PROMISING MATERIALS FOR HTGR HIGH TEMPERATURE HEAT EXCHANGERS

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Abstract

The service conditions for high-temperature heat-exchangers with helium coolant of HTGR's and requirements imposed on materials for their production are discussed.

The choice of nickel-base alloys with solid-solution hardening for long-term service at high temperatures is grounded.

Results of study on properties and structure of types Ni-25Cr-5W-5Mo and Ni-20Cr-20W alloy in the temperature range of 900°- 1,000°C are given. The ageing of Ni-25Cr-5W-5Mo alloy at 900°- 950°C results in decreased corrosion-mechanical properties and is caused by the change of structural metal stability. Alloy with 20% tungsten retains a high stability of both structure and properties after prolonged exposure in helium at above temperatures. The alloy has also increased resistance to delayed fracture and low-cycle fatigue at high temperatures.

The developed alloy of type Ni-20Cr-20W with microalloying is recommended for production of tubes for HTGR high-temperature heat-exchangers with helium coolant.

One of the main trends in atomic energy application equally with electric power output is production of high-potential heat for technological needs. Realization of this program is carried out by means of high-temperature gas-cooled reactors (HTGR's) with helium coolant.

Development of HTGR's offers the possibility of effective use of high-potential heat in nuclear-metallurgical systems, chemical, petro-chemical and other industries. One of the main problem of HTGR development is the choice of structural materials for tubes and tube elements of heat-exchangers.

The specific effect of helium coolant at high temperatures suggests some requirements for their choice. Prolonged service of heat-exchangers can lead to change in physical-mechanical properties of materials, primarily, strength and ductility. The high-temperature corrosion processes developed in helium atmosphere with active impurities as well as the possibility of carburization and decarburization, and some other processes of chemical interaction of impurities with the metal can be the reason of loss of strength, reduced high-temperature, heat-resistant and corrosion-fatigue properties. Since the conditions of prolonged accident-free operation of HTGR have the paramount importance, the main criteria of reliable estimation of intermediate heat-exchangers serviceability should be long-term strength and creep of metal at the operating temperatures in helium atmosphere. As a result of the specific helium effect the strength of metal can be reduced by 30-50%; in this case the creep rate increases twice or more. Thus, the correct selection and use of structural material assumes a significant importance in reliable and accident-free HTGR operation.

At present there are no valid data on the use of alloys for intermediate heat-exchangers. According to design requirements the material should ensure the service life for heat-exchangers for 10^5 hrs at 950°C; the stress level should be no less than 10MPa. Consider, that creep-rupture should not exceed 0.5 - 1%. Rather wide experience on study and evaluation of nickel-base alloys for operating temperatures of 850°- 900°C is accumulated in the U.S.S.R. and abroad.

Available high-temperature nickel-base alloys with intermetallic or carbide strengthening at temperatures above 900°C and prolonged service undergo inevitable loss of strength due to dissolution of intermetallic phase which is dispersion - strengthening for the solid solution. Besides, the presence of the secondary phases in the alloy structure can be the reason of crack initiation during prolonged service of metal; these cracks lead to brittle failure and decreased life under creep and cyclic loading.

Inconel 617 which is recommended by many firms as the main material for heat-exchanger tubes has the long-term strength no more than 0.9 MPa at 950°C for 10^5 hrs. The presence of cobalt up to 12% makes difficult its use from the ecological viewpoint. Some other deformed nickel-base alloys such as Incoloy 800H, 802, Hastelloy X and RX, developed specially for tubes of HTGR intermediate heat-exchangers have much more lower high-temperature strength. [3].

In recent years the studies carried out in our country, allowed to develop materials on the basis of nickel alloys with solid-solution hardening for the HTGR heat-exchangers. The common principles of hardening of such alloys are based on solubility of substitution elements: chromium, tungsten, molybdenum and others in the nickel bulk. According to this model the linear relationship is observed between the changes of lattice parameters while introducing substitution elements and the yield point of the alloy. It is known that chromium, tungsten and molybdenum which have the most of electron vacancies on the outer shells, reduce the stacking fault energy. This results in solid-solution hardening of the alloy due to dislocation dissociation with formation of stacking fault energy zones which impede transverse slip of the edge dislocations. Increased parameters of the crystal lattice, in its turn, make difficult high-temperature processes of deformation. At low stresses which are typical for long-term service life of tube metal in heat-exchangers, the introduction of tungsten and molybdenum into chromium - nickel alloys reduces actively diffusion processes. This promotes increased creep and oxidation resistance at high temperatures.

