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RADIATION-RESISTANT ALLOYS OF THE NICKEL-CHROMIUM SYSTEM

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Properties of some alloys of the nickel-chromium system are studied with the aim of determining the possibility of their use as structural materials for nuclear reactors. It is shown that at some compositions such alloys form a structure ensuring high process and service properties under irradiation in boiling water reactors and pressurized water reactors. Commercial production of these alloys has begun.

INTRODUCTION

Commercial high-strength nickel alloys of the Ni-Cr system have been developed in the 1950 – 1960s for blades of jet engine turbines of new generations. The compositions for the alloys were chosen so as to preserve high ductility characteristics in the process of production of parts from these materials and to ensure high-temperature strength in service at up to 900°C. This goal was reached due to the use of nickel-chromium alloys based on a solid solution of the f.c.c. phase of nickel (nichrome, inconel) and additives of molybdenum, which hardened the solid solution, and titanium and aluminum, which formed segregations of coherent phases of type $Ni_3(Ti, Al)$ (nimonic). In such alloys the content of chromium is limited to about 20 at.%[2] in order to avoid formation of "coarse" double-phase structures that lower the mechanical, physical, process, and operational properties of the alloys.

In foreign countries some of these alloys and their modifications have been studied as applied to the conditions of operation of structural materials in the nuclear power industry. Under the conditions of a reactor the materials exhibited high-temperature radiation-induced embrittlement associated with the accumulation of helium formed according to the nuclear (n, α)-reaction upon neutron capture by nickel. Under specific conditions this effect begins to manifest itself even at a temperature exceeding 450°C. For this reason high-nickel alloys have not been used as structural materials for nuclear reactor cores.

However, the Russian nuclear power industry uses nickel alloys bearing 42 – 44% Cr and 1% Mo (type KhNM) that ensure high process properties and radiation resistance.

RESULTS

Properties of Alloys of Type KhNM Used as Structural Materials for Nuclear Reactors

The position of alloys of type KhNM and high-strength nickel alloys (HSNA) in the Ni – Cr phase diagram is presented in Fig. 1.

In contrast to high-strength nickel alloys that keep the γ-phase based on the f.c.c. lattice of Ni in all temperature ranges important for the process (hot and cold deformation, welding, etc.), alloys of type KhNM undergo some phase transformations, namely, at a temperature below 1000°C the γ-phase decomposes yielding an α-phase based on the b.c.c. lattice of Cr; at a temperature below 590°C a Ni_2Cr phase with orthorhombic lattice appears.

Despite the seeming contradiction to the conventional approaches to creation of commercial deformable materials, alloys of type KhNM are well adaptable to manufacture. This is connected with the globular morphology of segregations of the chromium α-phase in the high-temperature range and with the slow occurrence of the process of formation of the ordered Ni_2Cr phase and of the chromium α-phase at low temperatures. In virtually any temperature range used for manufacturing parts alloys of type KhNM are based on a γ-phase that ensures high manufacturing properties. This is confirmed by high resistance of the alloys to formation of hot cracks in welding and by high mechanical properties of welded joints that do not require annealing [4, 5].

Due to the high content of chromium in alloys of type KhNM, their corrosion resistance is an order of magnitude higher than that of stainless steels, especially in tests for susceptibility to intercrystalline cracking (ICC) in water, including boiling one, and in aggressive media provoking ICC [6].

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[2] Hear and below in the text the content of elements in the alloys is given in atomic percent.

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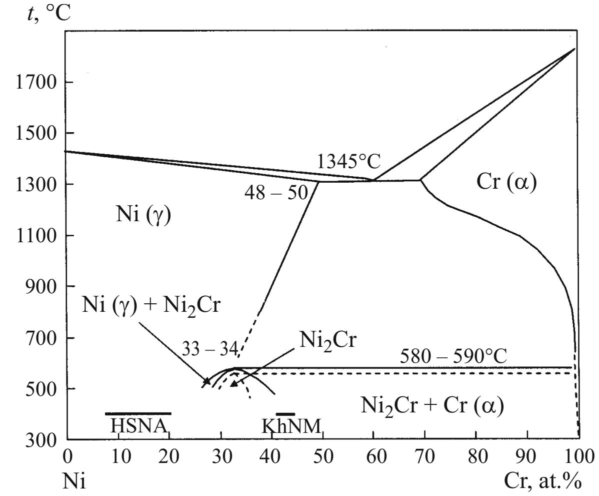

Fig. 1. Phase diagram of the Ni – Cr system and domains of alloys of types KhNM and HSNA [1 – 3].

