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INVESTIGATION OF THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF ALLOYS OF MOLYBDENUM DISILICIDE WITH NICKEL, COBALT, VANADIUM AND NIOBIUM

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INVESTIGATION OF THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF ALLOYS OF MOLYBDENUM DISILICIDE WITH NICKEL, COBALT, VANADIUM AND NIOBIUM

-USSR-

[Following is a translation of the article "Issledovaniye stroyeniya i fiziko-mekhanicheskikh svoystv splavov disilitsida molibdena s nikelem, kobaltom, vanadiyem i niobiyem" by Ye. M. Savitskiy and V.V. Baron in Doklady Instituta Metallurgii imeni A.A. Baykova (Works of the Institute of Mettalurgy imeni A.A. Baykova), No 5, Production Metallurgy, Physical Metallurgy, and Physicochemical Methods of Research, Moscow, 1960, pages 156-161.]

Investigations of the phase diagrams of the alloys of certain refractory metals with silicon (1--4) show that the silicides formed in the systems are likewise very refractory and many of them, unlike the metals forming them, possess chemical resistance to oxidation at high temperatures. One of these compounds is molybdenum dicilicide $MoSi_2$.

It is pointed out in the literature (5, 6) that this compound, which melts at 2030°, does not oxidize at 1650° and has great strength at high temperatures even in lengthy tests: with a 100-hour stress at 98° the strength of $MoSi_2$ is 21 kg/ sq mm. Its electric resistance is close to that of such materials as carbon steel, which evidences the metallic nature of this compound (7). However, because of the high brittleness of the alloys composed of molybdenum dicilicide, especially at room temperature, its use as a heat-resisting material is difficult.

In recent years a number of papers have appeared in print on the manufacture of metal ceramics consisting of a mixture of molybdenum dicilicide with various metallic additions (Pt, Ni, Co, Ti, Zn, Hf and others) introduced for the purpose of increasing plasticity (8-11).

As a result, metal-ceramic materials have been obtained with good strength at high temperatures and with a certain plasticity, but possessing low heat resistance.

There are almost no data on the structure and properties of cast alloys consisting of a mixture of molybdenum dicilicide with other elements, which is apparently due to the difficulties of obtaining such samples (refractoriness, oxidability of the component elements of the alloys, great hardness, brittleness, etc.).

The present work is devoted to a study of the properties and structure of alloys of molybdenum dicilicide with nickel, cobalt, vanadium and niobium. For this purpose we prepared alloys of the quasibinary sections $MoSi_2$-Ni, $MoSi_2$-Co, $MoSi_2$-V, and $MoSi_2$-Nb. The alloys were prepared in three ways: melting in an arc furnace in an argon or helium atmosphere with an infusible tungsten electrode; melting in a high-frequency vacuum furnace; and production of alloys by remelting the molybdenum dicilicide prepared in the arc furnace in an open high-frequency circuit with argon blast and subsequent introduction of the above-mentioned metals into the alloys. The composition of the cast alloys by charge and chemical analysis is given in table 1.

The alloys with niobium and vanadium were prepared in the arc furnace. The alloys with nickel and cobalt were at first melted in the high-frequency vacuum furnace and poured into a copper mold, but because of the difficulty of obtaining non-porous high-grade ingots in this manner, owing to the high melting point, this method of pouring was replaced by another and the samples consisting of Mo and Si with Ni or Co were prepared in an open circuit with argon blast. The initial material was molybdenum dicilicide, previously melted in an arc furnace, to which nickel or cobalt was then added.

We used metals of the following purity: molybdenum 99.9%, silicon 99.8%, nickel 99.9%, cobalt 99.5%, vanadium 95.6%, niobium 99.3%. Samples were made of the alloys for measuring the hardness, tensile strength and plasticity and for investigating the microstructure, as well as for determining the melting point of the alloys by the drop method.

The strength and plasticity of the brittle and very hard samples were determined under uniaxial compression and, in the case of alloys amenable to cutting, their properties under stretching were also determined.

