1. Introduction
Dispersion-hardening bronzes are among the best hardened conductive alloys (for example, heat- and electrically conductive ones) [1, 2]. However, the upper temperature limit at which such materials retain acceptable mechanical and conductive properties is restricted by the stability of inclusions of the hardening phase. Therefore, when developing new dispersion hardening alloys which are capable to maintain acceptable characteristics of performance at elevated temperatures, the problem of a fairly simple and effective assessment of the temperature stability of the hardening phases with respect to dissolution in the base remains relevant. Temperature dependencies of the content of dissolved elements in the base can serve as one of the indicators of such stability.

Preliminary studies [3] established interconnection between the configurations of solvus line and the polytherm of the electrical resistivity of the alloy as a whole for nickel-silicon bronzes belonging to the quasi-binary Cu – Ni2Si cross section of the state diagram of the Cu – Ni – Si system. For bronze K1H3 (Ukraine), the composition of which belongs to the indicated cross section, the temperature dependencies of the electrical resistivity were experimentally obtained [3]. Therefore, it seems appropriate to develop a mathematical model to determine the temperature stability of the hardening phases, based on the available information.

2. Background and means to solve the problem
For dispersion hardening copper conductive alloys, due to a rather small volume fraction of the dispersed phase, one can assume that indicators of the electrical resistivity are determined mainly by the resistance of the base (for K1H3 bronze - of a copper-based solid solution), and the effect of the dispersed phase is minor. Therefore, in the framework of the classical theory of electrical conductivity, the value of the electrical resistivity of the alloy at a given temperature can be represented as the result of the combined action of the following factors:

1. Interference to the movement of charge carriers (electrons) created by copper atoms, oscillating regarding to the nodes of the crystal lattice of the solid solution. This resistance R depends linearly on temperature t, as follows from the equation for the temperature dependence of the resistance of pure metals

\[ R(t) = R_0 (1 + \alpha t). \]

where \( \alpha \) is the temperature coefficient of resistance (K⁻¹).

The atoms of nickel and silicon, which are part of the solid solution based on copper, violate the regular arrangement of atoms in the crystal lattice, and thereby create additional obstacles to the movement of charge carriers. At the same time, there is Vegard's empirical law, which states a linear correlation between the properties of the crystal lattice of the alloy and the concentration of its individual elements at a constant temperature [4]. If this is correct and the content of impurity in the crystal lattice of the solid solution is small, we can assume that the obstacles to the flow of charge carriers due to the presence of lattice distortions created by nickel and silicon atoms linearly depends on the total content of these atoms in the solid solution.

3. Thermal vibrations of nickel and silicon atoms in the crystal lattice of a solid solution create additional obstacles to the movement of electrons. In the general case, the intensity of the influence of thermal vibrations of impurity atoms on the value of electrical resistance of a solid solution cannot be considered as equivalent to the intensity of the influence of thermal vibrations of copper atoms. However, the same as in the case with copper atoms, it increases linearly along with increasing of temperature. Therefore, the increase of electrical resistance created by thermal vibrations of impurity atoms is determined by the composition and temperature of the solid solution. The intensities of the influence of thermal vibrations of nickel and silicon atoms on the value of electrical resistance are not equivalent. But for alloys of the quasibinary Cu – Ni2Si cross section of the state diagram (when the transition to a solid solution of one of silicon atom is accompanied by the transition of two nickel atoms), one can consider only the total content of nickel and silicon in the solid solution (in [5] this concept for alloys belonging to the quasibinary cross section is indicated by the term "solubility of Ni2Si silicide in copper").

Within the framework of these assumptions, the temperature dependence of the electrical resistivity of the alloy can be represented as:

\[ \rho(t) = \rho_0 + \alpha t + \alpha_x [x(t) - x_0] + \alpha_{\chi} [x(t) - x_0]. \]  

