# TRANSLATION

ELECTROLYTIC SILICONIZING OF MOLYBDENUM FROM FUSED SALTS

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# ELECTROLYTIC SILICONIZING OF MOLYBDENUM FROM FUSED SALTS

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In recent years a great deal of attention has been devoted to the development and perfecting of methods of protecting high-melting metals and their alloys from oxidation, inasmuch as many properties of the protecting coatings depend on the method of their application. Thus silicon coatings on high-melting metals which assure protection up to the temperature of $1,700^0$, as a result of the formation on the surface of a compact film impenetrable to gas of rich $SiO_2$, generally have been obtained from the solid (1-5) or gaseous phase (6-7). The properties of such coatings have been well studied and described in the literature (8).

Considerably less often silicon coatings have been gotten by electrolysis from fused media (9, 10). In this work the structure and properties of the coatings have scarcely been investigated. However, the electrolytic

depositing of silicon and many other metals from fusions enables one to carry on the process at temperatures that are comparatively not very high, below the temperature of recrystallization of most metals. In the technological relationship for small-dimension parts the method assures good productivity.

In this connection in this work there were studied the conditions for depositing silicon on molybdenum with electrolysis of fused salts and the properties of the coating obtained. The siliconizing of molybdenum was done for the purpose of obtaining in the coating a heat-resistant di-silicide of molybdenum.

## Material and Method of Investigation.

The specimens investigated were made from rods of rolled molybdenum of the diameter of 7 x 16 mm and of the size 0.5 x 20 x 40 mm.

The surface of the specimens before the siliconizing is electrically polished in a solution of $H_2SO_4$ and $H_3PO_4$ (1:1) with a density of the current of 0.3-0.5 amp/$cm^2$, and a temperature of 90° in the course of 40 to 60 sec, after which the specimens are washed in water and dried.

As is noted in the literature, most in line with proper technology for siliconizing in fusions are the fluoride-silicate baths. Therefore the electrical depositing of silicon on molybdenum specimens was done in a fusion of the following composition: 33% $Na_2SiO_3$ and 67% NaF (9). The principle of the cell for the siliconizing of the specimens is shown in Fig. 4.

The temperature of the electrolysis was selected starting from the conditions of the depositing and the electrolyte. Thus the fusion of the given

composition at a temperature of 1,000° was viscuous and turbid, while at

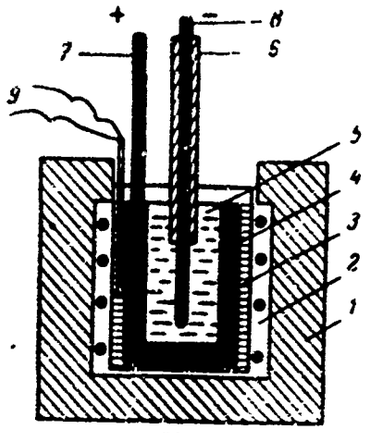


Fig. 1. Principle of the cell for siliconizing. KEY: (1) silit furnace, (2) porcelain cup, (3) filling of $SiO_2$, (4) graphite cup, (5) electrolyte, (6) protecting shell for molybdenum conductor shell being silicon carbide, (7) graphite conductor, (8) specimen, (9) thermocouple Pt-Rt (Po).

Fig. 2. Outer appearance of the specimen after siliconizing.

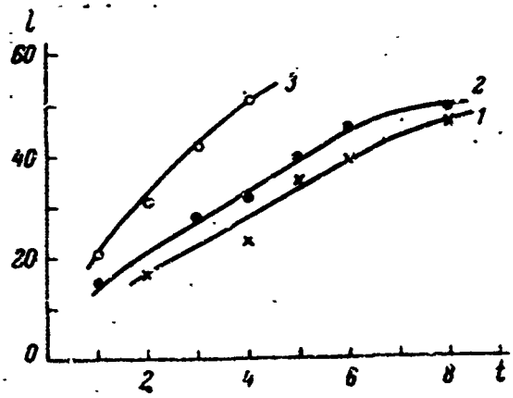


Fig. 3. Dependence of the thickness (l, μ) of the silicide layers on the duration (t, hour) of the electrolysis. $D_K$ (amp/cm$^2$): 1=0.05, 2-0.2, 3-0.3.