Study of the microstructure of the alloys with vanadium and niobium cast and roasted in a vacuum at 1200° for 6 hours showed that all of them are two-phased. The alloys contain-

Table 1

1 Состав по шихте, вес. %						2 Состав по хим. анализу, вес. %					
Mo	Si	Ni	Co	Nb		Mo	Si	Ni	Co	Nb	V
56,5	33,5	10	—	—	—	3 Осталь-	33,8	10,3	—	—	—
50,5	29,5	20	—	—	—	ное	29,02	19,1	—	—	—
44	26	30	—	—	—	»	23	28,75	—	—	—
38	22	40	—	—	—	»	16	36,35	—	—	—
31,5	18,5	50	—	—	—	»	15,1	51,04	—	—	—
25,5	14,5	60	—	—	—	»	12,7	57,66	—	—	—
25	14	61	—	—	—	»	8,8	61,28	—	—	—
22	13	65	—	—	—	»	13,21	64,99	—	—	—
20,9	12,1	67	—	—	—	»	11,94	66,56	—	—	—
20,2	11,8	68	—	—	—	»	12,1	66,1	—	—	—
19	11	70	—	—	—	»	10,8	64,49	—	—	—
13	7	80	—	—	—	»	7,38	80,12	—	—	—
6,5	3,5	90	—	—	—	»	3,37	90,63	—	—	—
56,5	33,5	10	—	—	—	»	31,74	—	10,02	—	—
50,5	29,5	20	—	—	—	»	27,7	—	20,4	—	—
44	26	—	30	—	—	»	24,6	—	39,9	—	—
38	22	—	40	—	—	»	22,4	—	40,1	—	—
31,5	18,5	—	50	—	—	»	18,59	—	49,78	—	—
25,5	14,5	—	60	—	—	»	14,98	—	59,9	—	—
19	11,0	—	70	—	—	»	10,96	—	69,4	—	—
13	7,0	—	80	—	—	»	7,06	—	80,04	—	—
6,5	3,5	—	90	—	—	»	3,56	—	89,59	—	—
56,5	33,5	—	—	10	—	»	32,0	—	—	10,46	—
50,5	29,5	—	—	20	—	»	28,5	—	—	20,38	—
44	26	—	—	30	—	»	27,5	—	—	30,8	—
38	22	—	—	40	—	»	22,5	—	—	39,34	—

Legend to Table 1: 1) Composition by charge, % by weight; 2) Composition by chemical analysis, % by weight; and 3) Residual.

[Table 1 continued on following page.]

Table 1 (Continued)

31,5	18,5	—	—	50	—	"	18,2	—	—	50,32	—
25,5	14,5	—	—	60	—	"	14,7	—	—	60,08	—
19	11	—	—	70	—	"	9,9	—	—	70,25	—
10	7,0	—	—	80	—	"	4,5	—	—	81,5	—
6,5	3,5	—	—	90	—	"	2,2	—	—	91,0	—
56,5	33,5	—	—	—	10	"	31,09	—	—	—	9,88
50,5	29,5	—	—	—	20	"	29,82	—	—	—	19,64
44,0	26	—	—	—	30	"	25,4	—	—	—	30,03
38	22	—	—	—	40	"	21,27	—	—	—	40,21
31,5	18,5	—	—	—	50	"	19,04	—	—	—	47,31
25,5	14,5	—	—	—	60	"	14,27	—	—	—	59,88
19	11,0	—	—	—	70	"	10,78	—	—	--	70,5
13	7,0	—	—	—	80	"	7,38	—	—	—	80,68
6,5	3,5	—	—	—	90	"	4,5	—	—	—	90,35

ing from 40 50 60% V have small quantities of inclusions of the second phase and apparently in these areas of concentration a metal compound is formed in this system, as indicated by the increased hardness and higher-melting point (about 1950°) as compared with the other alloys of this system. No solubility was observed in the solid state of the alloys in the intervals of concentration investigated.

The investigation of the microstructure of the alloys with nickel and cobalt case and roasted in air for 6 hours at 1200° revealed that solid solutions with a nickel or cobalt base are formed in these systems, and further increase in the $MoSi_2$ content results in the appearance of eutectic. The melting point of the latter in the $MoSi_2$-Ni system is about 1250°, and in the $MoSi_2Co$ system about 1300°. The other alloys also consist of two and three phases.

The hardness of the alloys was measured at 20 and 1000°.

