THERMAL STABILITY OF CHROMIZED MOLYBDENUM

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The improvement of the properties of molybdenum by chromizing [1-4] permits the use of this process for molybdenum parts operating at high temperature that are subject to thermal fatigue and thermal shock. The resistance of molybdenum to thermal shock and its thermal stability after chromosiliconizing by the W-2 process were investigated in [5-8].

We studied the thermal stability of MRN metallo-eramic molybdenum wire samples 1.2 and 1.5 mm in diameter and 24 and 55 mm long respectively. We also investigated wire 1.2 mm in diameter prepared from single crystals obtained by electron beam zone refining of TsM2A molybdenum rod.

The thermal stability was investigated in a specially built apparatus in which the wire was heated by passing a commercial-frequency electric current through it (Fig. 1). The temperature in the heated zone of the wire was determined by means of a Pyropto optical pyrometer, using a correction for the blackness of the oxide. The given temperature was maintained with a precision of ±10°C in the central section of the piece.

The testing conditions of the chromized molybdenum consisted of heating to 1200°C in 20 sec, holding 40 sec, cooling in air to ≤100°C in 60 sec. Such testing conditions amount to thermal shock [9]. The criterion of the thermal stability of the diffusion coating was taken as the number of cycles until the appearance of the first defect in the coating—the appearance of the characteristic white smoke (the formation of volatile molybdenum trioxide).

The samples were subjected to diffusion chromizing by different methods. The gaseous process was carried out in powdered mixtures of various compositions and also by the noncontact method in an atmosphere

Fig. 1
Diagram of the apparatus for testing thermal stability.
1) RNO-250-5 voltage regulator; 2) power transformer, 220/18 V, 2.2 kV; 3) screen; 4) sample; 5) Pyropto optical pyrometer.

Fig. 2
Effect of chromizing time on the thermal stability of molybdenum (chromized at 1100°C in powdered mixture of 70% Cr + 25% Al₂O₃ + 5% NH₄Cl). 1) Thermal stability of samples 1.2 × 24 mm; 2) thermal stability of samples 1.5 × 55 mm; 3) thickness of diffusion coating in relation to chromizing time.

TABLE 1

<table>
<thead>
<tr>
<th>Chromizing medium</th>
<th>Chromizing conditions</th>
<th>Phase composition of diffusion coating</th>
<th>Cr (%) in surface solid solution</th>
<th>Thickness of coating, μm</th>
<th>H*</th>
</tr>
</thead>
<tbody>
<tr>
<td>70% Cr + 25% Al₂O₃ + 5% NH₄Cl</td>
<td>1100°C 9 h</td>
<td>Traces Cr₂N</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid solution</td>
<td>92</td>
<td>19</td>
<td>200~675</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50% Cr + 43% Al₂O₃ + 7% NH₄Cl</td>
<td></td>
<td></td>
<td>Cr₂N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Solid solution</td>
</tr>
<tr>
<td>100% CrCl₂ (in stream of argon)</td>
<td>1100°C 6 h</td>
<td></td>
<td>-</td>
<td>12 (33% Fe)</td>
<td>8</td>
</tr>
<tr>
<td>100% Cr (vapor phase method, vacuum 10⁻⁷ mm Hg)</td>
<td>1150°C 8 h</td>
<td>Solid solution</td>
<td>49</td>
<td>17</td>
<td>335~675</td>
</tr>
</tbody>
</table>

* Microhardness at surface.

Chromizing conditions: Conditions under which the diffusion coating was formed. Phase composition of diffusion coating: The phase composition of the coating was determined by x-ray structural and local x-ray spectral analysis.* We also examined the microstructure and determined the microhardness of the diffusion coating. The test results for MRN molybdenum chromized by different methods are given in Table 1.

The nature of the diffusion coating depends not only on the chromizing method but also the composition of the powdered mixture used. Chromizing in a powdered mixture consisting of 70% Cr + 25% Al₂O₃ + 5% NH₄Cl produces a diffusion coating with approximately 100% Cr on the surface. The chromium concentration is about 50% after chromizing in vapor phase. Chromizing in a powdered mixture of 50% Cr + 43% Al₂O₃ + 7% NH₄Cl results in the formation of nitride (Cr₂N) in the form of a layer, below which is a zone of solid solution with a low chromium concentration (<36%). The chromium concentration of the coating is still lower after gas chromizing in an atmosphere of argon with CrCl₂ salt (12% Cr); the coating contains 33% Fe.

The heat resistance of chromized molybdenum depends on the nature of the diffusion zone, which can vary substantially in relation to the chromizing method used [4]. The chromizing method also has a substantial effect on the thermal stability. The thermal stability of MRN molybdenum was highest after gas chromizing in powder consisting of 70% Cr + 25% Al₂O₃ + 5% NH₄Cl, after which the chromium concentration of the diffusion coating reached 90%.

The oxide film of α-Cr₂O₃ formed in oxidation of the chromized surface has good protective properties [4]. However, the cyclic effect of the temperature and also the increase in the thickness of the film with increasing testing time weaken the adhesion of the oxide film to the metal and cause cracking at the oxide–metal interface. The magnitude of internal stresses in the surface layer resulting from the difference in the changes in volume of the metal and the oxide film (volume ratio equal to 2.07 [10]) depends on the heating rate. With slow heating and cooling the stresses in the oxide film are lower due to the relaxation process, which does not have time to be completed under conditions of rapid heating. With thermal cycling under thermal shock conditions the stresses in the oxide film increase considerably.

The higher the residual stresses in the coating resulting from the chromizing process [1] and the higher the internal stresses resulting from thermal cycling, the greater the effect on the formation of defects. Such stresses are observed even in pure metals [11] and in metalloceramic materials [3]. In this case changes in the shape of the metal can occur as the result of internal stress relaxation and the anisotropy of the thermal expansion coefficient.

The thermal stability of chromized molybdenum increases with the thickness of the diffusion coating up to a certain thickness (Fig. 2), evidently due to decreasing residual stresses with increasing thickness.

*N. V. Koryakin, V. P. Saperov, and A. N. Sokolov took part in this work.