The effect of the temperature on the electric resistivity of the quaternary alloys utilized in electronics

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The actual tendency in the world is to use the quaternary alloys in electro technique and electronics as springs, elastic elements good conductors of electricity, as well as in electric welding under pressure in points. In the literature of specialty there is no data regarding the behaviour of these materials in the heating process. From here our interest for the study of the electric resistivity of the quaternary alloys in the heating process appeared. In the present work the electric resistivity of the quaternary alloys CuNiAlSi is studied, in the process of heating with an experimental device specially conceived, as well as the study of the structure by spectrometry and diffractometry that spotlights the strong influence of the phenomenon of precipitation on certain intervals of temperature on the electric resistivity.

1. Introduction

Quaternary alloys CuNiAlSi used in electro-techniques and electronics present a significant variation of the characteristics depending on the temperature [1]. The properties of the quaternary alloys are determined by their structure. During the heating phenomenon of reorientation of the crystalline grains, phase's transformations, segregations and chemical reactions between the inclusions appear, all leading at modifications of the structure and implicitly of the properties. The heat treatment leads to the modification of the properties by the transformations that take place at different temperature levels [2]. The electric resistivity of the quaternary alloys is strongly influenced by the precipitation phenomenon that takes place at the heating of these ones.

2. Laboratory experiments

The electric resistivity of the materials is a size influenced by the structural modifications that appear during heating [3]. Into the work frame of the laboratory experiments determinations of the electric resistivity have been made depending on the temperature for the interval 20-550°C with a heating speed of 200°C/h. The determinations have been performed on the experimental device shown in the Fig.1 designed and produced for research and study.

The specific resistivity has been calculated with the relation:

$$\rho = \frac{\Delta U}{I} \frac{S}{l} \quad [\mu\Omega m] \quad (1)$$

where: ρ – electric resistivity, [$\mu\Omega$m]; ΔU – tension drop indicated by the millivoltmeter,[mV]; I – current intensity = 0.5A; S – sample section = thick.x b= 3× 3.5= 10.5 mm^2; l – sample length = 100 mm.

Replacing the data in the formula 1 we obtain:

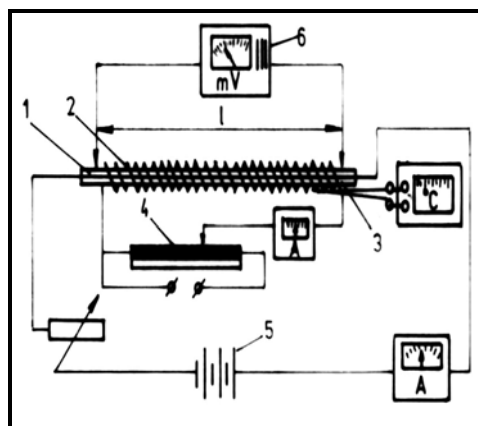$$\rho = \frac{\Delta U}{0.5} \frac{10.5}{100} = 0.21 \cdot \Delta U \quad [\mu\Omega m] \quad (2)$$

Fig. 1 The scheme of the device designed and produced for the study of the variation of the electric resistivity of the quaternary alloys depending on the temperature 1 – sample of quaternary alloy CuNiAlSi (L = 100 mm; thick.= 3 mm; width b = 3.5 mm); 2 – electrical resistivity for the cooling in air of the sample; 3 – thermo-couple NiCr-Ni; 4 – auto-transformer; 5 – source of direct current (I = 0.5A, U = 9V); 6 – millivoltmeter for the measurement of the tension drop on the sample.

In the Table 1 and Fig.2 the values of the measurements performed into the work frame of the laboratory experiments are shown.

Table 1. Electric resistivity ρ of the samples of quaternary alloys as a function of temperature.

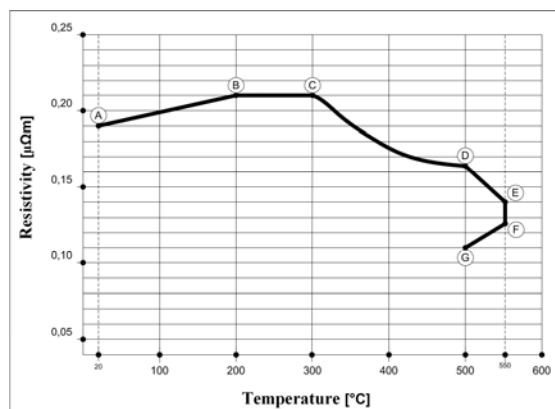| Cr. Nr.	Sample of quaternary alloy	Temperature °C	Tension drop ΔU, mV	Electric resistivity $\rho = 0.21 \cdot \Delta U$, μΩm
1	CuNiAlSi	20	0.90	0.190
		100	0.95	0.200
		200	1.00	0.210
		300	1.00	0.210
		400	0.83	0.175
		500	0.79	0.165
		550	0.67	0.140

Fig. 2. Variation of the electric resistivity with the temperature for the experimental samples of quaternary alloy CuNiAlSi

