Investigation of Electrical Resistivity of Ni-Cr-Al Alloys in Liquid and Solid State

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Abstract. The subject of the study was temperature dependence of electrical resistivity of alloys based on Ni-Cr-Al system in liquid and solid state. Objects of research were alloy compositions contained 10 and 15 % of chromium and alloyed by 5 and 10 % of aluminium each. The temperature dependences of electrical resistivity was a characteristic to commercial superalloys. It has been founded that the higher the amount of alloyed elements the lower critical temperature heating up to which leads to the formation of equilibrity and microhomogeneity of the melt structure and the lower the temperature of hysteresis of electrical resistivity polyterms. Melt state before crystallization has had a significant influence on solidification process and structure of alloys in solid state.

1. Introduction
The Ni-Cr-Al system occupies a special place in the development of dispersion-hardening nickel-based alloys [1]. The distortion of the crystal lattice of solid solutions based on nickel accrues continuously and smoothly with increasing number of alloying components and their concentrations. Apparently, this is due to the appearance of additional polar bonds in such alloys and the determining factor of phase stability is the electron concentration but not the difference in the dimensions of the atoms [2].

The alloying of nickel with chromium has a strengthening effect but mainly during short-term tests. The increase in the heat resistance of Ni, Cr-alloys is achieved by alloy age in particular by aluminum. Alloys are strengthened by creating a dispersive heterogeneous structure consisting of a γ-solid solution and a strengthening phase of Ni₃Al that is variable in solubility; therefore, dispersion hardening is possible because of heat treatment. Intermetallide Ni₃Al has a small area of homogeneity. Chromium is dissolved in small amounts in this phase.

In the ternary alloys of the Ni-Cr-Al system, the solubility of aluminum in the nickel-chromium solid solution is lower than in the alloys of the binary Ni-Al system. So, the isolation of the hardening intermetallic γ'-phase occurs at lower aluminum concentrations in comparison with the binary system. Consequently, substantial hardening can be obtained with significant amounts of aluminum and this dramatically reduces the ability of alloys to deform.

A general increase in the amount for intermetallic phase leads to an increase in the working temperature of the product. However, in this case it is necessary to take into account the technically feasible reduction in the plasticity of the alloy that is observed with an increase in the amount for intermetallic compounds and the possibility of changing in morphology of the strengthening phase as well.
The diagram approach used in the structural-phase analysis of alloys is developed for binary systems including Ni-Cr and Ni-Al systems [3,4]. As for ternary systems, the Ni-Cr-Al system in particular, the interest in research in this area is insignificant and the published results are few in number but they come into notice [5-7].

For example, L. Kaufman and H. Nesor [5] consider that Ni$_3$Al, NiCr, CrAl and CrNi compounds can be a part of the hard alloys of the Ni-Cr-Al system and Ni$_2$Al and Cr$_2$Al$_3$ are present in two structural modifications differing in the type of crystalline lattice. The sections at 1500 and 1800 K are presented as heterophase systems consisting of two condensed phases- liquid, i.e. melt and solid metal.

It is known that iron atoms are able to replace nickel and aluminum atoms in Ni$_3$Al intermetallic [6]. The electronic structure of chromium and iron atoms differs insignificantly. Therefore, despite the low solubility of chromium in the intermetallic compound, its presence is possible by the principle of substitution. In the Ni$_80$Cr$_9$Al$_9$W$_2$ alloy the quantitative ratios of γ and γ'-phases can be indeed represented as 0.05 and 0.95 respectively. The alloy Ni$_64$Cr$_27$Al$_9$W$_2$ containing less nickel but more chromium has a phase ratio close to the previous composition [6].

The results of research [7] indicate the presence of alloys of more complex composition. The authors of this paper indicate the possibility of existence in the Ni-Cr-Al system of atomic compositions of the type Al$_{81}$Ni$_3$Cr$_{16}$, Al$_{76}$Ni$_3$Cr$_{20,5}$, Al$_{71}$Ni$_3$Cr$_{19,5}$ etc along with binary alloys known as phases γ', α, β, μ, σ, θ.

Thus, combinational manifold of atomic clusters of the Ni-Cr-Al system indicates their considerable disequilibrium and inhomogeneity. The characteristic features of short-range order as a certain regularity in the arrangement of neighboring atoms are preserved during melting process and have a hereditary effect on the structure and properties of the melt [1,8-10]. Therefore, the information on duration of the period or the effective relaxation temperature of the structure of melt is needed during the design process of the melting modes of industrial high-temperature alloys. Data on alloys synthesized in the laboratory can serve as a guide.

2. Materials and methods

Modern methods of density studies by analyzing the intensity of penetrating gamma radiation, magnetic susceptibility and electrical resistivity are successfully used for research of physical properties of metals and alloys in a wide temperature range and solid-liquid phase transition. The latter method is the most informative, since it allows to determine contactless the conductivity type and the beginning of the structural ordering of intermetallics.

The electrical resistivity of the studied alloys has been investigated in a rotating magnetic field by the contactless method. The measurement procedure is described in the research [8] in sufficient detail.

Taking into account the results of studies of binary alloys [3,4], the compositions Ni + 10 and + 15 wt. % Cr each is aluminum alloyed in an amount of 5 and 10% by weight.