The combination of high level of mechanical characteristics ($\sigma_{0.2} = 500$ MPa, $\delta = 50\%$), high resistance to total corrosion and ICC including the case of loading (the highest stability according the GOST 5272 Standard), and satisfactory weldability with materials of different kind makes the alloys of type KhNM promising materials for high-stress peripheral equipment of water nuclear reactors, i.e., for the pipe systems of steam generators.

It is known that the initial properties of materials change substantially under the action of reactor radiation. The main factor limiting the life of structural materials in reactor cores is the radiation-induced embrittlement.

Today, the body of pressurized water reactors is made of pearlitic steels of type 15Kh2; the equipment inside the body is produced from austenitic stainless steels of type Kh18N10.

Figure 2 presents mechanical properties of pearlitic and austenitic stainless steels after irradiation in a reactor [5 – 7].

Growth in the strength parameters and decrease in the ductility parameters as a result of irradiation is typical not only for the steels considered but also for pure metals with different lattice types (Al, Cu, Ni, Nb, etc.) and their alloys.

It is known from the science of radiation materials that this behavior is a result of changes in the dislocation structure due to separation of flows of primary radiation-induced point defects, i.e., vacancies and intrinsic interstitial atoms (IIA). In early stages of irradiation IIA in annealed materials form dislocation loops, then a dislocation network, and finally a cellular dislocation structure with dislocation density of up to 10^{12} cm^{-2}. The process is similar to the evolution of dislocation structure in the absence of radiation damage due to deformation of the material at a relatively low temperature (strain hardening).

Alloys of type KhNM take a special place among numerous materials studied under the conditions of reactor radiation [4, 5, 8, 9] (Fig. 3).

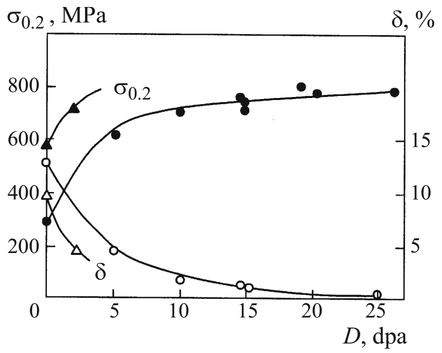

Fig. 2. Mechanical properties of structural steels after reactor irradiation (t_{ir} and $t_{\text{test}} = 250 – 370$°C) to different damaging dozes D: △, ▲) pearlitic steels; ○, ●) austenitic stainless steels.

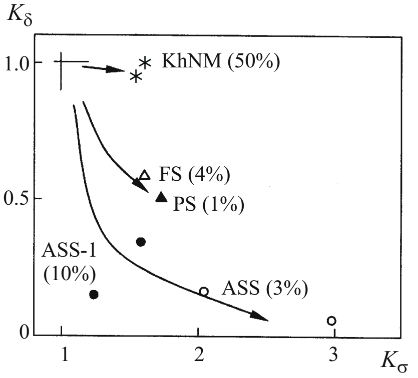

Fig. 3. Relative decrease in the ductility (K_δ) and growth in the strength (K_σ) for structural steels (ratios of initial values to values obtained after irradiation to a damaging dose of 10 – 15 dpa) at t_{ir} and $t_{\text{test}} = 250 – 400$°C (the parentheses contain the values of elongation after irradiation): FS) ferritic steels bearing 9 wt.% Cr; PS) pearlitic reactor body steels of type 15Kh2; ASS) austenitic stainless steels of type Kh18N10; ASS-1) austenitic stainless steels with elevated content of Ni (up to 25 – 45 wt.%).

For these alloys the traditional increase in the strength characteristics due to irradiation is not accompanied by substantial decrease in the ductility characteristics, which contradicts the established laws of behavior of materials under radiation damage or cold deformation.