Thus, the maximum hardening of the nickel solid solution can be achieved by summary alloying by chromium, tungsten and molybdenum (Figure 1), as a result of their combined effect on lattice parameters, stacking fault energy and diffusive mobility of elements. This fact permits to consider Ni-Cr-W and Ni-Cr-Mo-W alloys as the most promising, high-temperature materials for HTGR equipment.

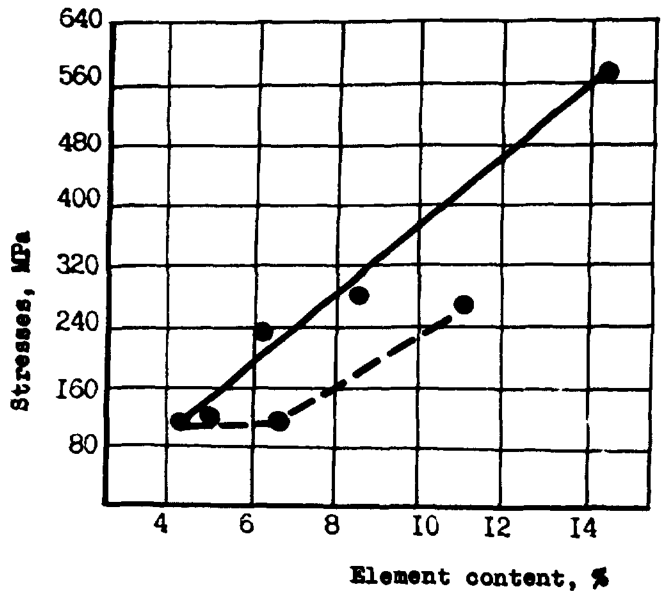

Fig.1 Effect of W and Mo on the long-term strength of type XH80T alloy at 750°C, 25 MPa.

——— 4.2% W + Mo (variable) ;
– – – 4.8% Mo + W (variable).

The relationship between metal diffusion parameters and high-temperature strength is determined by: some structural changes of alloy, grain size, state of grain boundaries, processes of strengthening and loss of strength due to alloying and phases formation. Introducing of tungsten and molybdenum into type XH80 alloy sharply increases high-temperature strength (Figure 1).

In γ- solid solution of nickel with 20-25% of chromium the short-range order is observed which is necessary to resist the fracture energy upon yielding and to increase high-strength properties. Based on physical-chemical performance of refractory elements, alloys with tungsten are much more hardened than the alloys with molybdenum. The most hardening effect on nickel-base alloys is achieved by simultaneous introducing chromium, tungsten and molybdenum.

In three-component, Ni - Cr - W, system the range of γ-solid solution existence with 20% of chromium at 1,200°C is restricted by 18% of tungsten [1]. Precipitation of the α- W phase in alloys with 20% chromium occurs when tungsten content is more than 20% ; in alloys with 15% of chromium the secondary phase appears in the presence of tungsten more than 26%.

The partial tungsten substitution by molybdenum is accompanied by the intermetallic μ-phase ($Ni_7 Mo_6$) precipitation, which promotes the loss of strength and decreased high-temperature strength of the alloy [2].

While developing alloys with solid-solution hardening we based on the following:

- the average number of electron vacancies, N_v, should be less than the critical average number, N^c, and, more or equal to 1.9 ;
- the lattice parameters of the substitution element should be no less than 3.58 Å ;
- summary chromium and tungsten content should be 37 - 41%.