Laboratory experiments regarding the variation of the electric resistivity of the quaternary alloys CuNiAlSi with the temperature spotlight the following phenomenon:

- AB (20-200 ºC)- linear increase of the electric resistivity with the temperature $\rho T = \rho o(1+ \alpha \Delta T) \rightarrow$ no precipitation phenomenon take place;
- BC (200-300 ºC)- precipitation of the chemical compounds Ni_3Al, Ni_2Si takes place with a constant intensity maintaining the values of the electric resistivity;
- CD (300-500 ºC) – precipitation with high intensity of the chemical compounds based on Ni and Al that leads to the resistivity decrease;
- DE (500-550 ºC)- precipitation with high intensity of the chemical compounds Al_2Cu, Cu_3Al that leads to the sudden variation of the resistivity;
- EF- maintaining at 550 ºC for the definitization of the precipitation phenomenon – that provokes a decrease of the electric resistivity;

- FG- the beginning of the slow cooling process that leads to the continuous decrease of the electric resistivity due to the finalization of the precipitation processes.

3. Study of the quaternary alloys structure by diffractometry

The presence of the chemical compounds that precipitate on certain temperature intervals is spotlighted by diffratograms by the study of the intensity maxima [4,5]. The diffractometric research puts into evidence the high intensity peaks and low intensity peaks associated with the presence of the solid solutions and chemical compounds which precipitate and which influence significantly the values of the electrical resistivity, implicitly of the conductivity [6,7]. This way the differences between the cast condition and the heat treated condition of the quaternary alloy is spotlighted.

The samples have been taken from the quaternary alloy being in cast condition 1 and treated in salt bath at 50 ºC, maintaining 5 min/mm of thickness, cooling in water + ageing 1.5 hours at 490 ºC, cooling in water. The characteristics of the diffractometric analysis are: X-ray CoK_α filtered, current intensity 10 mA, voltage 30 kV, precision of determination of peak position ± 0.02 degrees 2θ, precision of determination of inter-planar distance >1:20000. The diffractograms on the samples taken of the quaternary alloy are shown in the Figs. 3 and 4.
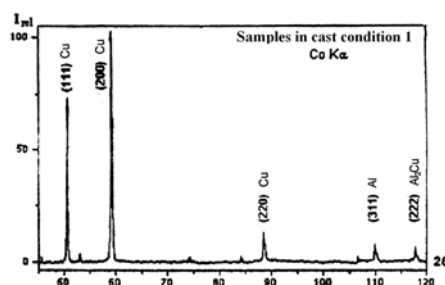

Fig. 3. The diffractogram of the sample of quaternary alloy CuNiAlSi (92,5% Cu, 2% Ni, 4,5% Al, 1% Si) in cast condition 1.
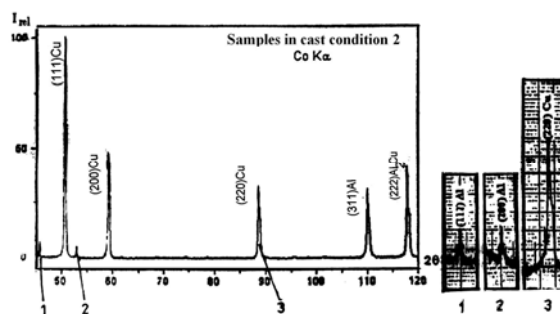

Fig. 4. Diffractogram of the sample of quaternary alloy CuNiAlSi in treated condition (hardening in salt bath + ageing).

The XRD analysis spotlighted the following aspects :
- the net constants are close in what concern the size related to the net constant of the pure copper,
  - Cast condition: a = 3.615 Å (by respect to a_{Cu} = 3.6078 Å at 20°C);
  - Treated condition: a = 3.616 Å;
- average dimension of the mosaic blocks,
  - Cast condition: D = 48.2 nm;
    - Treated condition: D = 19,8 nm;
- micro-distortions of order II and III,
    - Cast condition: ε = 0.391×10^{-3} daN/mm^2
    - Treated condition: ε = 0.189×10^{-3} daN/mm^2
- the cast sample has a layer number of crystallites with the planes (200) parallel to the sample surface, in comparison with the heat treated sample;
- the cast sample has a smaller number of crystallites with the planes (111) parallel to the sample surface, in comparison with the heat treated sample;
- in cast condition the samples are characterized by big dimensions of the mosaic blocks and a higher level of distortions;
- following the heat treatment, the dimensions of the mosaic blocks decrease 2,4 times and the micro-tensions decrease 2 times;
- the approximate maintaining of the net constant size and the high level of the distortions even after the treatment suggest the existence of the interstitial atoms and the substitution of the Cu atoms [8];
- the peaks of high intensity correspond to the α solid solutions of Cu and the maximums of low intensity correspond to the compounds based on Al (Al_2Cu, Cu_3Al, Ni_3Al), precipitated, that lead to the non-linear variation of the electric resistivity with the temperature;
- the precipitates identified in very small quantity don't appear on the diffractograms and the absence of certain precipitates is due also to the fact that their planes are not parallel to the sample surface.

