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TRANSLATION

PROBLEM OF THE BEHAVIOR OF HEAT RESISTANT ALLOYS IN CONTACT WITH SODIUM IN STRESSED STATE

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PROBLEM OF THE BEHAVIOR OF HEAT RESISTANT ALLOYS IN CONTACT WITH SODIUM IN STRESSED STATE*

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To explain the action mechanism fo sodium on the properties of alloys in connection with the detected effect of strengthening, observed on a series of alloys at 1000°C and 200 hr. exposure, additional investigations.

It was established on the basis of the carried out experiment that in EI437A, EI437B and EI617 alloys, when the samples are filled with

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*In this report are given results of investigations which appear to be a continuation of work on studying the behavior of heat resistant alloys during contact with sodium, published in Trudy MAI, ed. 123, Oborongiz, 1960.

filtered sodium, any noticeable change was not observed in the duration of the strength in comparison with samples not filled with sodium. The microhardness curves retain the previously established rule for alloys, working in a technical sodium medium, and the increase in microhardness of these alloys is slight. In the surface of samples, contacting with sodium, the diffusion layer is not observed metallographically, and a layer which exists when nonpurified sodium is filled.

In this report a chemical analysis of the sodium is not made because it is unknown what admixtures existed in it, and, consequently, to exclude their effect was found to be impossible.

It is known that the formation of various compounds on the surface of contact materials is connected, mainly, with the presence of admixtures in liquid metal.

From results of investigating samples, filled with filtered metal, is evident that an increase in strength, microhardness, the formation of a dark diffusion layer cannot be connected with the action of the very sodium.

To explain the possibility of sodium diffusion and its effect on changes taking place in the surface layer, Cand. of Tech. Sc. G. N. Dubinin carried out (by a method developed by him) a gas sodying of nickel and EI437A and EI617 alloys in sodium chloride vapors. Sodium chloride, being brought in contact with the object at 1000° dissociates, formed sodium vapors. The time of gas nitration constituted 25 hours. It was established that as a result of gas nitration, surface microhardness of the nickel with sodium contact rises somewhat (Fig. 1).

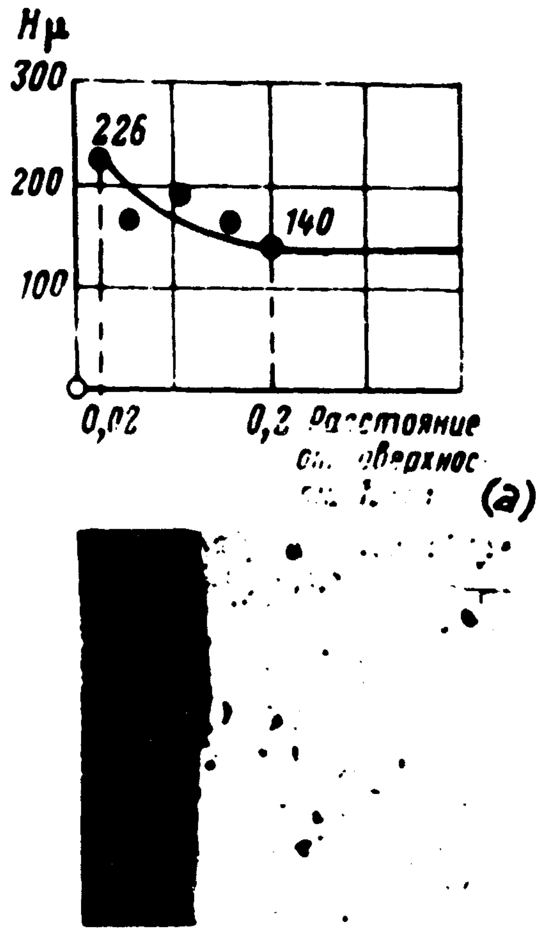

Fig. 1. Microhardness changes in surface layer of nickel after gas nitration. a - distance from surface h mm.

In alloys at a certain distance from the surface is observed a microhardness "dip" (Fig. 2). The presence of sodium in the surface layers was established with the aid of a qualitative spectral analysis.

It is known that corrosion of structural materials becomes especially intensified in the presence of an oxygen admixture in liquid metal. The presence of oxygen in sodium leads to surface oxidation of structural materials, and, what is more important — to intercrystalline destruction of stressed objects.

