

Refining Metallized Molybdenum Concentrate by Means of a Low-Temperature Plasma-Forming Mixture

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Abstract—The low-temperature treatment of metallized molybdenum concentrate with plasma-forming gas is analyzed. The phase composition, chemical composition, and structure of the refined product are carefully studied.

Keywords: metallized molybdenum concentrate, plasma-forming gas, impurities, vapor tension, refining, phase composition, microstructure

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The expanded production of special steels calls for corresponding increase in the production of the necessary alloying materials, whose quality must also be improved. This is particularly true of ferroalloys, which are used in the production of most special steels and alloys [1, 2]. Molybdenum is a very common alloying element. In the production of special steels, a particular challenge is the sharp increase in the prices of ore concentrates and alloying materials [3]. Resource conservation is essential in ensuring stable growth in the production of alloying materials and special steels.

The production of alloying materials based on rare refractory elements by traditional furnace heating with aluminum offers little scope for further improvements in quality. That limits the applicability of the products or entails additional expenditure in removing impurities from the melt in the production of special steels. The highly efficient use of metallized molybdenum concentrate in the production of special steels was reported in [4, 5].

By the reduction of an element in a heterogeneous system, an alloying material with qualitatively new properties may be obtained [6, 7]: specifically, with relatively low apparent density of the briquets (3.2–3.4 g/cm³) and a developed reaction surface. The density of fused molybdenum is 10.23 g/cm³. Thanks to the rapid solution of molybdenum in the metal melt, the excellent reducing properties of the components in the new alloying elements, and other properties, the assimilation of molybdenum chromium, tungsten, and vanadium may be increased by 4–10% in comparison with roasted molybdenum concentrate, while the time for alloying of the melt may be reduced by a factor of 7–8 in comparison with standard ferromolybdenum concentrate [4–7].

However, the presence of accompanying impurities—sulfur, phosphorus, and fusible nonferrous metals—significantly limits the applicability of the new alloying metal. If present at levels of 10^{−3} or 10^{−4}%, the fusible nonferrous metals solidify to form fusible and brittle layers at the grain boundaries. That impairs the bond between the grains and gives rise to hot and cold brittleness. It also results in intergrain creep under prolonged loads in high-temperature steels and alloys. Accordingly, the applicability of a particular alloying material is determined by the permissible impurity content. To improve the quality of refractory metals, they are refined by vacuum—arc and electron—arc remelting [2]. However, these methods are not widely used on account of the complex equipment required and the high costs of refining molybdenum.

In the present work, we assess relatively inexpensive methods of improving the quality of metallized molybdenum concentrate: in particular, low-temperature treatment by plasma-forming gas. We consider the physicochemical aspects of such treatment and also the phase composition, chemical composition, and structure of the refined product.

We study metallized molybdenum concentrate (ferromolybdenum sponge corresponding to Technical Specifications TU 48-5-224-81) with the addition of iron shot to improve its thermal conductivity. In refining, we treat briquets of the metallized molybdenum concentrate with plasma-forming mixture produced in an arc generator at temperatures above 3473 K. The content of the natural gas used in producing the refining gas is as follows: 91.66% CH₄, 3.70% C₂H₂, 1.12% C₃H₈, 0.30% C₄H₁₀, 0.18% C₄H₈, 0.08% C₅H₁₂, 0.09% C₅H₁₀, 0.28% C₆H₁₄, 0.21% C₇H₁₆, 2.14% N₂, and 0.24% CO₂ (C_{1.0834}H_{4.1138} = 97.62%), plus industrial-grade oxygen.

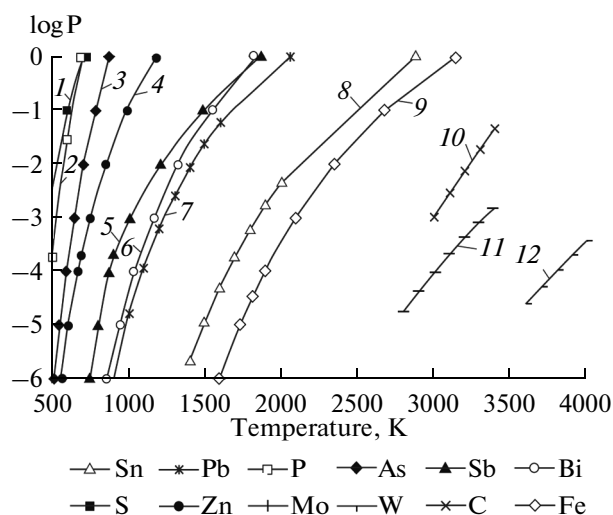
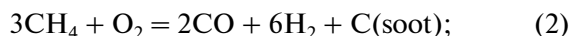
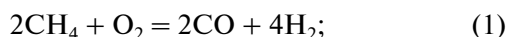


Fig. 1. Temperature dependence of the logarithm of the vapor tension P (atm) for the basic components and impurities in ferromolybdenum sponge [12].