The samples used for electrical resistance studies have been melted in a vacuum induction furnace in an argon atmosphere at a temperature of 1500°C. The reliability of the compositions is confirmed by atomic absorption analysis. The concentration of gases in the various samples has differed insignificantly and amounted to ~ 0.003 wt. % [O] and ~ 0, 001% by weight [N].

The duration of structural relaxation has not exceeded 7 minutes. Proceeding from this, during the measurement of $\rho$ the exposure period at each temperature has been established within 10-12 minutes.

3. Experiment and discussion

As results of the experiments it has been shown that, the form of the temperature dependence of the resistivity $\rho (t)$ is a characteristic of high-temperature alloys [1,9].

A typical form of the $\rho (t)$ dependence is shown in figure 1. The general patterns inherent in the studied high-temperature nickel alloys are as follows:

- sigmoid character of the location of polytherms during heating and cooling, branching or hysteresis of polytherms;
- the interval of thermal stability (Δtts) of the primary structure of the melt located between the liquidus temperature (tl) and the abnormal temperature (tan), i.e. Δtts = tan - tl and fluctuated within the limits of 50-260°C;
- abnormal temperature (tan) - the beginning of intensive restructuring of the melt structure;
- critical temperature (tc) – the temperature, heating to which leads to irreversible restructuring of the structure of the melt;
- the temperature range of the intensive reorganization of the melt structure – Δtirs is located between the temperature of the anomaly and the hysteresis temperature of the polytherm, i.e. Δtirs = th - tan (th -temperature of hysteresis);
- coefficient of intensive restructuring of the melt structure Cirs = Δρh / Δtirs, where Δρh is the hysteresis value of the polytherm ρ for th; the index of Cirs is used as an analog of the activation energy for express analysis of the structural rearrangement process.

The phenomenon of hysteresis of polytherm ρ (t) is observed only when a certain melt temperature is reached usually corresponded with the initial stage of a sharp increase in the electrical resistivity (tan) and stabilized at a temperature (th) (figure 1).

4. Results and discussion

The study results of temperature dependence of physical properties of the PG-SR1 alloy are given in figure 1.

![Figure 1. Typical form of the temperature dependence of the electrical resistivity (ρ) of high-temperature nickel alloys.](image)

The temperature dependences of the electrical resistivity of Ni-Cr-Al alloy system are shown in figure 2. All of them also have a form of characteristic of high-temperature nickel alloys.

It is found that the most thermally stable is the structure of the alloy containing Ni + 10% Cr + 5% Al as evidenced by the lowest value of the coefficient dρ / dt.

Aggregate of data indicates that the initial state of the melt is microinhomogeneous, the atoms of the doping components form independent structural groups that inherit the features of the solid state. After heating the melt to ta1 its structure becomes more homogeneous which is apparently due to the destruction of nonequilibrium associations and the formation of a melt based on liquid nickel.

The well-known information on the dependence of the critical temperature (tc) and hysteresis of polytherms (th) from the degree of alloying of the samples has been also confirmed. It has been established that the greater the alloy doping the lower the critical temperature heating to which increases the equilibrium and microhomogeneity of the melt structure and the lower the hysteresis temperature of the polytherm ρ (figure 2).
Upon repeated examination of noncrystallized samples, the polytherms $\rho$ of the second measurement cycle has coincided with the cooling polytherm of the first cycle. However, cooling to room temperature has passed through the stage of $\gamma'$-phase separation at temperatures of 1100-1050°C which has had an effect on the formation of the solid metal structure. Upon repeated examination of such samples, the polythermal heating-cooling hysteresis has been observed but the hysteresis value has not exceeded 20% of the $\Delta \rho$ of the first study cycle.

![Figure 2. Temperature dependences of the electrical resistivity of Ni-Cr-Al alloy system.](image)

The influence of the heating temperature of the Ni + 15Cr + 10Al alloy on the supercooling value $\Delta t = t_t - t_c$, the parameters of the dendritic cell of the cast metal $d_{II}$ and the ductility for hot deformation $\delta$ are shown in figure 3 and indicates the essential role of the state of the structure of the melt before solidification.

![Figure 3. The effect of the alloy composition on the critical temperature ($t_t$) and the hysteresis temperature of the polytherm ($t_h$) of the electrical resistivity (a) and the effect of the melting temperature on the supercooling interval $\Delta t$, the parameter of the dendritic cell of the cast metal $d_{II}$ and the relative elongation of $\delta$ at 1000°C temperature of the Ni + 15% Cr + 10% Al alloy (b). 1 - Ni + 5% Cr + 5% Al; 2 - Ni + 10% Cr + 10% Al; 3 - Ni + 15% Cr + 5% Al; 4 - Ni + 15% Cr + 10% Al.](image)
5. Conclusion
The results of the temperature dependences research of the electrical resistivity has shown that after melting the initial state of the Ni-Cr-Al melt has been microinhomogeneous, the atoms of the doping components have formed independent structural groups inheriting the solid-state signs. After heating the melt above the hysteresis temperature, its liquid structure has become more homogeneous which is apparently due to the destruction of nonequilibrium associations and the formation of a solution based on liquid nickel.

It has been established that the higher alloy doping the lower the critical temperature, the heating up to which increases the equilibrium and microhomogeneity of the melt structure and the lower the hysteresis temperature of the polyntherm of electrical resistivity.

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