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Effect of Cerium and Lanthanum Additives on the Phase Composition of the Copper-Nickel Alloys

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Abstract. An experimental study of the phase composition for nine samples of the Cu–Ni–Ce–La alloys with different content of components was carried out. The nickel concentration in the experimental samples varies from 3 to 40 wt. %, the sum of cerium and lanthanum concentrations was not exceed 7 wt. %. Alloys samples of the system Cu–Ni–Ce–La were studied using scanning electron microscopy and microprobe analysis, as well as X-ray analysis. Also, Vickers micro hardness was measured on the cross sections of the experimental samples. In this work, the conditions of intermetallic compounds formation in the as-cast samples were studied. The results of the work can be used for the technological processes analysis of copper and copper-based alloys production.

Introduction

Copper-nickel alloys are widely used in engineering, thanks to their good mechanical properties, corrosion resistance and special electrical properties, they can be easily treated by pressure in hot and cold conditions. Most of these alloys are deformable materials [1]. The nickel concentration in copper-nickel alloys varies widely (depending on the alloy grade) from 3 wt. % to 40 wt. % of nickel content.

On the other hand, bronze with addition of the rare earth elements (in particular, cerium and lanthanum) is of interest due to the successful combination of high heat resistance and electrical conductivity. In addition, the additives of cerium and lanthanum reduce the grain size in the structure of copper and copper alloys [2–11]. In particular, the work [11] indicates a significant positive effect of rare earth metal additives on the structure and mechanical properties of as-cast alloys with Cu–30Ni composition.

However, the phase composition of the Cu–Ni–REM (REM – rare earth metals) alloys systems is not well studied. For example, there is no data on the phase diagram representation of the Cu–Ni–Ce–La system. However, the literature provides some information on double and triple systems including copper, nickel, cerium and lanthanum.

Cu–Ni system is characterized by unlimited solubility of components, both in solid and liquid state [12], the same can be said about Ce–La system [13]. According to the phase diagram of the Cu–Ce [14], the system has five compounds: Cu_6Ce, Cu_5Ce, Cu_4Ce, Cu_2Ce, CuCe, where only Cu_6Ce and Cu_2Ce are congruently melted. It should be noted that the solubility of cerium in solid copper according to [15] is only 0.2 wt. % at 870 °C and does not exceed 0.05 wt. % at 300 °C. In the system Cu–La there are six possible compounds [16]: $Cu_{37}La_3$, Cu_6La, Cu_5La, Cu_4La, Cu_2La, CuLa, where only Cu_6La and Cu_2La are congruently melted. However, the solubility of lanthanum in solid copper is comparable to the solubility of cerium. The Ni–Ce system is also characterized by a low solubility of cerium in solid nickel, in this system the following intermetallides can be formed: $CeNi_5$, Ce_2Ni_7, $CeNi_3$, $CeNi_2$, CeNi, Ce_7Ni_3 [17, 18]. The Ni–La system is characterized by the formation of eight intermetallic compounds: $LaNi_5$, La_2Ni_7, $LaNi_3$, La_7Ni_{16}, La_2Ni_3, LaNi, La_7Ni_3, La_3Ni; solid solutions are absent in this system [19].

According to the experimental data [20], in the Cu–Ni–Ce system it is possible to form a number of solid solutions of intermetallic compounds $Ce(Ni,Cu)_6$ and $Ce(Ni,Cu)_5$ in the copper and nickel enriched area. The solubility of nickel in the Cu_6Ce compound can reach 5 at. % [20]. In the Cu–Ni–La system, the formation of a $La(Cu,Ni)_5$ solid solution is possible [21], there is also data on the presence of a triple compound $La_{10}Cu_{85}Ni_5$ [21, 22].

However, despite of numerous studies on double phase diagrams and some available information on triple phase diagrams, the phase equilibria representation of the Cu–Ni–Ce–La system remains unclear.

The aim of this work is to study experimentally the effect of cerium and lanthanum additives on the phase composition of copper-nickel alloys.

Experimental Research

The compositions of the experimental samples are given in the Table 1. Electrolytic copper (99.99 wt.% of purity), electrolytic nickel (99.5 wt.% of purity), metal cerium (99.9 wt.% of purity), metal lanthanum (99.9 wt.% of purity) are used for alloys casting. Alundum crucibles are used for melting at a temperature of 1450–1500 °C in the laboratory induction furnace, where a heater acts as a graphite vessel, inside of which a reducing atmosphere is created for metal protection from oxidation. By the end of metal melting, the crucibles were kept in the working volume of the furnace, without reducing the temperature for about 15–20 minutes. The crucibles were covered with a graphite cap. The samples were cooled in the air without removing the cap.