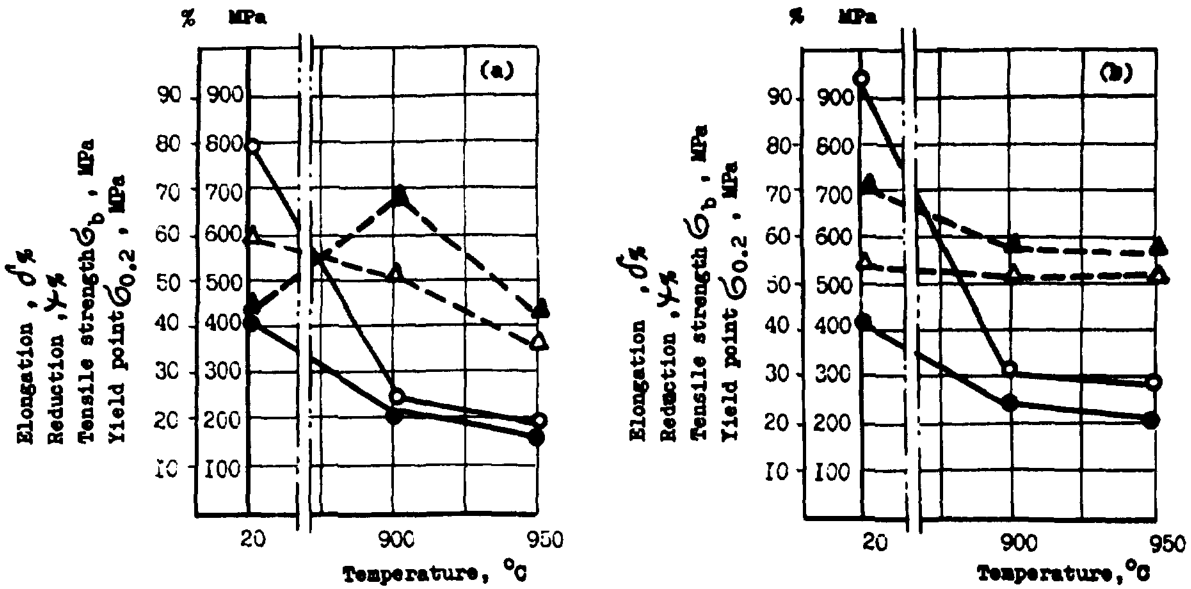

Fig.2 Mechanical properties of alloys at 20 , 900 and 950°C
(a) - Ni-25Cr-5W-5Mo alloy ; (b) - Ni-20Cr-20W alloy
o—o σ_b; Δ- -Δ δ ;
●—● $\sigma_{0.2}$ ▲- -▲ ψ .

When making up the Table of experimental nickel base alloys the following ranges on complex alloying were chosen: 17 -27% of chromium, 5 - 20% tungsten and 5 - 18% molybdenum. Chromium content was varied at constant tungsten and molybdenum content and, conversely, the content of tungsten and molybdenum, or each of them was varied at constant chromium content.

The use of the method of orthogonal regressions allowed to define the experimental compositions as well as the independent effect of each alloying element and their summary influence on service performance.

Combined study of technological, strength, fatigue and corrosion-mechanical properties of experimental compositions allowed to choose two basic alloys with the optimal alloying. They are: Ni - 20Cr - 20W and Ni -25Cr - 5W - 5Mo.

Comparative test results for the given compositions in the temperature range of 20 - 950°C showed that Ni-20Cr-20W alloy has the advantage of mechanical properties over alloy with tungsten and molybdenum (Figure 2).