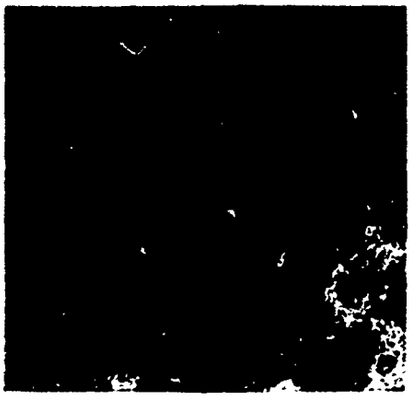

Fig. 4. Microstructure of silicon coating on molybdenum after siliconizing in the fusion. Magnification 340.

1,100 it glows and its viscosity becomes less. Such a temperature is enough for getting a uniform coating, since a higher temperature can bring about recrystallization processes in the metals to be covered and deteriorate their strength properties.

It is known also that the silicon coatings of a thickness of more than 100 $\mu$ differ in having increased brittleness, especially at low temperatures (11). We did the precipitating for the purpose of obtaining coatings with a thickness of not more than 50 $\mu$ with a density of the current of from 0.05 to 0.3 amp/cm$^2$ and time of 1, 3, 4, 6, and 8 hours. After the electrolysis the specimens were cooled in the air to room temperature and washed in hot water. The coating had a smooth surface of dark-gray color (Fig. 2).

The silicon coverings on molybdenum were investigated by metallographic, X-ray, and spectral methods.

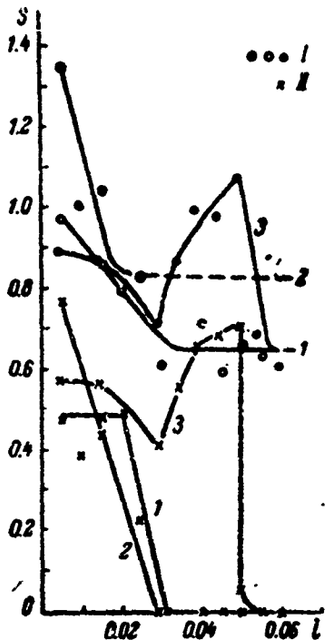


Fig. 5. The transverse (S) line of silicon and molybdenum as a function of the depth (l, mm) of the coating at $D_K$ = 0.2 amp/cm$^2$.

Time of electrolysis (hour) 1 = 1, 2 - 3; 3 = 6, I = Mo 2816.15, II = Si 2881.56.

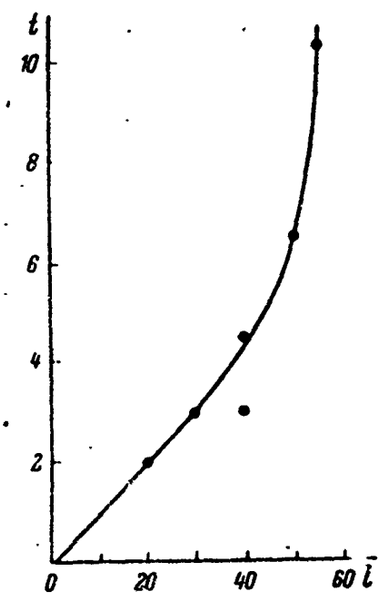


Fig. 6. Stability of electrolytic silicon coating as a function of the thickness.

For the metallographic analysis the investigated specimens were wetted with plastic AKR-7 and subjected to mechanical grinding and polishing. In accordance with the depth of the coating there was measured the microhardness on the instrument PMT=3 with a load of 20 g. The X-ray structure layer analysis was done the URS-50I stand in copper radiation. Layers of the coating were taken off by emery paper, after which the surface was rubbed with alcohol. The photographing of the spectra* of the investigated layers of the coatings was done on the quartz spectograph of medium dispersion the ISP-28. As a source of excitation there was used the generator DG-2 in the mode of operation of the high-frequency spark with a force of the current of 0.5 amp.