Table 1. Compositions [wt. %] used for the experimental study* and its results.

No.	Ni	Ce	La	*HV*	Phases**
1	40.10	0.68	0.97	1770	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$
2	10.06	3.52	3.34	1660	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La
3	10.13	0.87	0.99	1207	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$
4	10.11	0.64	2.59	1457	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La
5	5.19	0.09	0.26	950	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$
6	5.16	0.58	0.61	1090	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La
7	5.09	1.93	0.58	1130	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La
8	3.14	0.89	1.10	1110	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La
9	3.12	1.75	0.98	1170	(Cu,Ni)-solid solution, $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La

* Cu – balance; ** MRSA and XRD complex data.

Sample composition analysis was carried out by determining the content of nickel, cerium and lanthanum on the atomic emission spectrometer with inductively coupled plasma OPTIMA 2100 DV (Perkin Elmer).

X-ray diffraction (XRD) on the cross sections of the polished samples was conducted using the multi-purpose diffractometer D8 ADVANCE, Bruker, with Cu K_{α} radiation.

Structures of experimental samples were studied using a JEOL scanning electron microscope (SEM) with JSM–6460LV modification, equipped with an energy dispersion spectrometer of Oxford Instruments for qualitative and quantitative micro-X-ray spectral analysis (MRSA).

Measurements of Vickers HV microhardness were carried out using hardness testing machine FUTURE–TECH FM–800 with Thixomet PRO software, applying the loading of 100 grams at least at ten points for each samples.

The results of the study are shown in the Table. The microstructures of the samples No. 1, 2, 5 and 8, obtained by SEM, are shown on Fig. 1. The elements distribution along the selected scanning line (according to SEM and MRSA) for sample No. 9 is shown on Fig. 2.