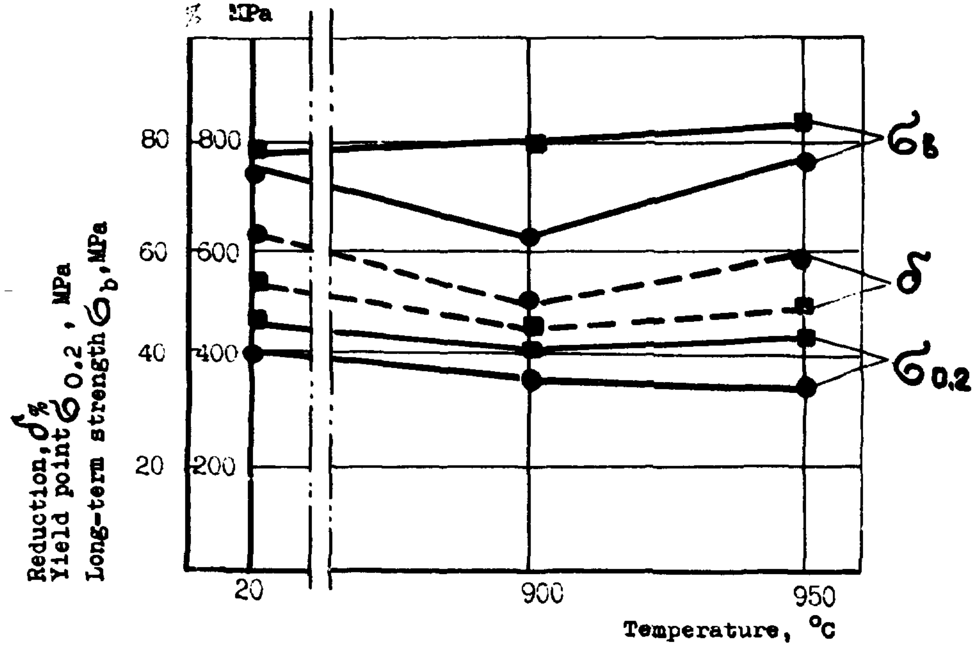

Fig.3 Mechanical properties of alloys after thermal ageing at 900, 950°C for 3,000 hrs
o - Ni-25Cr-5W-5Mo
■ - Ni-20Cr-20W

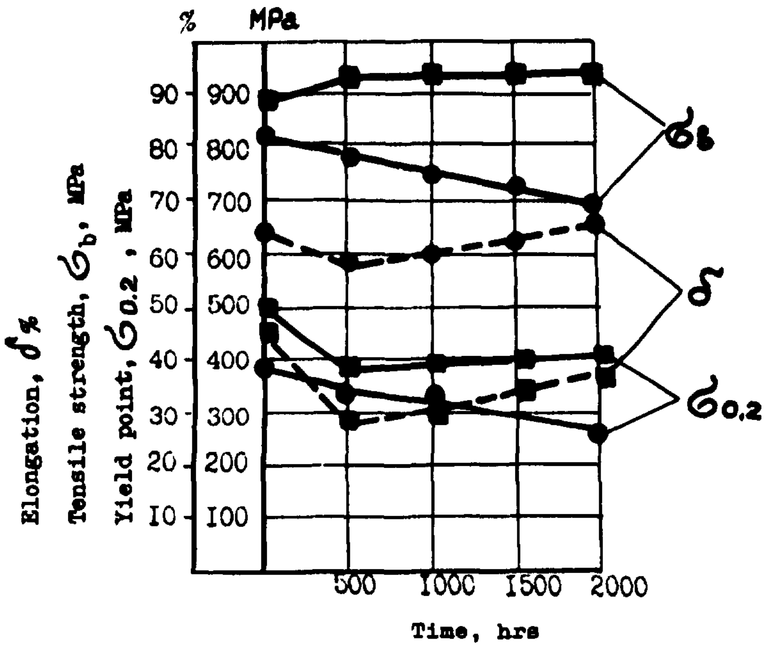

Fig. 4 Mechanical properties of alloys at 20°C, after ageing in helium at 950°C.
● - Ni-25Cr-5W-5Mo alloy;
■ - Ni-20Cr-20W alloy.

Prolonged ageing at 900-950°C markedly decreases strength and ductility characteristics of Ni-25Cr-5W-5Mo alloy (Figure 3).

The mechanical properties of the Ni-20Cr-20W alloy upon ageing for 5,000 hrs at the given temperatures change only sligtly (Figure 4). Here, some increasing tensile strength due to α - W phase precipitation is observed.

Upon ageing in helium atmosphere in the range of operating temperatures of 900 - 950°C the alloy properties are defined by the change of structural stability, morphology and the mode of the secondary phase distribution.

The ageing of Ni-25Cr-5W-5Mo alloy leads to significant decreasing strength properties (Figure 4) and accompanied by a large carbide phase precipitation in the surface layers (Figure 5). The depth of changed structural layer reaches 100 - 200 μm. The internal oxidation of grain boundaries is also observed. These structural changes are the reason of alloy failure upon ageing in helium.

(x200)