Cand. of Techn. Sc. N. V. Karyakinax made an x-ray analysis of the surface of samples from EI617 alloy for the purpose of explaining the period of the hard solution lattice on the surface, and also to detect its oxidation.

In order to reveal the lines of oxides, the surface of sample channel was established under an angle of $\sim 25^{\circ}$ in direction of the primary beam of rays for the obtainment of previous roentgenogram lines, close to which are situated the oxide lines.

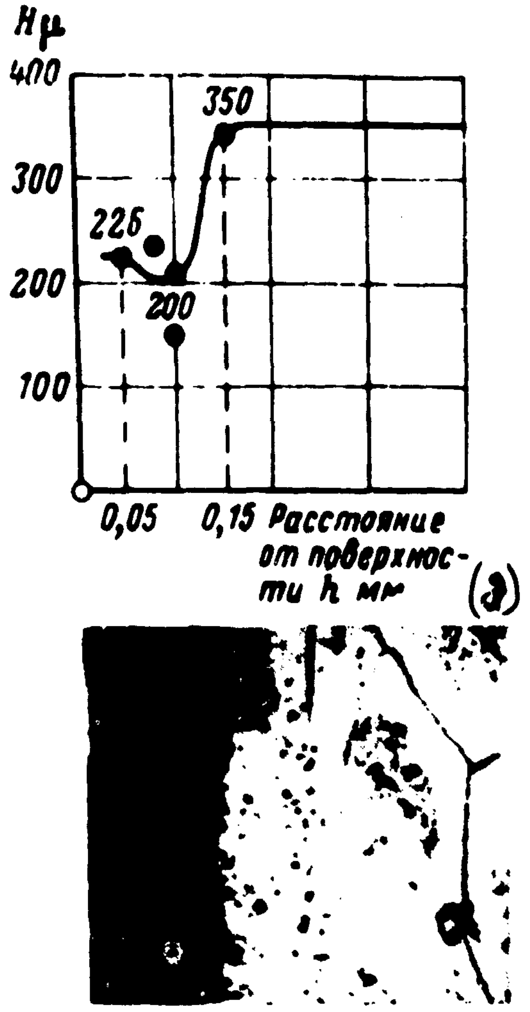

Fig. 2. Microhardness changes in surface layer of EI437A alloy after gas nitration. a - distance from surface h mm.

To measure the period of the crystalline lattice of solid solution on the surface of sample channel was applied a thin layer of powder of platinum standard. The sample was placed under an angle of 90° in direction to the beam of x-rays to obtain lines with greater Broegg angles. Calculation of the period of crystalline lattice of the solid solution was carried out by a line, obtained from plane [024]. Accuracy of calculation ± 0.002 Å. Results of analysis are given in Table 1.

It was established on the basis of the carried out analysis that in all instances, except the initial one, the surfaces have oxides. In the process of oxidation a reduction takes place in the parameter of solid solution (in connection with the possible impoverishment of same with the alloying elements).

During the analysis, because of the complexity of the obtained Roentgenogram, it was impossible to establish what effect of sodium of various purity has on the change of lattice parameters after reaction with unpurified sodium. Oxidation of contact surface may be accompanied by a change in chemical composition under the film, and consequently, by a change in stability of surface layer.

Table 1

Samples	State of sample from EI617 alloy	Characteristic of roentgenogram	a Å (of solid solution)
Basic	after thermal and mechanical treatment	no oxide lines	3.574
Without sodium	after long lasting tests at 1000°C $\sigma = 3.5$ kg/mm^2	oxide lines available	3.551
With unpurified sodium	after long lasting tests at 1000°C $\sigma = 3.5$ kg/mm^2	oxide lines available in unknown phase	——
With filtered sodium	after long lasting tests at 1000°C $\sigma = 4$ kg/mm^2	oxide lines available	3.547

Since carbon appears to be a highly probable admixture in sodium, preliminary carbonization of alloy EI617 surface was carried out and the duration of the process was determined.

It was established on the basis of carried out tests, that carbonization of internal surface does not lead to an increase in lasting duration, but the diffusion layer is analogous to the one obtained during contact with nonpurified sodium.