where \( \rho_0 \) is the electrical resistance of the alloy in equilibrium state at 0°C (Ohm·m), which takes into account, inter alia, obstacles to the movement of charge carriers due to the presence of impurities in the solid solution at 0°C; \( \alpha t \) is the coefficient which takes into account obstacles to the movement of the electron flux caused by the thermal vibrations of copper atoms at temperatures other than 0°C (Ohm·m²/°C); \( \alpha_x \) is the coefficient which takes into account obstacles to the movement of charge carriers caused by distortions in the crystal lattice of copper created by the presence of impurity atoms (nickel and silicon) in it at temperatures other than 0°C (Ohm·m·%); \( x(t) \) is the “Ni2Si silicide content” in a copper-based solid solution at temperature t (wt.%); \( x_0 \) is the “Ni2Si silicide content” in a copper-based solid solution at 0°C (wt.%); \( \alpha_{\chi} \) is the coefficient which takes into account obstacles to the flow of charge carriers due to thermal vibrations of impurity atoms (nickel and silicon) in the crystal lattice of the solid solution at temperatures other than 0°C (Ohm·m²/°C·%).

Abstract: The possibility of assessing of the temperature stability of the hardening phases of dispersion-hardened alloys with the help of polytherms of electrical resistance is experimentally confirmed. For alloys compositions of which belong to the quasi-binary Cu - Ni2Si cross section of the state diagram of the Cu - Ni - Si system, a procedure has been developed for calculating of the content of elements dissolved in the phase, based on copper, using data on temperature dependences of the electrical resistivity on temperature, presented in the form of regression equations. In the future, it is possible to use the developed model to assess the temperature stability of dispersed phases in alloys of more complex systems (for example, such as Cu - (Ni - Si) - (Fe - Cr - C)).

KEYWORDS: HARDENING PHASES, POLYTHERM OF ELECTRICAL RESISTANCE, REGRESSION EQUATIONS
3. Solution of the problem under consideration

It is often difficult to bring the alloy at a temperature of 0 °C to a state which is close to equilibrium state as much as possible in order to determine experimentally the value of \( \rho_0 \). In this case, it is possible to provide calculations in a relative coordinate system, which implies determining of the content of elements dissolved in the base at a given temperature relative to their content at some randomly selected (“reference”) temperature \( t_{01} \). Obviously, the value of the (“reference”) temperature should be chosen based on the convenience of achieving of the state of the solid solution which is the closest to equilibrium one at this temperature.

To shift the reference point of the values of resistivity to temperature \( t_{01} \), expression (1) is reduced to the form

\[
\rho(t) = \rho_{01} + \alpha_1(t-t_{01}) + \alpha_2 \left[ x(t) - x_0 \right] + \alpha_3 \left[ x(t) - x_0 \right] (t-t_{01}),
\]

where \( x_0 \) is the “content of silicide Ni \(_2\)Si” in a solid solution based on copper at \( t_{01} \); \( \rho_{01} \) is the value of the specific electrical resistance of the alloy determined by the polytherm at the “reference” temperature \( t_{01} \). This addendum takes into account the influence of all the above mentioned factors on the movement of charge carriers at temperature \( t_{01} \).

For K1H3 bronze, it is convenient to take \( t_{01} = 550 \) °C as the “reference” temperature (the optimal temperature of artificial aging of the hardened alloy [5]). For this temperature \( x_{550} = 1.59 \) wt. % [5] and \( \rho_{550} = 11.718 \times 10^{-8} \) Ohm m [3].

4. Results and discussion

The values of the coefficients, \( \alpha_1 \), \( \alpha_2 \), and \( \alpha_3 \), were determined by substituting in (2) the values of the specific electrical resistance of bronze K1H3 \( (\rho(t)) \) which were experimentally determined in [3], and also the equilibrium compositions of the solid solution, which were determined from the state diagram [5], at the corresponding temperatures.