Fig.5 Microstructure of Ni-25Cr-5W-5Mo alloy after ageing in helium at 950°C

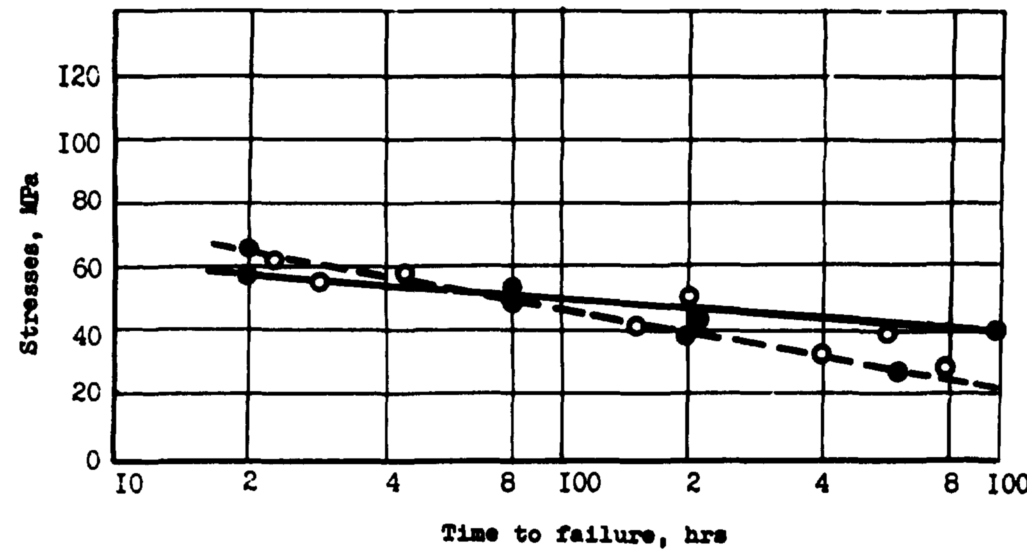

Fig.6 Long-term strength of Ni-20Cr-20W and Ni-25Cr-5W-5Mo alloys in the air and helium at 950°C.
_____ Ni-20Cr-20W ● - air
– – – Ni-25Cr-5W-5Mo o - helium

Alloy with 20% tungsten retains higher structural stability upon ageing in helium; in this connection there is stability of properties close to that of as-quenched metal. Heat- and inter-granular corrosion resistance of this alloy is 2 - 3 times higher as compared to type Ni-25Cr-5W-5Mo alloy.

The comparative tests on high-temperature strength of two types of nickel-base alloys in helium and in the air at operating temperatures showed that Type Ni-20Cr-20W alloys have higher strength properties by 15-20%; it may be explained by solid-solution hardening produced by 20% of tungsten (Figure 6).

Tensile strength of this alloy is 25 MPa in helium atmosphere at 950°C for 25,000 hrs. This alloy appears to have considerable promise from the viewpoint of necessary service performance.

The study on alloy resistance to low-cycle loading under conditions close to service ones showed that low-cycle metal fatigue of both compositions in the temperature range of 650 - 850°C is quite the same; in practice all experimental points lie on one curve.

Comparative tests of alloys at 950°C and cyclic deformation of 0.5 - 5.0% and service life up to 10^3 as well as cyclic deformation of 0.2 - 0.5% and service life up to 10^4 cycles showed the advantage of Ni-20Cr-20W alloy as related to low-cycle fatigue resistance. Note, that the metal of Ni-25Cr-5W-5Mo alloy had much more loss of strength in the deformation range of 0.2 - 0.4%.

Thus, the combined investigations of physical-mechanical properties of nickel-base alloys with solid-solution hardening by chromium, tungsten and molybdenum demonstrated that the most promising is the Type Ni-20Cr-20W alloy (from the point of service performance) as applied to intermediate heat-exchangers of HTGR's.

The nickel-base alloy developed in the U.S.S.R. which has about 20% chromium and 20% tungsten with complex microalloying features satisfactory strength- and ductility properties in the temperature range of 20 - 950°C.

T, °C	MPa		%
	$\sigma_{0.2}$	σ_b	
20	350 - 385	785 - 840	40 - 60
950	165 - 195	190 - 215	30 - 40

Heat-resistance of the alloy at 950 and 1,000°C for 3,000 hours in helium atmosphere with the oxidation potential of $\bar{O}/S$ = 0.1 - 0.4 and carburization potential of $\bar{C}/S$ up to 0.05. Test results showed that in spite of some decreasing mechanical properties for the first 500 hours of ageing, the following long exposure at the above temperatures markedly stabilize the properties. The mechanical properties of the alloy at 20°C after ageing at 950 and 1,000°C are, practically, the same (Figure 7). The tensile strength maintains the level of as-recieved metal; the yild point decreases up to 30-32 MPa and ductility up to 40 - 50%.

High-temperature strength properties of the alloy (σ_b, $\sigma_{0.2}$) aged at 950°C are slightly above as compare to those of the alloy aged at 1,000°C. Ductility properties at these temperatures are , practically, equal (Figure 8).