This was done by the method of pressing in a pobedite [alloy of tungsten carbide particles cemented with cobalt] cone with loads of 50 and 100 kg. In heating to 1000°, the alloys of molybdenum with silicon and vanadium and of molybdenum with silicon and niobium were blasted with argon to protect them from oxidation. The alloys of the $MoSi_2$--Ni section proved very hard at room temperature, especially with a 50% Ni, 18.5% Si and 31.5% Mo content. The hardness of this alloy reached 700 kg/sq mm. With increase of the nickel content the hardness drops and with an alloy having 90% Ni it reaches 170 kg/sq mm. At 1000° the hardness values are much less; the greatest hardness in this case is acquired by alloys containing small quantities of nickel (for example 10%) and constructed mainly of $MoSi_2$. An increase in the nickel content to 50% lowers the hardness of these alloys at 1000°. When its concentration is from 50 to 90%, the hardness of the alloys changes little and averages 50 kg/sq mm (Table 2).

Table 2

Properties of Mo--Si--Ni Alloys

(1) Содержание Ni, вес. %	(2) Твердость при 90° $H_к$, кг/мм²	(3) Твердость при 1000° $H_к$, кг/мм²	(4) Прочность при сжатии $\sigma_{в_{сж}}$, кг/мм²	(5) Прочность при растяжении $\sigma_в$, кг/мм²	(6) Пластичность при сжатии ε, %	(7) Пластичность при растяжении δ, %
10	390	310	16	—	0	—
20	450	175	26	—	0	—
30	560	90	36	—	0	—
40	620	75	62	—	0	—
50	730	50	112	—	0	—
60	620	60	60	—	0	—
61	620	65	35	—	0	—
65	540	45	130	—	30	—
67	590	55	135	—	20	—
68	540	50	170	—	45	—
70	560	40	240	18	53	0
80	410	45	250	85	49	4
90	170	35	—	55	61	31
100	80	—	—	30	—	80

Legend: (1) Ni content, % by weight (2) Hardness at 90% H_K, kg/sq mm (3) Hardness at 1000° H_K, kg/sq mm

(4) Strength under compression $\sigma_{B_{comp}}$: k/g sq mm

(5) Strength under tension σ_B, kg/sq mm

(6) Plasticity under compression ε, %

(7) Plasticity under tension δ, %

Table 3

Properties of Mo--Si--Co alloys

Содержание Co, вес. % (1)	Твердость при 20° H_K, кг/мм² (2)	Твердость при 1000° H_K, кг/мм² (3)	Прочность при сжатии $\sigma_{B\ сж}$, кг/мм² (4)	Прочность при растяжении σ_B, кг/мм² (5)	Пластичность при сжатии ε, % (6)	Пластичность при растяжении δ, % (7)
10	1000	125	0,5	—	0	—
20	300	150	17	—	0	—
30	620	440	19	—	0	—
40	470	175	1,0	—	0	—
50	490	105	31	—	0	—
60	450	75	110	—	0	—
70	450	50	215	46	20	0
80	430	40	225	98	28	1,5
90	350	39	190	66	30	2,1
100	200	30	55	—	32	—

Legend: (1) Co content % by weight (2) Hardness at 20° H_K, k/g sq mm (3) Hardness at 1000° H_K, k/g sq mm

(4) Strength under compression $\sigma_{B_{comp}}$: k/g sq mm (5) Strength under tension σ_B, kg/sq mm (6) Plasticity under compression ε, %

(7) Plasticity under tension δ, %

Table 4

Properties of Mo--Si--V alloys

(1) Содержание V, вес. %	(2) Твердость при 20° H_K, кг/мм²	(3) Твердость при 1000° H_K, кг/мм²	(4) Прочность при сжатии $\sigma_{B\,сж}$, кг/мм²	(5) Пластичность при сжатии ε, %
10	940	400	0,6	0
20	830	390	3	0
30	620	495	10	0
40	610	400	4	0
50	590	535	3	0
60	1500	—	10	0
70	830	745	42	0
80	620	390	53	0
90	590	165	165	13,7
100	250	—	140	0

Legend: (1) V content, % by weight (2) Hardness at 20° H_K, k/g sq mm (3) Hardness at 1000° H_K, k/g sq mm

(4) Strength under compression $\sigma_{B compr.}$ kg/sq mm (5) Plasticity under compression ε, %