The plasma-forming gas is the superheated product of the gas–oxygen conversion of natural gas with an optimal ratio of the oxygen and natural gas. In such conversion, the following reactions occur



The optimal ratio of the oxygen and natural gas ($\alpha = 0.49\text{--}0.51$) ensures high activity of the reducing mixture. That rules out contamination of the molybdenum with carbon from Eq. (2) or its secondary oxidation in Eq. (3). The plasma-forming gas is a mixture of ionized hydrogen and carbon-monoxide molecules. A coaxial plasmatron is used as the reaction chamber; it consists of a reactor with a receiver made of carbon–carbon composites.

The plasmatron is a cylinder (diameter 0.8 m, height 1 m) with an expansion in the lower section containing the receiver (metal capacity >50 kg). To increase the reaction surface of the plasma-forming gas and the metal melt, the interior of the reactor is corrugated. The power of the plasmatron is 1 MW.

The phase composition of the samples is investigated on a DRON-6 diffractometer in radiation from a copper cathode with a nickel filter, on the basis of the recommendations in [8]. The scanning conditions are as follows: 40 kV, 20 mA. The phases are identified by comparing the experimental interplane distances d_{hkl} with tabular values [9, 10].

The microstructure of the samples is investigated on a REM-161 scanning electron microscope with an X-ray microanalysis system, by the method in [11]. The accelerating voltage is 20 kV; the electron-probe current is 58–86 μA . The working distance to the

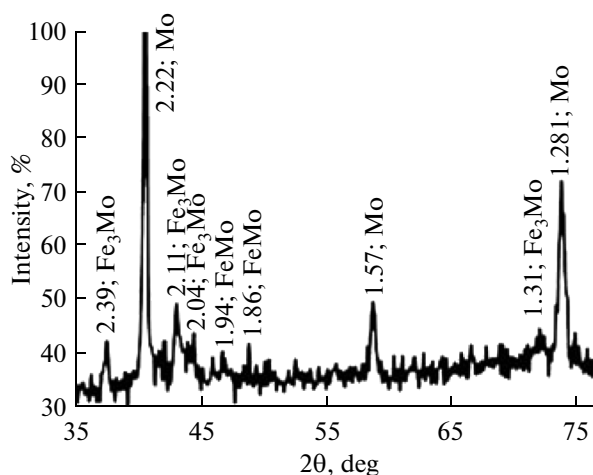


Fig. 2. Section of the diffraction pattern for a fused ferro-molybdenum sample obtained when ferromolybdenum sponge is treated by plasma-forming gas.

investigated surface is 10.2–10.5 mm. The chemical composition of the phases is determined without the use of standards, by calculating the fundamental parameters: the probe's correction factor for electron reflection and the absorption of the characteristic X-rays and fluorescence.

Analysis of the vapor tension of the harmful impurities—sulfur, phosphorus, and fusible nonferrous metals—on the basis of literature data (Fig. 1) indicates that it tends to increase with increase in temperature and is 1 atm within the range 702–2882 K [12]. This confirms that the impurity content of metallized molybdenum concentrate with added iron filings may be reduced by low-temperature treatment with plasma-forming gas. In the course of treatment, the impurities vaporize and leave the metallized molybdenum concentrate. At the same time, the vapor tension of molybdenum and iron (and the accompanying tungsten impurity) will be several orders of magnitude lower. That indicates negligible losses of the required elements with the gases on vaporization. In treatment, the carbon content may be reduced on account of partial vaporization with increase in its vapor tension and also thanks to the release of carbon in the secondary reduction of the oxide component in the metallized molybdenum concentrate at elevated temperatures, with the formation of carbon oxides.

Table 1 presents the chemical composition of the initial materials and the intermediate and final products, along with the residual impurity content in the fused ferromolybdenum obtained when ferromolybdenum sponge is treated by plasma-forming gas ($\alpha = 0.49$) at 3347 K for 310 s.

It is evident from the X-ray phase data (Fig. 2) that the high-intensity diffraction peaks for metallic molybdenum are accompanied by lower-intensity peaks for iron–molybdenum intermetallides (Fe_3Mo and FeMo).

