STRENGTH CHARACTERISTICS OF MOLYBDENUM IN HIGH-TEMPERATURE GAS MEDIUM

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ABSTRACT

In this work the creep of molybdenum sample is studied in high-temperature gaseous medium under homogeneous static load. The typical behavior of molybdenum is investigated for different concentration of gas corrosive medium. As a result the asymptotic behavior of molybdenum is determined in a first approximation for the above-mentioned conditions.

Keywords: corrosive gas, creep, high-temperature, molybdenum.

1. INTRODUCTION

Development and application of various methods of construction elements' strength characteristics improvement by treatment and sputtering of their surfaces by some substances can appreciably modify the modern materials. These methods of treatment lead to the technological structural inhomogenity of the construction elements. Thus it is important to study physical, chemical and mechanical properties of such elements. Among the progressive techniques of physical-mechanical characteristics improvement we can name the focused radiation-beam furnish of surfaces. It changes the structure of surface layers and makes the sample to be inhomogeneous across its section.
The aim of this work is the study of the influence of gaseous medium (at hand ammonium, nitro-hydrogen, nitro-hydrogen-ammonium and argon) on a creep of molybdenum for high temperatures.

2. EXPERIMENT'S TECHNIQUE

The techniques of experimental investigation lays in determination of sample's durability in zone of high-temperature corrosive gaseous medium under uniaxial loading. Experiments for investigation of strength characteristics of molybdenum under the physical fields were conducted on modernized apparatus designed in Institute of Strength Problems of NASU [1]. For the experiments we take flat samples of chemically-pure molybdenum of $110\times5.7\times0.5$ mm. Highly refined gas mixture is pumped into optically transparent reactor of quartz (with the sample in it) that was in one of the focuses of ellipsoid mirror heating chamber. The sample was heated by focused radiation-beam technique to 600^{o}C. In 30 min temperature in heating zone was 1000^{o}C. The loading on sample was stepping and the creep diagram was automatically recorded.
In experiment the series of samples was divided on some equal parts, each of them was tested under the different physical fields. Duration, level and intensity of loading for every part of samples are determined experimentally. The results for every chosen factor are analyzed and compared with standard part tested in inert medium (argon) under the same loading and

temperature conditions. To minimize the error in statistical calculations the main relative error was calculated and compared with normative values.

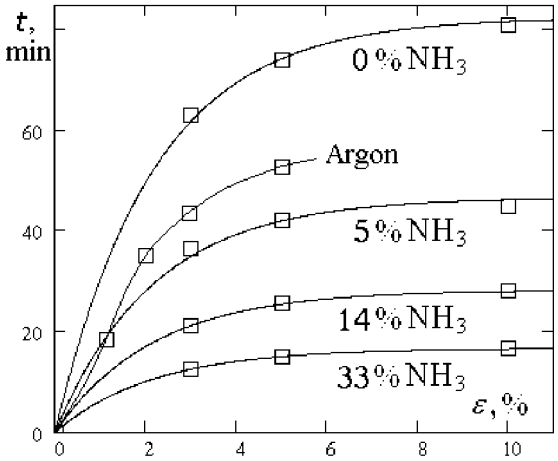

Figure1. Plots of high-temperature creep.

3. RESULTS

Results of the conducted experiments show that the most increase for strength can be achieved in nitro-hydrogen mixture and the most decrease – for gaseous ammonium (Fig.1). So, for example, the time for the value of relative deformation to take three definite levels is shown in Table 1.

Table 1. Experimental data on relative deformation vs. time.

e%	Time, min.			
	Concentration of NH_3 in $(N_2 + H_2)$, %			
	33	14	5	0
3	12.5	21	36.5	63
5	15	25.5	42	74
10	16.5	28	45	81

It is important, for our view, that the relative elongation of molybdenum samples considerably increase under the action of corrosive medium. This elongation after the failure was almost twice larger than their deformation in inert (argon) medium, and it takes place for nitro-hydrogen as well as fro mixtures with different concentrations of ammonium.
It should be noticed that the influence of nitro-hydrogen mixture on surface layers of molybdenum samples considerably increase their resistance to loads for high temperatures. In other words, the creep speed of molybdenum decrease almost twice. The ammonium mixture leads to opposite results (Fig.1). Even its negligible concentrations (5%) in nitro-hydrogen mixture crucially increase the creep speed for the samples and for concentration of 33% its influence is at the rate as fro pure ammonium. This tendency can be explained as follows. Nitration of fire-resistant alloys is made in two ways – formation of nitride surface layers and internal nitration, that chemically similar to internal oxidation. Both of the processes can affect the strength of construction materials [2].
Fine-dispersated nitride phases generated by internal nitration lead to dispersing strengthening that considerably improve strength characteristics of metals and alloys.