The comparison of the data obtained with the results of study on mechanical properties after thermal ageing in the air indicates a slight helium effect on properties change in the process of ageing. Strength- and ductility properties after 3,000 hours of ageing in helium are close to those of the metal aged in the air under similar conditions.

In the nickel-base alloy strengthened by 20% chromium and tungsten at 950 - 1,000°C the reactions of formation and dissolution of α - W phase carbides responsible for the strengthening and the loss of strength take place.

$$\gamma + M_6C \text{ ——— } \alpha - W + \gamma$$

$$\gamma + \alpha - W \text{ ——— } M_6C + \gamma + M_{23}C_6$$

These processes are controlled by diffusion of alloying elements and pass slowly for alloys with chromium and tungsten.

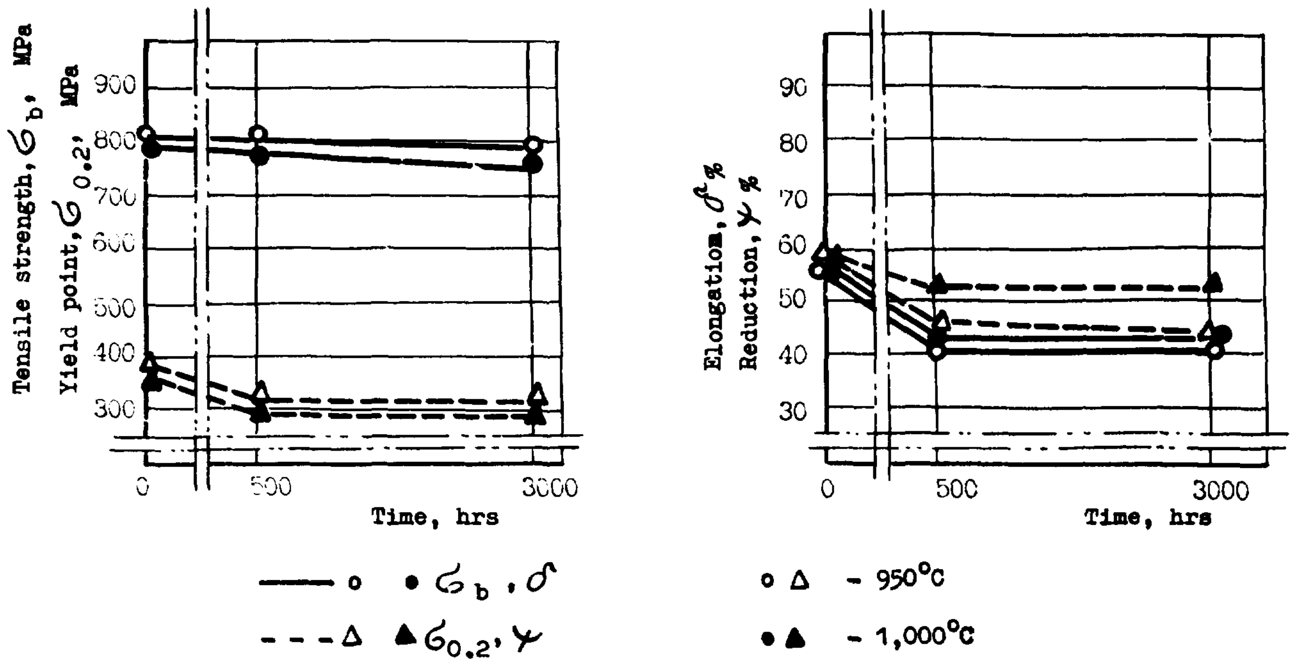

Fig. 7 Mechanical properties of Ni-20Cr-20W alloy at 20°C after ageing in helium at 950°C and 1,000°C.

Upon prolonged high-temperature exposure the balance on structural compounds characterizes stability of the structure and mechanical properties of the alloy.

Studies on the alloy phase composition under different regimes of ageing at 950 and 1,000°C showed that in the initial period of ageing (~ 500 hrs) followed by some loss of strength (Figures 7 and 8) there was precipitation of finely dispersed carbides M_6C and $M_{23}C_6$ preferentially at grain boundaries and some of α- W phase. Prolonged ageing up to 3,000 hrs at 950°C leads to redistribution of carbides in the grain volume and additional precipitation of the α- W phase. The common quantity of precipitated phases upon ageing retain equal value 2.3 - 2.6%. This ensures the high stability of structure and mechanical properties of the alloy after ageing (Figure 7).

