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INFLUENCE OF THERMOMECHANICAL TREATMENT ON STRUCTURAL-PHASE TRANSFORMATIONS AND MECHANICAL PROPERTIES OF THE Cu–Al–Ni SHAPE-MEMORY ALLOYS

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Using the methods of optical and electron microscopy and electron and X-ray diffraction analyses, the influence of thermomechanical treatment on the mechanical properties, average grain size, and structural and phase transformations is investigated in the Cu–Al–Ni *triple alloys exhibiting a shape memory effect. In the alloys under study with a fixed content of 3wt%* Ni *the concentration of aluminum was varied from 9 to 14 wt%. It is shown that in the alloys subjected to thermal treatment, including forging and homogenizing annealing using controlled recrystallization in the austenitic state followed by quenching, the grain-boundary disintegration and segregation disappear. It is found out that the microstructure of the alloys in the hot-forged and hardened states with the content of aluminum 9–10 wt%. consists of the grains of the average dimensions within 60–80 μm, with the content of aluminum 10–12 wt% – 100–350 μm, while in the alloys with the content of aluminum up to 14 12 wt% the average grain size reaches 1 mm. According to the data of mechanical testing at room temperature, with a decrease in the content of aluminum the ultimate tensile strength (σ_{UTS}), the yield strength (σ_M) and the relative elongation (δ) increase. An improvement of the mechanical properties of the alloys is attributed to the grain structure refinement of the β_2-austenite and package substructure of the β'_1- and γ'_1-martensites as the content of aluminum in the alloys decreases. For instance, in the fine-grained alloys containing 9.2 and 9.5 wt%* Al *the value of relative elongation remains at a high level (>10%), while for the other alloys with 10–14 wt%* Al *it does not exceed 5%. As the content of aluminum in the alloys decreases, the character of the specimen fracture under uniaxial tension changes (from brittle to ductile).*

Keywords: shape memory, mechanical properties, structure, martensitic phases, thermomechanical treatment.

INTRODUCTION

Among the scientific events of practical importance in the XX century was the discovery of highly reversible thermoelastic martensitic transformations (TMTs) in the Cu–Al–Ni alloys by the soviet scientists G. V. Kurdyumov and L. G. Khandros [1]. More recently the shape memory effects (single and thermocyclically reversible shape memory effect (SME), pseudoelasticity, and a number of other anomalies) observed in different alloys have been attributed to them [1–9]. It is well known that TiNi-based alloys possess the best complex of SME and other physical-mechanical properties [1–8]; their unique practical applications are widely reported in the literature (see, e.g., [10, 11]). On the other hand, after certain heat and thermomechanical treatments they by no means always exhibit the physical-mechanical characteristics demanded in practical applications.

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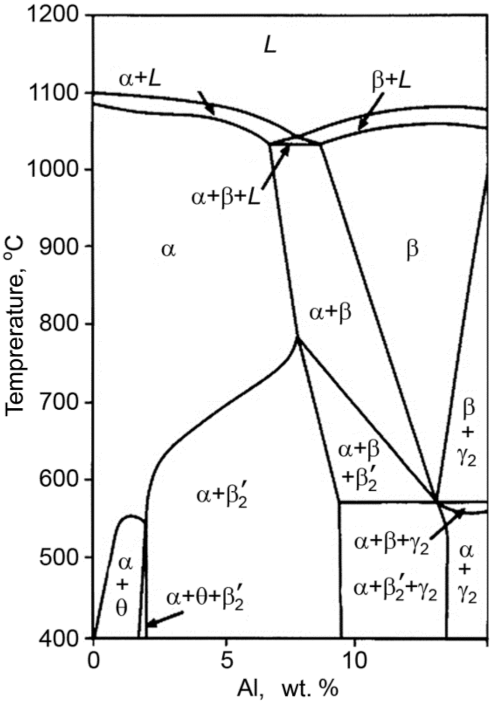

Fig. 1. Phase equilibrium diagram of the Cu–Al – 3 wt% Ni alloy.

Ternary β-alloys of copper, such as Cu–Al–Ni, Cu–Zn–Al, and Cu–Zn–Sn, are by far less expensive, they have better heat and electrical conduction, as well as better manufacturability compared to, e.g., TiNi-alloys [1, 4]. Moreover, in the single crystalline state they demonstrate excellent SME characteristics [1]. In the coarse-grained polycrystalline state they, however, possess extremely low ductility, crack resistance, and fatigue life, especially in the temperature interval of martensitic transformations, which rules out manifestation of the SMEs commonly observed in their single crystals. One of the reasons for intercrystalline fracture is the high anisotropy A = C44/C' ~ 12–13 of the elastic moduli of the copper alloys, which are metastable with respect to the TMTs [1, 9], while for the elastic-isotropic low-modulus TiNi-alloys A is found to be ~1–2 [3, 5–8]. In the alloys with a high elastic anisotropy during a TMT, the stresses localized, especially at the grain boundaries, are the higher, the larger the grains of the alloy [1]. A heterogeneous decomposition of these alloys also results in lower ductility, especially in the coarse-grained state. Brittle intercrystalline fracture is thought to be the principal reason preventing their wider practical application. By decreasing their grain size it is possible to diminish the role of the above factors in embrittlement of the alloys. On the other hand, a variety of the methods for grain structure refinement in the copper alloys using alloying additions, plastic deformation, rapid solidification, powder metallurgy, and some other techniques ended in a failure [1, 4, 12]. The purpose of this work is to study the influence of the high-temperature thermomechanical treatment on the grain size, structural-phase transformations, and mechanical properties of the Cu–Al–Ni ternary alloys with a shape memory effect, which were doped with 9 to 14 wt% aluminum.

