For specimens of the alloy $MoSi_2$+5%Si, the load increase to 10 kg/mm^2, owing to increased plasticity, does not lead to a breaking, which indicates the possibility of obtaining greater camber, that that which could be detected on the given setting.

Conclusions

As a result of the conducted experiment, the conditions of the extraction were studied of the solid disilicide of molybdenum by the method of hot compression (baking under pressure) of the mixture of fine powders of molybdenum and silicon at comparatively low temperatures (1100-1200°).

The systems and conditions are established for the preparation

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of solid specimens by repeated hot compression (caking) of the powdered disilicide.

The conformity of the specimens to the disilicides of molybdenum ($MoSi_2$) is confirmed by the X-ray and chemical analysis, and also by metallo-graphic investigation, and by a determination of the micro-solidity and blister-resistance of the specimens.

The hot solidity (to 1000°), the micro-solidity and blister-resistance (at 1200°) of the obtained specimens of the disilicide were defined.

By the investigation of the alloys $MoSi_2$ with a surplus of silicon in the mixture against a stoichiometric composition, it was shown that 5% surplus of silicon is conducive to obtaining solid specimens with optimum mechanical properties. The breaking

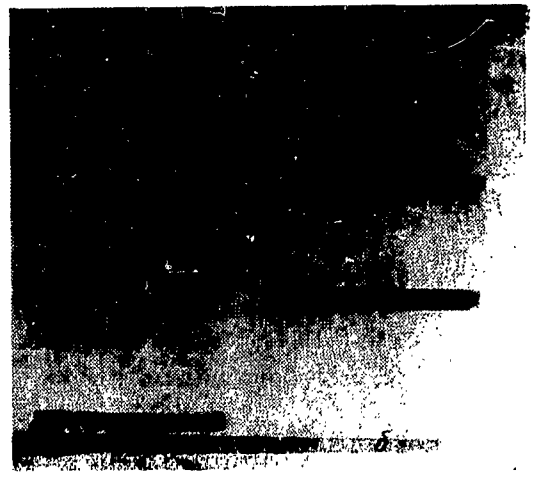

Fig.7. Specimens of $MoSi_2$ (b) and $MoSi_2$ + 5% Si (a) after the test for bending at 1200° temperature.

point for bending was defined for the indicated specimens at 20, 1000, 1100 and 1200°.

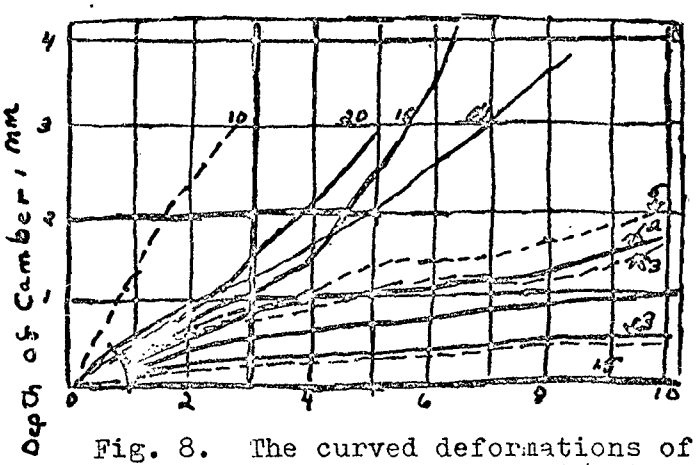

Fig. 8. The curved deformations of the specimens $MoSi_2$ and $MoSi_2$ + 5% Si under prolonged bending:

_____ $MoSi_2$; ---- $MoSi_2$ + 5% Si. (on the curves the values show σ at kg/mm^2)

By the method of testing for protracted bending at 1200° in a special setting, the plastic deformation of the specimens of pure $MoSi_2$ and $MoSi_2$ +5% Si was computed at comparatively small loads, according to the camber of the specimens.

FOOTNOTES

[a] Work conducted in 1952-1953.

[b] Powdered molybdenum disilicide was also obtained by roasting a mixture of Mo + Si at a specified temperature in a hydrogen atmosphere, in muffled, alundum electric furnaces, used in the production of hard alloys.

[c] The experiment for heat-stability was carried out by Engr. A. B. Platov.

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