When irradiated in a reactor to a damaging dose of 32 dpa (dislocation per atom) these alloys exhibit a combination of properties unusual for structural materials, i.e., an inconsiderable decrease in the ductility (reduction of total elongation from 50 to 40%) at simultaneous increase in the yield strength by more than a factor of 1.5 (from 500 to 800 MPa) [6].

Preservation of ductility at high radiation damage doses has made it possible to use alloys of type KhNM as a structural material for high-duty core parts, i.e., for systems for controlling the protection of nuclear reactors. The possibility of the use of such alloys for internal devices and bodies of

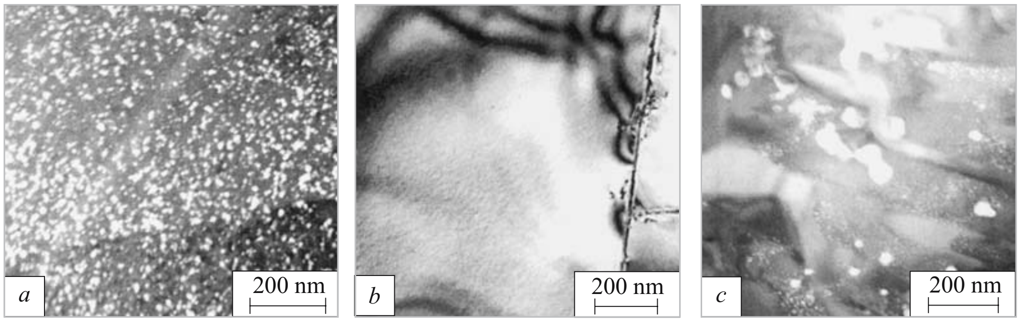

Fig. 4. Structure of alloys Ni – 35% Cr – 1% Mo (*a*), Ni – 41% Cr – 1% Mo (*b*), and Ni – 48% Cr – 1% Mo (*c*) after annealing at 450°C for 40,000 h.

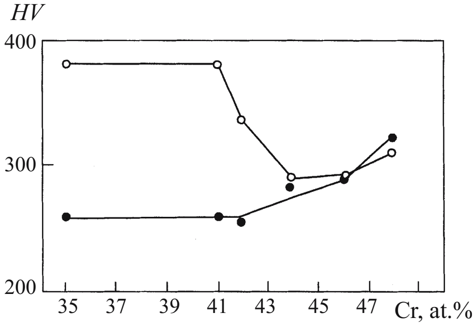

Fig. 5. Microhardness of alloys of type KhNM after γ-hardening (●) and after annealing at 450°C for 40,000 h (○).

pressurized water reactors with service life of up to 100 years is studied [4, 5].

Structure of Alloys Prior to Irradiation

The Ni – Cr phase diagram (see Fig. 1) has a domain of ordering for compositions close to the Ni_2Cr compound. The boundaries of the domain of ordering below 550°C presented in Fig. 1 have been determined by extrapolation because of the slow occurrence of the reaction. In accordance with Fig. 1, alloys of type KhNM (42 – 44% Cr + 1% Mo) in the operating temperature range can belong either to a single-phase domain (Ni_2Cr) or to a double-phase domain (Ni_2Cr + Cr) of the equilibrium phase diagram.

In order to determine the low-temperature domain of the Ni – Cr phase diagram in the presence of 1% Mo and at 35 – 48% Cr more exactly, alloys preliminarily homogenized and hardened from the γ-range were annealed at 300 – 450°C with a hold of up to 40,000 h. After the hardening the alloys were represented by a nickel-base solid solution with f.c.c. lattice.

After annealing at 350°C for 40,000 h the phase composition of all alloys bearing from 35 to 47% Cr did not change and exhibited only the initial γ-phase detected during hardening.

The occurrence of phase transformations at 450°C changed depending on the chromium content. In the alloy with 35% Cr after annealing we detected two phases, namely, the initial γ-phase and an ordered Ni_2Cr phase (Fig. 4*a*).

The alloys bearing from 41 to 44% Cr turned out to be the most resistant to the decomposition of the initial γ-phase. In the alloy Ni – 41% Cr – 1% Mo (Fig. 4*b*) an x-ray diffraction analysis showed the presence of only γ-phase. In the alloy with 44% Cr we observed features of pre-segregations of chromium α-phase.