Table 1. Chemical composition of the initial materials and intermediate and final products, %

Material	Mo	C	S	P	Si	Cu	W	O	As
KMo-2 annealed molybdenum concentrate (Technical Specifications TU 14-5-88-77)	55.8	0.07	0.12	0.037	3.22	0.88	0.15	27.2	0.036
FMo ferromolybdenum (State Standard GOST 4759-79))	58.5	0.08	0.12	0.05	1.00	0.80	6.50	0.07	0.030
KMM-2 metallized molybdenum concentrate (TU 48-5-224-81)	70.6	0.73	0.082	0.030	2.45	0.71	0.17	0.78	0.036
Fused metallized molybdenum concentrate after treatment by plasma-forming gas	84.9	0.05	0.001	0.001	0.015	0.04	0.16	0.01	0.08
Metallic molybdenum:									
vacuum-sintered powder (in heaps)	The remainder**	0.006	—	—	0.002	0.005	0.01	0.0023	Not regulated
after refining electron-beam treatment	The remainder***	0.01—0.02	—	0.001—0.02	0.004	0.0001—0.002	—	0.005	Not regulated
after vacuum-arc melting with reducing agent	The remainder****	0.002	—	—	—	0.001 Cu, Ni	—	10 ⁻³ —10 ⁻⁴	Not regulated
Material	Sn	Sb	Bi	In	Pb	Cd	Cr	Fe	Impurities
KMo-2 annealed molybdenum concentrate (Technical Specifications TU 14-5-88-77)	0.04	0.01	0.003	0.22	0.01	0.1	—	2.14	The remainder*
FMo ferromolybdenum (State Standard GOST 4759-79))	0.02	No limit	The remainder	—					
KMM-2 metallized molybdenum concentrate (TU 48-5-224-81)	0.035	0.01	0.004	0.08	0.068	0.001	0.07	16.13	The remainder*
Fused metallized molybdenum concentrate after treatment by plasma-forming gas	0.002	0.0008	0.0007	0.0016	0.0005	0.00005	0.001	14.57	—
Metallic molybdenum:									
vacuum-sintered powder (in heaps)	0.03	—							
after refining electron-beam treatment	0.001—0.002	—							
after vacuum-arc melting with reducing agent	0.005—0.03	—							

* Accompanying impurities: Al, Ca, Mg in oxide form.

** Besides Mo, we note 0.006% N, 0.0005% H₂, 0.01% Mn, and 0.05% Ni.

*** Besides Mo, we note 0.005% N.

**** Besides Mo, we note 10⁻³—10⁻⁴% N and 3 × (10⁻⁴—10⁻⁵)% H.

The phase composition is confirmed by scanning electron microscopy and X-ray microanalysis (Fig. 3, Table 2). Visually and on the basis of the chemical composition in spectra 1–14 (Table 2), the presence of three phases in the sample may be established. In Fig. 3a (magnification ×1000), the lighter particles

with rounded edges (spectra 4–6) correspond to a phase with a relatively high molybdenum content. The Mo content in those particles is 85.00–85.98 wt %; the remainder is Fe. These inclusions measure 20–70 μm. Study at larger magnification (×5000) indicates that they have noneutectic or eutectoid structure of sponge

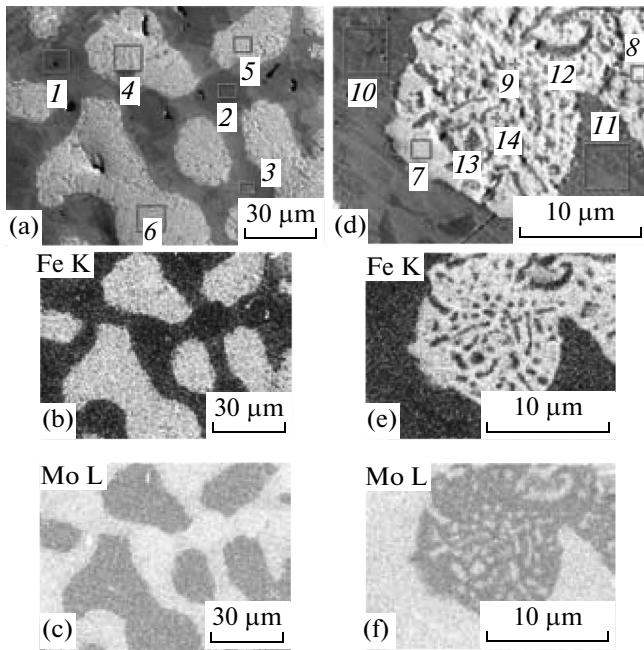


Fig. 3. (a, d) Microphotographs of samples of refined ferromolybdenum sponge at magnifications of $\times 1000$ (a) and $\times 5000$ (d); (b, c) distributions of the elements according to characteristic X-rays for Fig. 3a; (e, f) the corresponding distributions for Fig. 3d. More intense coloration corresponds to higher content of the element.