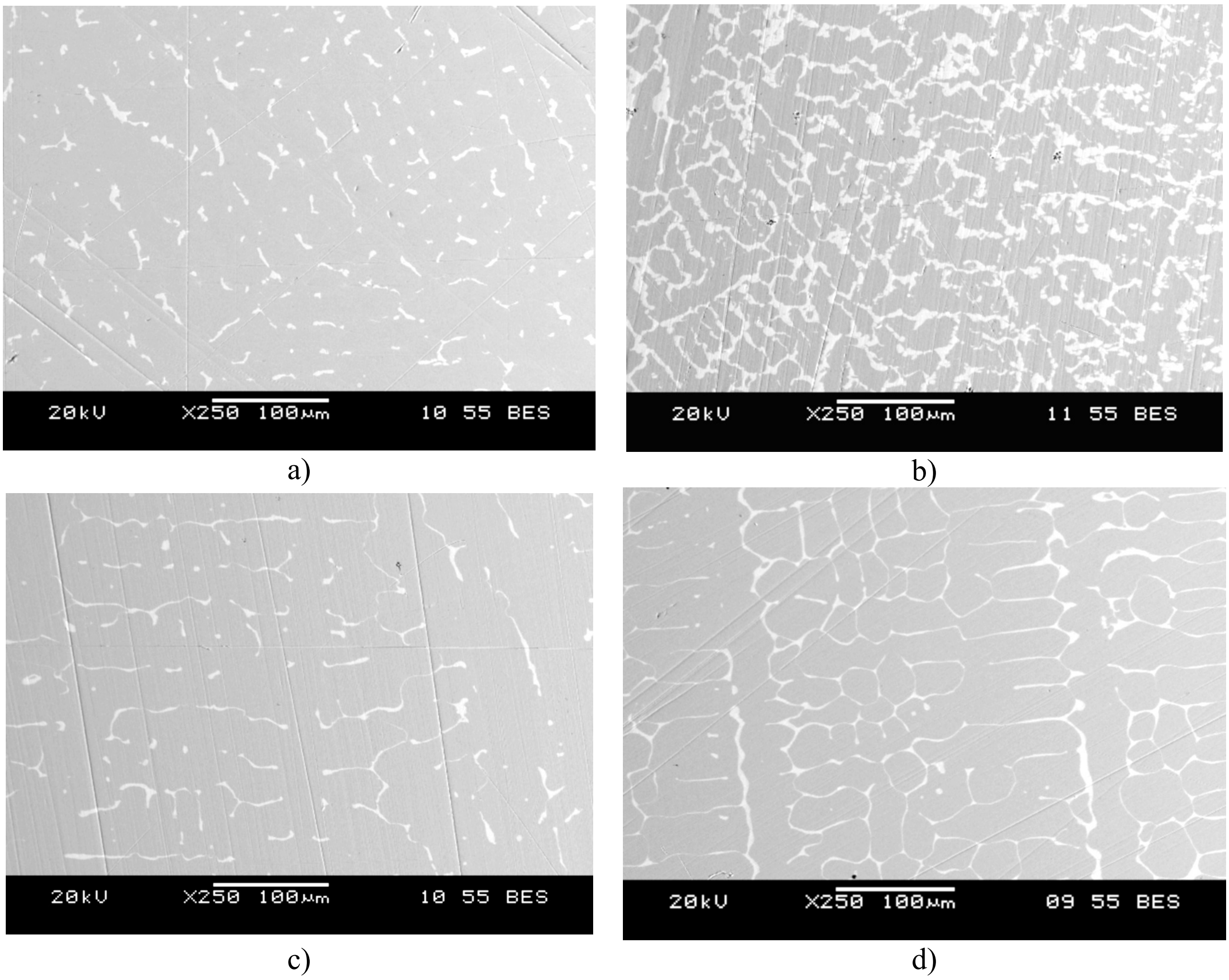

Fig. 1. The structure of experimental samples (according to SEM): a) No. 1; b) No. 2; c) No. 5; d) No. 8.

Results and Discussion

In the experimental samples the precipitations of intermetallic compounds were found, which include rare earth metals.

According to Fig. 1, for copper-nickel alloys with small additives of cerium and lanthanum, the structure of the eutectic type is typical. When the concentration of rare earth metals is increasing, the eutectic component becomes larger, while the solid solution cells (Cu,Ni) are refined. More low-melting intermetallic compounds are located on the grain boundaries of copper-nickel solid solution.

With decreasing of nickel concentration and increasing of cerium and lanthanum concentrations in the experimental samples their phase compositions are changed.

For samples No. 1, 3, 5 with sufficiently low concentrations of rare earth metals, the precipitates are homogeneous and represent a solid solution of $(Ce,La)(Ni,Cu)_5$. The ratio of total concentrations of cerium and lanthanum to the nickel concentration for these samples is: 0.041 for sample No. 1; 0.183 for sample No. 3; 0.068 for sample No. 5.