When the chromium content was increased to 46 – 48%, the structure had three phases, i.e., the initial γ-phase, a chromium-base α-phase with b.c.c. lattice, and a phase with a lattice parameter corresponding to an ordered Ni_2Cr phase. In the alloy with maximum content of chromium (48%) we observed regions of discontinuous decomposition over grain boundaries, which consisted of alternating plates of an α-phase and of the initial γ-phase bearing coherent particles of an ordered Ni_2Cr phase (Fig. 4*c*).

On the whole, x-ray diffraction and electron microscopic studies showed that the right boundary of the “ordering dome” in the Ni – Cr phase diagram with 1% Mo at 450°C was close to the chromium content of 41%.

This conclusion correlates with the data on measured microhardness of annealed alloys given in [10] (Fig. 5).

According to the data of [10, 11], we present in Fig. 6 the values of relative changes in the microhardness, electrical resistivity, and impact toughness of the alloys.

The resistivity and the impact toughness for chromium concentration range of 35 – 48% have less manifested dependences than the microhardness and show a tendency to stabilization of the values for from 41% Cr to 46% Cr (Fig. 6). The impact toughness declines the most considerably in the alloys bearing 35 and 48% Cr, which corresponds to formation of double-phase (the initial γ-phase + Ni_2Cr) or three-phase (the initial γ-phase + Ni_2Cr + α-phase) structures.

The results of the studies performed show that alloys of type KhNM (41 – 44% Cr and 1% Mo) belong most probably to the double-phase domain of Ni_2Cr + Cr-base α-phase. However, after annealing at 450°C for 40,000 h all the alloys studied were far from the equilibrium state, whereas the alloys of type KhNM were in a virtually stable γ-phase state.

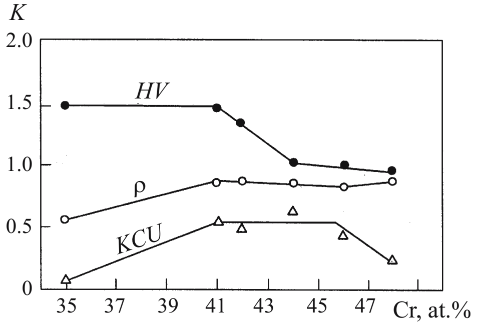

Fig. 6. Variation of the microhardness (*HV*), electrical resistivity (ρ), and impact toughness (*KCU*) [*K* is the ratio of the initial value (after γ-hardening) to the final value (after annealing at 450°C for 40,000 h)] of alloys of type KhNM with different chromium content.

The high resistance of the alloys of type KhNM to decomposition of the initial γ-phase (preservation of high ductility characteristics) has been confirmed indirectly by other experiments performed at a temperature of up to 400°C for up to 130,000 h [5, 6]. After 80,000 h of testing of tube specimens at 400°C under pressure the ductility did not change relative to the initial sate, and no structural changes were detected by the electron microscopic method.

Structure of Alloys after Irradiation

The structure of alloys irradiated in a reactor at 350°C is presented in Fig. 7 [12, 13].

In the initial state the dislocation density in the alloy was $(1 - 2) \times 10^{9}$ cm^{-2}.

In the alloy Ni – 44% Cr – 1 % Mo (type KhNM) irradiated at 350°C to 32 dpa we observed individual loops with dislocation density of about 2×10^{10} cm^{-2} (Fig. 7*a*). No gas-vacancy pores were detected under the resolution used.

In the alloy Ni – 51% Cr – 1% Mo a typical structure of secondary radiation damage formed already at a damage dose of 11 dpa at 350°C (Fig. 7*b*); the pattern was usual for nickel-bearing structural materials, i.e., weaved dislocations (with density of about 7×10^{10} cm^{-2}) and gas-vacancy pores (with mean diameter of about 1×10^{-6} cm at concentration of about 3×10^{15} cm^{-3}). The design swelling of this alloy was 0.15%.

For austenitic stainless steels [14] irradiated below 400°C the dislocation density is 10^{11} cm^{-2} up to a damaging dose of 38 dpa, which is close to the values obtained for the alloy Ni – 51% Cr – 1% Mo. The radiation behavior of this alloy (hardening accompanied by decrease in the ductility) should not differ from the behavior of typical structural steels used in nuclear reactors (see Figs. 2 and 3).