type (Fig. 3d). Against a relatively light background (with 88.54–91.53 wt % Mo; spectra 7–9, 14), we see darker layers (with 60.89–61.17 wt % Mo; spectra 12 and 13), which will presumably be deposited on solidification or cooling of the sample. Hence, the lighter

Table 2. Results of X-ray microanalysis for the sections of a sample of refined ferromolybdenum sponge in Figs. 2a and 2d, wt %

Spectrum	Fe	Mo	Total
1	47.68	52.32	100
2	50.06	49.94	100
3	45.03	54.97	100
4	14.79	85.21	100
5	14.02	85.98	100
6	15.00	85.00	100
7	11.46	88.54	100
8	11.09	88.91	100
9	8.47	91.53	100
10	42.29	57.71	100
11	40.30	59.70	100
12	39.11	60.89	100
13	38.83	61.17	100
14	10.87	89.13	100

phase may be regarded as metallic Mo with substitutional Fe atoms in its crystal lattice. The darker phase may be identified, with reasonable confidence, as Mo–Fe intermetallides.

The space between the lighter particles is filled by dark phase, including lighter regions with relatively high Mo content of 57.71–59.70 wt % (Fig. 3d, spectra 10 and 11) and darker sections with a lower Mo content of 49.94–52.32 wt % Mo (Fig. 3a, spectra 1 and 2). These sections may reasonably be assumed to be the intermetallides FeMo and Fe₃Mo; that agrees with the X-ray structural results. The overall distribution of chemical elements in the characteristic X-rays of the sample includes sections where Mo and Fe atoms are concentrated (Figs. 3b, 3c, 3e, and 3f); this confirms our previous findings.

As shown by our research, the refining of metallized molybdenum concentrate by plasma-forming mixture reduces the impurity concentration by factors of 10–20 for arsenic, 4–10 for antimony, up to 25 for tin, 10–18 for bismuth, 6–20 for zinc, 100–150 for lead, and 1.5–2.5 for phosphorus. The purification is greater than for vacuum–thermal treatment, while the impurity evaporation is an order of magnitude faster. The rate of decarburization and removal of certain impurities is 5–6 times that for electron-arc refining of molybdenum, thanks to the sharp increase in vapor pressure of the vaporizing elements, the increase in diffusion coefficient in the gas, and the faster mass transfer, resulting in higher flow rate of the plasma-forming gas above the surface of the molybdenum melt.

After refining by plasma-forming mixture, the metallized molybdenum concentrate takes on crystalline structure, which is practically the same as the structure of molybdenum after electron-arc remelting. The density of the final material is increased to 10.17 g/cm³. The molybdenum-bearing material produced may more expediently and efficiently be used in the smelting of 79NM precision alloys, ЭИ943 stainless steel, and powder high-speed steels, without any constraints.

CONCLUSIONS

Experience in the production and use of metallized molybdenum concentrate in the manufacture of high-speed steels permits reduction in the losses of alloying elements by 4–10% and increase in the rate of molybdenum solution in the metal melt by a factor of 7–8.

Refining of metallized molybdenum concentrate by low-temperature plasma-forming mixture improves its quality and expands its applicability. The concentration of impurities—fusible nonferrous metals, sulfur, phosphorus—is significantly lower, and practically 100% reduction of molybdenum is achieved.

X-ray structural phase analysis shows that fused ferromolybdenum obtained by treating ferromolybdenum sponge with low-temperature plasma-forming

mixture contains three main phases: metallic molybdenum and the intermetallides FeMo and Fe₃Mo. By scanning electron microscopy and X-ray microanalysis, we establish the configuration of the phases and inclusions, as well as the distribution of the chemical elements. The results are in good agreement with X-ray structural data.

The molybdenum alloys refined by low-temperature plasma-forming mixture permit the production of a broader range of steels and alloys. They may be effectively used instead of metallic molybdenum in the smelting of 79NM precision alloys, ЭИ943 stainless steel, and powder high-speed steels, without any constraints.

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