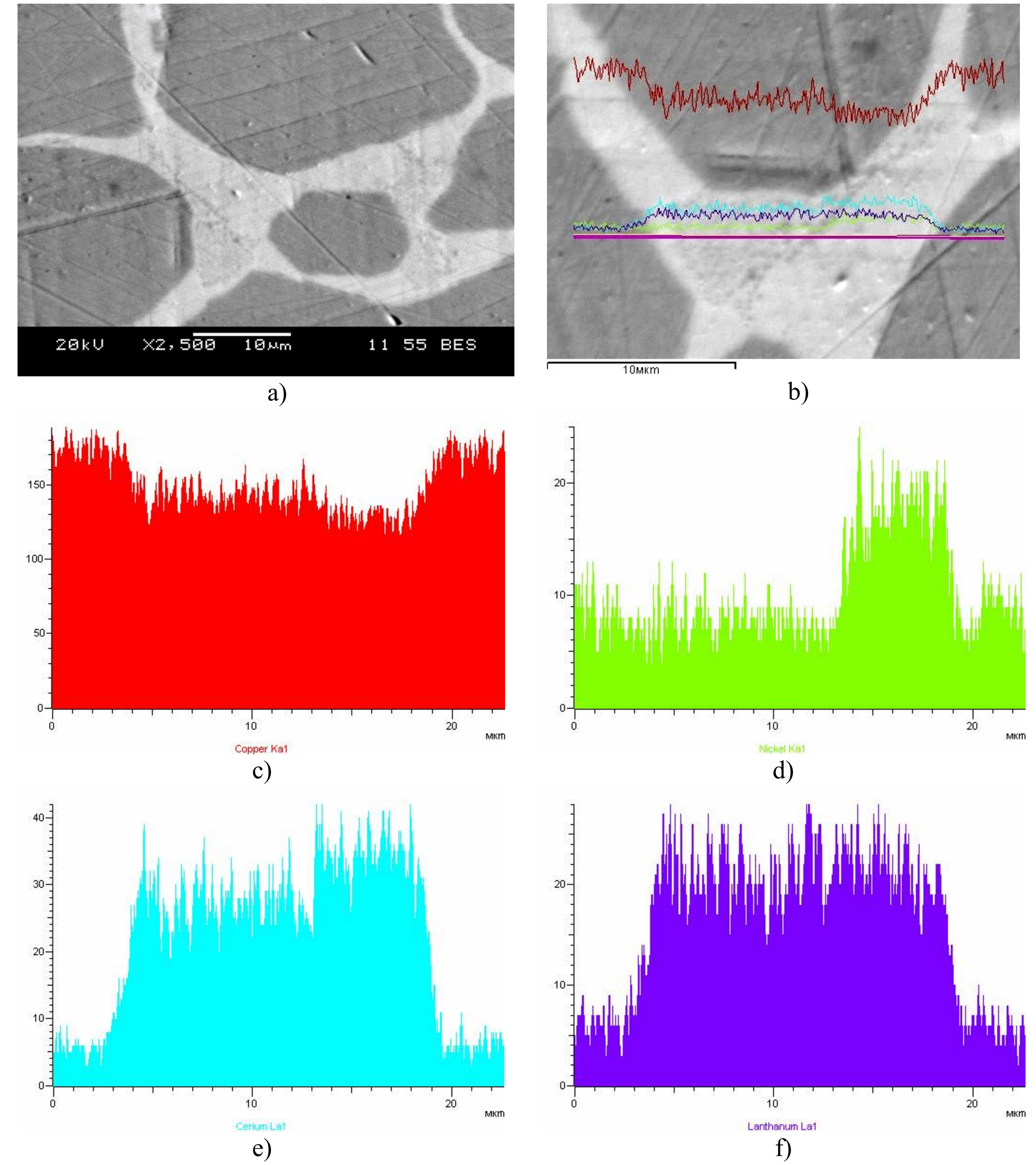

Fig. 2. The structure of the sample No. 9 (according to SEM and MRSA): a) the general view of the precipitates (with magnification 2500x); b) area zoom (with magnification 5000x) indicating the line along which the scan was carried out; c) copper distribution along the scanning line; d) nickel distribution along the scanning line; d) cerium distribution along the scanning line; e) lanthanum distribution along the scanning line.

In the other samples, the precipitations of $(Ce,La)(Ni,Cu)_5$ and other intermetallic phases based on Cu_6Ce and Cu_6La are observed. According to Fig. 2, intermetallic compounds are located along the grain boundaries of (Cu,Ni) solid solution. Apparently, during the crystallization of experimental samples, the crystals of solid solution are primarily formed from the metal melt, only then the relatively refractory nickelides of rare earth metals are formed, and then the compounds of rare earth metals with copper. The ratio of the concentrations sum of cerium and lanthanum to the concentration of nickel for these samples is: 0.682 for sample No. 2; 0.320 for sample No. 4; 0.231 for sample No. 6; 0.493 for sample No. 7; 0.634 for sample No. 8; 0.875 for sample No. 9.

The microhardness of the experimental samples is sufficiently strong dependent on the concentrations of nickel, cerium and lanthanum. The higher the concentrations sum of these elements leads to the higher the microhardness value.

Conclusions

Effect of cerium and lanthanum additives on the phase composition of copper-nickel alloys was studied. With a ratio of the concentrations sum of cerium and lanthanum to the concentration of nickel in the samples composition do not exceeding 0.2, in addition to (Cu,Ni)-solid solution in the ingots volume, a single intermetallic $(Ce,La)(Ni,Cu)_5$ is observed. With increasing of this ratio value, the intermetallic phases $(Ce,La)(Ni,Cu)_5$, Cu_6Ce, Cu_6La are formed, that segregates on the boundaries of the (Cu,Ni)-solid solution. The microhardness of the experimental samples is sufficiently strong dependent on the concentrations of nickel, cerium and lanthanum. The higher the concentrations sum of these elements leads to the higher the microhardness value.

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