This can be proved thermodynamically. For reaction

$$4Mo + 2NH_3 = 2Mo_2N + 3H_2 \qquad (1)$$

Gibbs free energy (ΔG^o) for a wide range of temperatures (500÷1000°C) is the negative value (see Table 2), that means that this reaction should be intensive in every gaseous medium with ammonium and it leads, as mentioned above, to deep internal nitration with creation of large disperse nitride compounds, that bring down the strength of material. Besides of basic chemical ammonium-molybdenum reaction the dissociative decomposition of ammonium should take place. It is well known [3], that molybdenum and his nitrides are good catalysts for such a reaction. Intensive heterogene-catalitic process on samples' surfaces have to assist the material's strength decrease as a result of catalytic corrosion of sample's surface layers [4].

Table 2. Experimental data on relative deformation vs. time.

T, °C	ΔG^o, kJ/mol	
	(1) $4Mo + 2NH_3 = 2Mo_2N + 3H_2$	(2) $4Mo + N_2 = 2Mo_2N$
0	–66.9	–50.1
500	–112.5	–19.5
700	–136.3	–9.0
1000	–176.1	+4.0

In nitro-hydrogen mixture nitration of surface layers of the sample can take place only as follows

$$4Mo + N_2 = 2Mo_2N \qquad (2)$$

This reaction is thermodynamically possible for investigated temperature interval, but Gibbs free energy, as it can be seen from Table 2, is sufficiently smaller than for the first reaction. Nitrogen molecule, N_2 is sufficiently stable (opposite to ammonium, NH_3) and hardly dissociate to atoms. This yields that it is usually impossible to obtain Mo_2N by direct synthesis from its elements. It can be stated that nitrogen molecule dissociation more often can take place where excess of free energy exists, i.e., in dislocations vertexes etc. This can probably leads to creation of small dispersive phases or pre-phase formations that assist the dispersive strengthening of material. In this process the hydration of nitride formations by hydrogen molecules of mixture does not take place because this reaction, that is inversion of reaction (1), Gibbs free energy is definitely positive value for a wide range of temperatures.

Analyzing the experimental data of creep in gas corrosive medium creep curves can be approximated in coordinates (e,t) fixing deformation values in time (tab. 1). As mentioned above, experimental data cited in tab. 2 are obtained for creep of molybdenum sample for different proportions of high-temperature gas medium. For the first proportion dependence is found in the form

$$t = l\left(1 - e^{-be}\right), \qquad (3)$$

with help of the least square method. The values of founded coefficients are $l = 16,7$, $b = 0,46$. To disclose dependence $t - e$ in standard form (exponential or power) is impossible using a single function of chosen class. Defining expressions of viscoelasticity for

the considered experimental research are essentially nonlinear that makes no use in determination of creep curves in standard form (for example in the form of Prony series). Form of eq. (3) is only used to define intermediate and limiting values of creep curves.

Fixing parameter b parameter l can be found for other data sets obtained for studied concentrations. Values of approximation parameters for four data sets are cited in tab. 3.

Table 3. Parameters of creep curves

	1	2	3	4
l	16,7	28,2	46,6	82,4
b	0,46			

Corresponding creep curves with experimental points are shown on Fig. 1. According to eq. (3) parameter l is the limiting time ($\lim_{e \to \infty} t = l$) which can be regarded as sample durability. Exponential regression in the best way fits dependence l - c (Fig. 2):

$$l(c) = \exp(-0,15 + 4,17 \times c) + 17,47. \qquad (4)$$

Maximal error of empiric curve (4) is within limits of 3 minutes. Eq. (4) can be used to determine parameter l for the given volume content of gas mixture c ant to define for this parameter creep curve in the form (3).

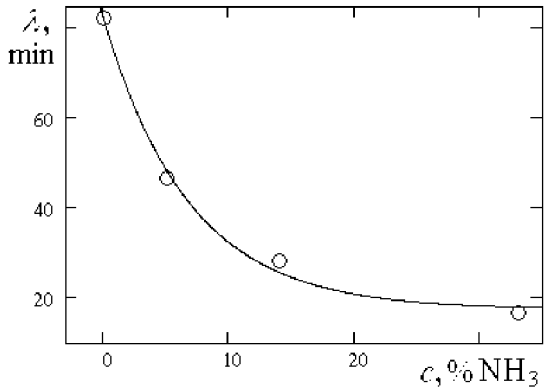

Figure2. Durability of molybdenum sample.

4. CONCLUSIONS

Influence of mentioned chemical processes leads to essential changes in physical mechanical characteristics of molybdenum. High-temperature creep rate and deformability appreciably increase in ammonia medium. Deformations being equal, high-temperature creep rate is several times smaller in nitrohydrogen gas mixture than in ammonium. Ammonium essentially enhance high-temperature molybdenum properties while nitric ammonium gas mixture essentially decreases its high-temperature creep rate.

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