The specimens of wire with a diameter of 2 x 50 mm covered with silicon were tested for heat resistance. For heating the specimens there was used the electrical system of the resistance furnace of the type TGV-1M, into which instead of a molybdenum heater there was put the molybdenum specimen. The temperature of the heating of the specimen was measured by the optical pyrometer OPPIR-017.

Results of the Experiments and Their Evaluation.

The silicon coating obtained under the given conditions of electrolysis is firm, and has a thickness of from 10 to 50 μ. As is shown in Fig. 3 the

*The spectral analysis was done by G. V. Chentsova and L. P. Tomilova.

**Figure 7. Microstructure of the silicon coating after testing for heat resistance at 1600° during 7 hours.**

**Magnification 340.**

thickness of the covering formed grows with the increase in time and strength of the electrolysis current. Meanwhile the change in the thickness of the coating for low current (0.05 amp/$cm^2$) from the continuity of the electrolys takes on an almost linear dependence, whereas with densities of the current of 0.2 and 0.3 amp/$cm^2$ it approaches the parbolical.

In accordance with the data of the metallographi and X-ray analyses the covering obtained with the electrolysis for 1, 3, and 4 hours is single-phase and consists of disilicide of molybdenum $MoSi_2$ (Fig. 4). The microhardness of this layer changes in accordance with the depth from 1349 to 976 kg/$mm^2$.

The increase in the time of the electrolysis up to 6-8 hours brings about the formation of a two-phase coating consisting of disilicide of molybdenum $MoSi_2$ and silicide $Mo_5Si_3$. The latter appears in layers adjacent to the molybdenum. The microhardness of the two-phase layer changes in accordance with the depth from 1214 to 875 kg/$mm^2$.

The character of the distribution of the elements in the coating (Fig. 5), established by layer spectral analysis, also indicates that with short durations of the electrolysis the intensity of the lines of the elements monotonically goes down with depth, whereas with long durations of the electrolysis it noticeably increases with the depth. Such a peak in the change of the lines of the elements can be brought about by the formation of silicide of molybdenum at a given depth of the coating.

As is shown by the X-ray analysis in the case of long durations of the electrolysis for about 8 hours in the surface layers of the coatings sometimes along with disilicide of molybdenum there appear small quantities

of silicide of molybdenum $Mo_3Si$, which is connected apparently with some corrosion of the surface layers of the coating in the fused electrolyte.

As a result of the analysis of the coatings obtained we selected the following system of electrolytical siliconizing in fusion: temperature 1100°, density of current 0.3 amp/$cm^2$, time 4 hours, which assured the obtaining of a layer of 50 $\mu$. The siliconized specimens were tested for heat resistance by heating them with current up to the temperature of 1600°. The stability of the electrolyte coating as a function of the thickness is shown in Fig. 6.

The experiments showed that the investigated coating of the thickness of 50 $\mu$ protects molybdenum from oxidation up to 1600° during the course of 7 to 8 hours. In this situation the thickness of the coating as compared with the original increases by a factor of 1.5.

After testing for heat resistance the coating consists of silicide of molybdenum $Mo_3Si$, which has a microhardness of 1214 kg/$mm^2$ (Fig. 7). The most serious breakdown of the coating was observed at the places of the contacts cooled by water, in view of the poor heat resistance of the covering at low temperatures. The results of the determination of the heat resistance of the electrolytical coating fully agree with the literature data (11).

## Conclusions.

(1) There was developed a mode of operation of electrolytical siliconizing of molybdenum in a fusion: temperature 1100°, density of current 0.3 amp/$cm^2$, and time 4 to 6 hours with which there was obtained a compact smooth coating on the molybdenum which consisted of disilicide of molybdenum $MoSi_2$.

(2) An electrolytic coating of a thickness of 50 $\mu$ assures protection of the molybdenum against oxidation at a temperature of 1600° during 7 to 10 hours.

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