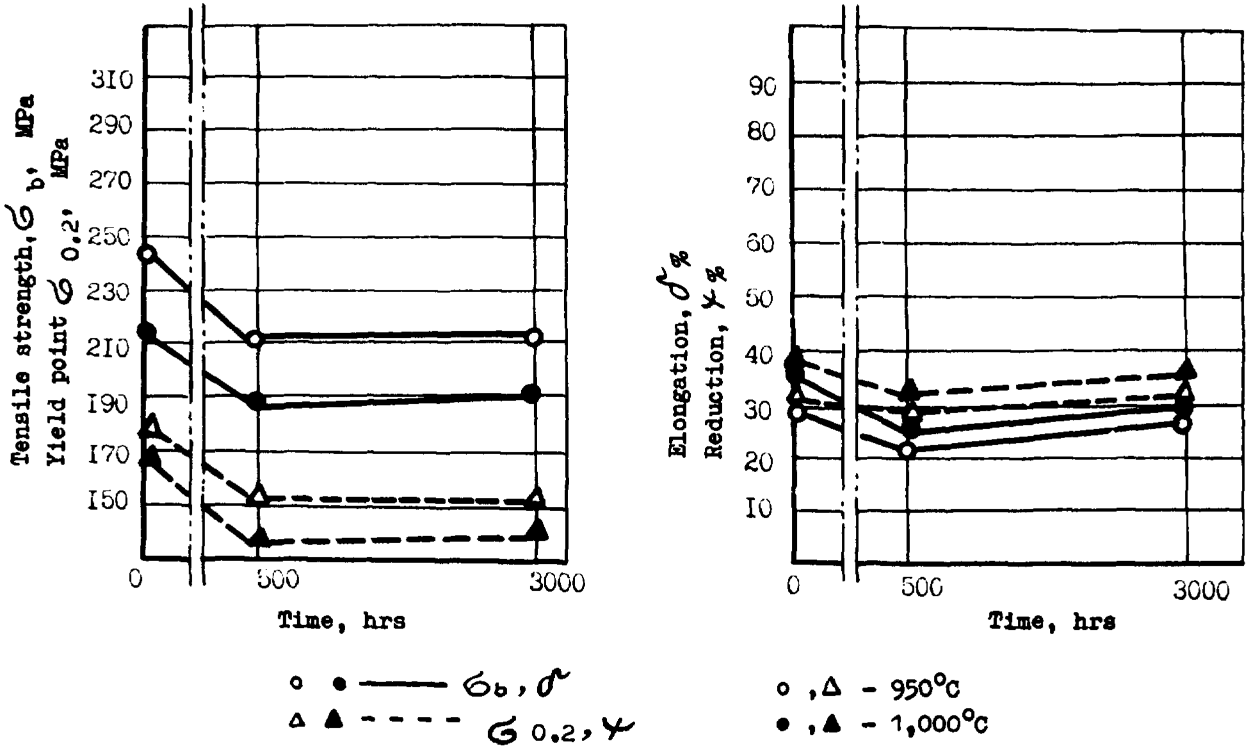

Fig 8 Mechanical properties of alloy Ni-20Cr-20W after ageing in helium at 950 and 1,000°C

Prolonged ageing at 1,000°C promotes dissolution of initially precipitated carbide $M_{23}C_6$ and α - W phase with formation of duplex M_6C carbide, the strengthening effect of which is known to be less than of α-W phase. In this connection the decreasing strength properties is observed as compared to the alloy aged at 950°C (Figure 8).

So, it can be concluded that our alloy has rather a high structural stability and satisfactory mechanical properties at long-term exposure to helium atmosphere at the coolant operating temperatures.

Long-term strength of the alloy at 950°C in the air and helium is practically equal; it is 20 MPa for 10,000 hours.

Extrapolation of results obtained for 100,000 hours shows that tensile strength at the given temperature is 12 MPa. This exceeds requirements imposed on heat-resistance of materials for tubes and tube elements of heat-exchangers in reactors with helium coolant.

The alloy is introduced by metallurgical industry as related to melting and deformation. At present the industrial production of range of tubes takes place.

Alongside the nuclear power the alloy can be used as corrosion-resistant and high-temperature material in chemical, petrochemical, metallurgical and other fields of industry.

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