4. Study of the structure by spectrometry

For the determination of the type of precipitate the study of the structure by spectrometry is necessary. The study puts into evidence the precipitation of different chemical compounds on certain temperature levels [9,10]. This way, during the heating process, the influence of the presence of certain precipitates on the electric resistivity can be determined.

The samples taken from the quaternary alloy CuNiAlSi being in treated condition have been submitted to the analysis by spectrometry by extraction of ions with the laser micro-probe. The exciting has been made on the precipitates present in the micro-structure. The diameter of the crater produced by the laser fascicle by local vaporization of the material has been smaller than the diameter of the precipitate. By the analysis effected four types of precipitates have been visualized, having the chemical composition obtained by spectrometry and shown in table 2.

Table 2 Precipitates determined by spectral analysis of the sample of treated quaternary alloy.

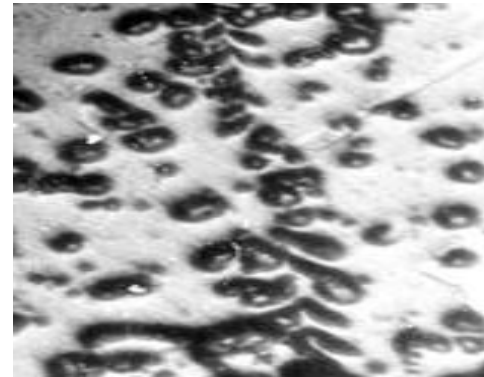| Crt. Nr.	Precipitate's size	Chemical composition of the precipitate, %			
		Cu	Al	Ni	Si
1	Big	28	69,8	2	-
2	Medium	3	16	80,7	-
3	Medium	79,5	18	2	-
4	Small	3	78,6	-	18,1

Fig. 5 Quaternary alloy CuNiAlSi treated (hardening in salt bath + ageing 490ºC/1,5 h/water). Electronic microscopy (x2500)- big density of non - coherent precipitates in the base matrix.

Depending on the chemical composition of the 4 types of precipitates (percentages of the chemical composition) and the optically visualized size, the probable chemical formulas of the precipitated compounds are the followings:
- pos.1 – big precipitates, formula Al_2Cu →low resistivity, leads to a resistivity variation with high intensity;
- pos.2 – medium precipitates, formula Ni_3Al→leads to a resistivity variation with a medium intensity;
- pos.3 – medium precipitates, formula Cu_3Al→ low resistivity, leads to a resistivity variation with high intensity;
- pos.4 – small precipitates, formula Ni_2Si→high resistivity, leads to a resistivity variation with the temperature with a constant intensity.

The precipitates of bigger dimensions of type Al_2Cu and Cu_3Al have a more reduced electric resistivity determining an accentuated variation of the resistivity with the temperature [11].

The maxima of low intensity from the diffract-gram correspond to the compounds on Al basis, respectively Al_2Cu, Cu_3Al, Ni_3Al, precipitates that determine a non-linear variation of the electric resistivity with the temperature on the precipitation interval.

The maxima of high intensity correspond to the copper α solid solutions that have a low electric resistivity;

Following the heat treatment (salt hardening + ageing), due to the accentuated phenomenon of precipitation of the basis component elements of Cu and Al, of the decrease of mosaic blocks dimensions and of the micro-stresses, the electric resistivity of the quaternary alloys decreases in comparison with the values of the resistivity of the quaternary alloys in cast condition.

The intensification of the precipitation phenomenon leads to the diminishing of mosaic blocks dimensions of 2,4 times and of the micro-distortions values of ord. II and III of about 2 times. These aspects create the accentuated diminishing of the electric resistivity and the abrupt variations in a narrow temperature interval (500-550 °C).

From the crystallographic point of view the precipitation phenomenon leads to the diminishing of the number of crystallites with the planes (200) parallel to the sample surface and the increase of the number of crystallites with the planes (111) parallel to the sample surface. These aspects create the variations of the electric resistivity, the slow decrease in the interval 300-500°C and the abrupt decrease in the range 500-550 °C [11].

5. Conclusions

In the case of the utilization of the quaternary alloys CuNiAlSi of high purity, as elastic elements and materials destined to welding by pressure in points in the electronics field, where the maintaining of the resistivity in a narrow interval of values is needed, the long duration functioning in the interval 500-550 °C has to be avoided, because in this interval, due to the finalization of the precipitation process, abrupt variations of the electric resistivity take place. In the interval 20-500 °C, the quaternary alloys present regions with linear variations and regions with constant resistivity values. These regions define an optimum interval in what concerns the utilization in the electronics field, as the resistivity variation on the whole is not significant.

By studying the variation of the chemical composition of the quaternary alloys a formula is obtained, that can ensure a controlled variation of the electric resistivity with the temperature on large temperature intervals.

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