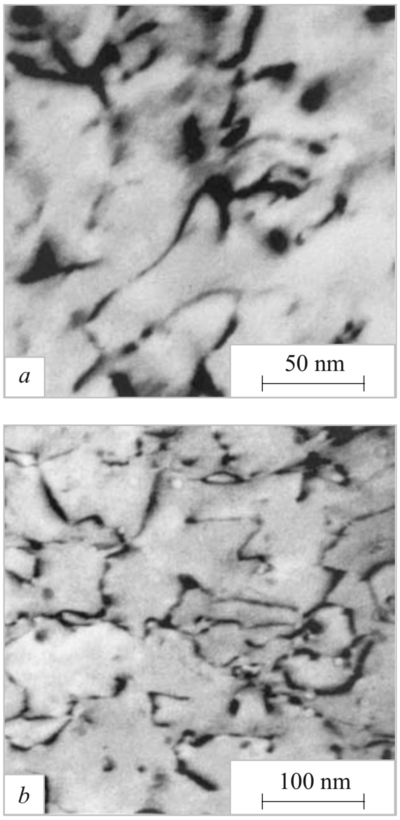

Fig. 7. Structure of alloys Ni – 44% Cr – 1% Mo (*a*) and Ni – 51% Cr – 1% Mo (*b*) after irradiation at 350°C to a damaging doze of 32 dpa and 11 dpa, respectively.

DISCUSSION OF RESULTS

Comparison of the values of dislocation density and of the increment of the yield strength of the structural materials considered shows that the radiation density of dislocations observed in alloys of type KhNM and their loop morphology cannot explain the growth in the yield strength by a factor of 1.5 – 1.6, which might be an indication of formation of a special kind of structure in the alloys due to irradiation.

The absence of gas-vacancy pores in alloys of type KhNM is a sign of low mobility of transmutation helium; for the vacancy mechanism of diffusion this mobility depends on the concentration of vacancies, while the low dislocation density is a sign of low concentration of IIA. The low quasi-stationary concentration of primary point defects (vacancies and IIA) is a feature of accelerated recombination. The accelerated recombination is another indication of formation of a special structure in the alloy.

Alloys of type KhNM lie in a narrow domain of chromium concentration. A shift in the chromium concentration within several atomic percent causes decomposition of the initial metastable γ-phase either due to ordering processes (for Cr content below 41%) or due to processes of segregation of a chromium-base b.c.c. phase and of an ordered Ni$_2$Cr phase (for Cr content above 44%). Thus, in alloys of type KhNM the formation of dislocation cascades under irradiation and the corresponding nonuniform distribution of alloying elements can result in the formation of clusters of an ordered orthorhombic Ni_2Cr phase and of a chromium-base b.c.c. phase in the γ-phase matrix; according the equilibrium phase diagram the latter phase can contain up to 35% Ni at high temperatures. With allowance for the considerable difference in the atomic densities of the f.c.c. phase, the orthorhombic lattice of Ni_2Cr, and the b.c.c. lattice of Cr, this process should lead to the appearance of local dynamic dilatations in the alloy, which can increase substantially the radius of spontaneous recombination of close-lying radiation point defects.

The hypothetical three-phase state forming due to irradiation can also explain qualitatively the effect of growth in the strength characteristics of KhNM-type alloys without considerable reduction of the ductility characteristics.

CONCLUSIONS

1. The processibility of Ni – Cr alloys in cold and hot deformation and welding, as well as the enhanced corrosion resistance are explainable by the high resistance of the high-temperature γ-phase based on f.c.c. nickel lattice to decomposition at chromium content of 42 – 44 at.%.

2. We presume that the high radiation resistance of alloys of type KhNM is connected with the formation under irradiation of a three-phase structure based on the initial γ-phase in a state of unstable equilibrium between an ordered orthorhombic Ni_2Cr phase and a b.c.c. phase of chromium.

3. Preliminary analysis of phase diagrams shows that the metastable phase observed in alloys of type KhNM can be realized in other systems of transition alloys. If the mechanism of formation of radiation-resistant structures suggested for alloys of type KhNM is confirmed, this might pave the way for creation of a new class of "self-organizing" radiation-resistant materials for nuclear power engineering.

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