Table 5

Properties of Mo-Si--Nb alloys

(1) Содержание Nb, вес. %	(2) Твердость при 20° H_K, кг/мм²	(3) Твердость при 1000° H_K, кг/мм²	(4) Прочность при сжатии $\sigma_{в\ сж}$, кг/мм²	(5) Пластичность при сжатии ε, %
10	720	—	40	0
20	780	—	12	0
30	880	—	0	0
40	780	—	70	0
50	490	—	18	0
60	830	—	30	0
70	590	—	55	0
80	590	—	205	4
90	390	340	185	15
100	150	70	—	41

Legend: (1) Nb content, % by weight (2) Hardness at 20° H_K, k/g sq mm (3) Hardness at 1000° H_K, kg/sq mm

(4) Strength under compression $\sigma_{B\,compr.}$ kg/sq mm (5) Plasticity under compression ε, %

The strength of alloys with small nickel contents is small and they are brittle. With increase in its content, the strength grows, and alloys with 70 and 80% Ni are strongest (240-250 kg/sq mm). An alloy with 90% Ni does not shatter under compression.

The plasticity of alloys grows with increase in nickel content and in an alloy with 80% Ni it is 49% under compression, and in an alloy with 90% Ni it is 62%.

In stretching tests the alloy with 80% Ni (σ_B = 85 kg/sq mm) proved the strongest and the alloy with 90% Ni the most plastic (δ = 31%).

A similar change in hardness at 20 and 1000° and of strength under compression and tension was also observed in alloys of the $MoSi_2$-Co section with an increase in the cobalt content (Table 3), with the sole difference that the greatest hardness in this case was observed in the alloy with 30% Co. Alloys with 70-80% Co possess the greatest strength under compression (200-220 kg/sq mm). Under tension the strength of the alloy with 80% Co is greatest and amounts to 98 kg/sq mm. The plasticity of alloys with cobalt is less than that of alloys with nickel, and in the alloy with 90% nickel it is 30% in the compression tests and 2.1% under tension.

The alloys of the $MoSi_2$-V and $MoSi_2$-Nb section proved very hard not only at room temperature, but also at 1000°. The alloys with vanadium are especially hard when they contain 60% of this metal. The hardness of the alloy with 50% V exceeds that of the pobedite cone at 20 and 1000°. It remains high when the vanadium content is 70-80% (Table 4). The alloys possess low strength under compression up to 70% V, but it grows with further increase of its content, and in the alloy with 90% V it is 165 kg/sq mm, which is greater than the strength of vanadium itself.

The $MoSi_2$-V samples oxidate strongly at high temperatures and especially with a high concentration of vanadium. Plasticity is detected only in the alloy containing 90% V and allowing of settling by 14% before shattering.

The hardness of the alloys of the $MoSi_2$-Nb section is somewhat lower at room temperature than in the preceding case, but at 1000° the softening of the alloys is less and their hardness is so great that we did not succeed in measuring it with the pobedite cone (Table 5). One can only note that the alloy with 90% Nb at 1000° has a hardness of 310 kg/sq mm.

The strength of alloys with a small niobium content is also very low, especially in alloys with 30% Nb. When its content is raised to more than 30%, the strength grows and reaches a maximum at 80% NB (205 kg/sq mm). The strength of niobium under compression could not be determined because of its considerable plasticity.

The plasticity of the alloys of the $MoSi_2$-Nb system is low and only when the Nb content is 90% is the alloy deformed before shattering under 15% compression. The oxidability of the alloys with niobium at 1000° is considerably less than when vanadium is added.

CONCLUSIONS

1. The alloys of the $MoSi_2$--Ni, $MoSi_2$--Co, $MoSi_2$--V and $MoSi_2$--Nb sections at room temperature possess high hardness and low strength and plasticity when they contain less than 60-70% by weight of the added elements. Hardness at 1000° is also high and reaches especially great values in alloys with niobium and vanadium (500-900 kg/sq mm). The strength of the alloys grows when the content of metals added to the $MoSi_2$ is increased above 60-70%, and remains high in all alloys except those with vanadium, being 200-250 kg/sq mm.

2. The most promising in their mechanical properties and their resistance to oxidation at high temperatures are the alloys of the Mo-Si-Ni and Mo-Si-Co systems in the concentration interval from 70 to 80% Ni and from 70 to90% Co. These alloys possess considerable strength, plasticity and comparatively high hardness at 1000°, and can be subjected to mechanical working.

The alloys with a high niobium content (80-90%) also possess considerable strength and very high hardness at 1000°, oxidizing moderately at high temperatures.

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