To ensure a more complete verification of the adequacy of the obtained results, the group of data used in the calculation of the coefficients did not include information on the electrical resistivity and composition of the solid solution for temperatures lower than \( t_{01} = 550 \) °C. It should be emphasized that the number of obtained equations exceeds significantly the number of sought-for unknowns. Therefore, an overdetermined system of equations was solved by minimizing the residuals using the least-squares method. The calculated results give the following values of parameters: \( \alpha_1 = 0.0077 \times 10^{-8} \) Ohm m°C; \( \alpha_2 = 2.5004 \times 10^{-8} \) Ohm m%/%; \( \alpha_3 = 0.00346 \times 10^{-8} \) Ohm m/(C %). The value of \( \alpha_1 = 0.0077 \times 10^{-8} \) Ohm m°C is close to the tabular value of the absolute temperature coefficient of the specific electrical resistance of pure copper (according to [6] \( \alpha_1 = 0.00736 \times 10^{-8} \) Ohm m°C). Even with the above assumptions, the calculation error is 4.6%. The results of comparison show a good coincidence between the experimentally determined temperature dependences of the electrical resistivity of K1H3 bronze and those ones which were calculated analytically using (2) (Fig. 1), including results for temperatures below 550 °C, which were not used for determining of the parameters of the model. It is also worth to pay attention on the accuracy of model's predictions (2) of the linear cross section of the polytherm of the K1H3 bronze electrical resistance at temperatures exceeding the solvus temperature (843 °C), although the experimental points lying on this segment also were not used in calculations of the model parameters. The presence of this segment is associated with the completion of dissolution of the components of nickel silicide in the base. \( \mathrm{Ni}_2\mathrm{Si} \) phase which is a source of saturation of the copper-based solid solution with nickel and silicon is already absent in the structure of K1H3 bronze at temperatures above 843 °C (these elements are already completely dissolved in the base). Therefore, upon further heating, the specific resistance of the alloy increases only due to an increase of the average amplitude of atomic vibrations at the nodes of the crystal lattice. The action of only one factor, the intensity of the influence of which on the resistance value depends linearly on temperature, leads to the appearance of an almost rectilinear site on the polytherm.

However, the determination of the contents of dissolved elements in a phase based on copper (for equilibrium conditions of the coordinates of points lying on the solvus line) with the usage of experimental data on the polytherms of the electrical resistivity of the alloy is of the greatest practical interest. For this purpose, expression (2) should be submitted in the form:

\[
x(t) = \frac{\rho(t) - \rho_{01} - \alpha_1(t-t_{01})}{\alpha_2 + \alpha_3(t-t_{01})} + x_{01},
\]

Literature data on the coordinates of points belonging to the solvus line of the quasibinary Cu – \( \mathrm{Ni}_2\mathrm{Si} \) cross section of the state diagram of the Cu – Ni – Si system [5] are in good correlation with the

Figure 1 - Temperature dependence of the specific electrical resistivity of the bronze K1H3.
- - according to experimental data
. . . - calculated by the equation (2)

Figure 2 - Temperature dependence of the \( \mathrm{Ni}_2\mathrm{Si} \) content in copper based solid solution on alloys belonging to the quasibinary cross section of the Cu – Ni - Si system
- - experimental data [4]
- - calculated for K1H3 bronze according to the temperature dependence of resistivity
values of calculated electrical resistivity [3] (according to expression (3)) (Fig.2). It should be noted that there is a good coincidence between the data on the compositions of the solid solution at temperatures up to 550 °C, information about which was not used in the calculation of the coefficients of the model. It should be noted that (3) can also be used to assess the temperature stability of dispersed phases in alloys of more complex systems (e.g., Cu - (Ni - Si) - (Fe - Cr - C)) for which state diagrams are absent in literature sources (therefore, it is not possible to obtain a priori information on the equilibrium composition of the solid solution at a “reference” temperature). Although in this case, expression (3) allows to obtain only the differences $x(t) - x_{01}$, however, this may be quite sufficient to estimate the temperature stability of the dispersed phases.

5. Conclusions

The aggregate of the above mentioned facts allows to assume that the developed model describes quite adequately the interrelation between the value of the electrical resistivity of the alloy and the content of dissolved elements in the base. Therefore, the presence of empirical data on the polytherms of electrical resistivity allows to determine analytically the content of elements dissolved in the base of alloy at various temperatures. Having made additional assumptions, it is possible to use the developed model in the future to assess the temperature stability of the dispersed phases in alloys of more complex systems (for example, such as Cu - (Ni - Si) - (Fe - Cr - C)).

6. References

3. Khristenko V.V. Effect of the content of dissolved elements in the copper-based phase on the polytherm of the electrical resistance of quasi-binary Cu - Ni - Si alloys of the cross section of the state diagram of the Cu - Ni - Si system. - Casting processes, 2012, № 2, p. 73 - 77. (Khristenko V.V., Kirievsky B.A, Trubachenko L.N.) (Russian)