Since phenomena, observed in alloys during reaction with sodium, cannot be fully explained by the presence of carbon in role of admixture in sodium, to explain the nature of the obtained layer, chief scientific worker N. F. Lashko carried out and x-ray structural layer-by-layer analysis of residue, electrolytically brought up from the surface layer of alloy EI617 after 25 hour contact with sodium.

Separation of residues was carried out in electrolyte No. 81 in which the solid solution is dissolved and phase Ni_3 (Al, Ti) is reinforced.

As the result of layer-by-layer x-ray structural analysis it was established in the first surface layer at a depth of 0.04 mm, the presence of $Me_{23}C_6$ carbide type with a parameter $a = 10.684$ Å and high dispersion titanium nitride with parameter $a = 4.25$ Å. The relative amount of titanium nitride in the first layer is considerably greater than in the second and third.

In the second layer at a depth of 0.07 mm was also detected carbide type $Me_{23}C_6$ and less dispersed titanium nitride. In the third layer, at a depth of 0.11 mm are present these phases, carbide has a parameter $a = 10.698$ A. titanium nitride by dispersity - is approximately equal to the parameter of the second layer.

Consequently, the action of the alloy with sodium, having admixtures, leads to the possibility of forming on the surface of new titanium nitride and carbide phases, hampering the development of creep processes in the region of high temperatures.

The mechanism of sodium effect on the surface of heat resistant alloys appears to be a complex one, not excluded is the possibility of diffusion of the very sodium in the basic metal and, furthermore, of greater importance are such admixtures as oxygen and carbon which react with the basic metal, changing its properties.

At the time of testing at 1000°C the alloys behave as follows:

a) in the absence of contact with sodium in the sample is formed a greater neck, as a result of which the working area at constant outer load decreases, actual stresses rise and the material acquires considerable creep at a relatively small load;

b) in the presence of contact with sodium because of formation, the neck in the surface diffusion layer is not formed, the working area changes little (all the way up to destruction), actual stresses in the creep process rise in a smaller degree and the sample endures for a long time greater outer loads.

The effect of the diffusion layer can be used when carrying out a special reinforcement of chemical-thermal treatment of the alloys, if they work in the field of high temperatures when the danger of the greater tendency of material to creep becomes real.

As is known in the field of relatively low temperatures (700-800°C) when testing alloys of EI437 type the neck during long lasting tests is not formed and destruction is preceded by a small deformation. Naturally, in these conditions, the strengthening effects should not be effective, and it is actually not observed when testing alloys EI437, EI617, and EI827 at 700-800°C.

Reaction with sodium at these temperatures cause brittle destruction of the alloys. It is also necessary to mention that the effect of strengthening in connection with the formation of a diffusion

Fig. 3. Structure of EI617 alloy after testing in a medium of nonpurified sodium at 1000°C for a period of 500 hours.

layer may disappear at very long exposures, when a sharp brittling of the alloy will lead to a reduction of separation resistance.

Tests, carried out within a period of 500 hours and over, confirm this situation. Hardening of alloys, working in contact with sodium in isothermal conditions and in the absence of circulation at temperatures of 1000°C for a period of 200 hours appears to be a special case of the behavior of the alloys, when the corrosion effect still remains calm to a larger degree and the effect of the diffusion layer predominates which hampers the development of creep processes.

At much longer lasting tests the corrosion effect will be greater.

It was established on the basis of metallographic analysis that there is a sharp surface corrosion destruction of nickel alloys, being in contact with sodium at 1000°C, being in a stressed state for a period of 500 hours. Corrosive destruction, having basically an intercrystalline nature, reaches depths of $\sim$0.03 mm for samples, filled with filtered sodium and $\sim$ 0.05 - 0.08 mm for samples filled with nonpurified sodium (Fig. 3).

Since to these tests were subjected samples with a thickness of wall $\sim$ 2 mm, the corrosive effect at the depth of 0.08 mm still does not appear in the characteristics of long lasting strength. When changing over into thin-walled constructions the corrosion injury at a depth indicated above will substantially reduce the work section of the sample and reduce its ability to work.

Conclusion

A study of the reaction mechanisms of sodium on heat resistant alloys points toward its greater role in changes of structural and surface properties of the layer of admixtures situated in alkaline metal.

In case of greater content of admixtures in sodium at long lasting contact is sharper; also, the corrosion effect of the surface.