1. EXPERIMENTAL MATERIAL AND PROCEDURE

In this study we used eleven Cu–Al – 3 wt% Ni ternary alloys with the content of aluminum varied from 9 to 14 wt% (with an accuracy of ±0.1 wt%), taking into account a triple-point phase-equilibrium diagram of the vertical section of the Cu–Al–Ni three-component system, which is given in Fig. 1 [1]. The alloys were produced by the electric-arc melting from high-purity Cu, Al and Ni (99.99%) in a refined helium atmosphere. For the sake of

TABLE 1. Data of Chemical Microanalysis of the Hardened Alloy Cu – 13 wt% Al – 3 wt% Ni

Element	Integral composition, wt%	Matrix, wt%	Region 1, wt%	Region 2, wt%	Region 3, wt%
Aluminum	13.0	13.2	10.3	10.1	9.6
Nickel	3.0	2.9	2.7	2.1	4.0
Copper	84.0	83.9	87.0	87.8	86.4

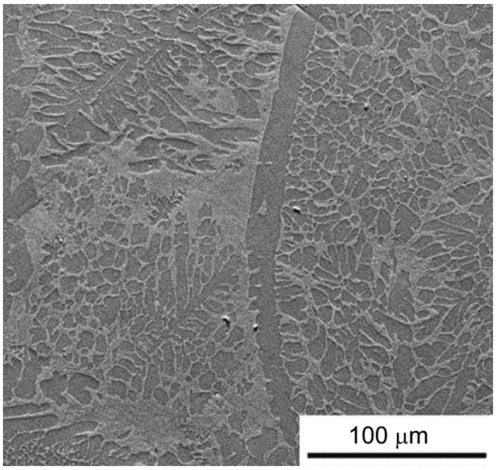

Fig. 2. Chemical segregation pattern in the as-cast Cu – 14 wt% Al – 3 wt% Ni alloy after its quenching from 1223 K for 10 min.

homogenization, the alloys selected by their chemical composition were subjected to long annealing at (1173 ± 25) K in an inert argon medium. The alloy ingots were cooled in air. The alloys heated to 1223 K were forged to form a 12×12 mm bar, followed by cooling in air. Then they were quenched into water at room temperature after heating of the bars at 1223 K for 10 min.

The structure, phase composition, and martensitic transformations were investigated using the methods of X-ray diffraction at $\theta/2\theta$ and optical and electron microscopy. The X-ray analysis was performed in a DRON-3M apparatus in the copper radiation monochromatized by a graphite crystal.

The following facilities of the UrB RAS IMP Collaborative Access Center were used in the investigations: JEM 200 CX (maximum accelerating voltage 200 kV) and Tecnai G^2 30 (maximum accelerating voltage 300 kV) transmission electron microscopes and a Quanta 200 scanning electron microscope (accelerating voltage 30 kV) equipped with a Pegasus system. The mechanical properties were measured in an Instron 5982 universal testing machine via tensile loading of standard cylindrical specimens measuring 3 mm in diameter and 20 mm in gage section at room temperature.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The experiments have shown that as-cast coarse-grained alloy ingots during cooling in air were partially disintegrated to form α, β, β_2, and γ_2- phases, where α is a three component FCC ($A1$) solid solution, enriched with copper compared to the β-matrix (lattice period $a_\beta \approx 0.289$ nm, $a_\alpha \approx 0.361$ nm), β'_2 is a BCC ($B2$)-phase based on Ni–Al–Cu (lattice period is close to 0.29 nm), γ_2 is a phase based on intermetallic Cu_9Al_4 with a cubic lattice of the $D8_3$ type, which also contains nickel (lattice period is close to 0.87 nm).

Quenching of as-cast alloys in water from 1223 K (10 min) after the preliminary homogenizing procedure practically ruled out their disintegration, except for the two-phase (β+α) alloys with 9.2 and 9.5 wt% Al, but it did not stop segregation in them (Fig. 2). As an example for one of the experimental alloys with 13 wt% Al Table 1 lists the

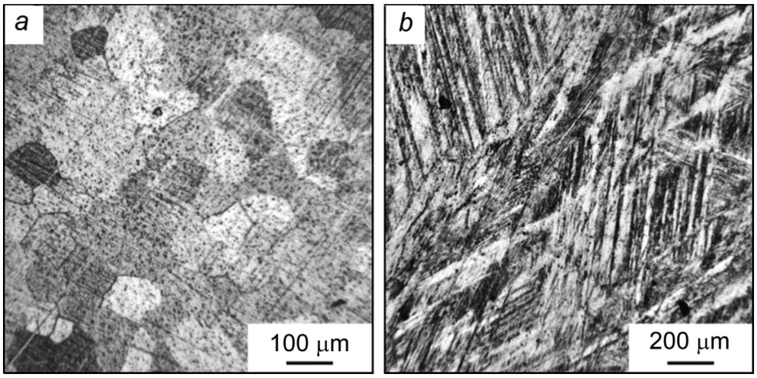

Fig. 3. Microstructure of the Cu – 9.5 wt% Al – 3 wt% Ni (*a*) and Cu – 14 wt% Al – 3 wt% Ni (*b*) alloys after their thermomechanical treatment.

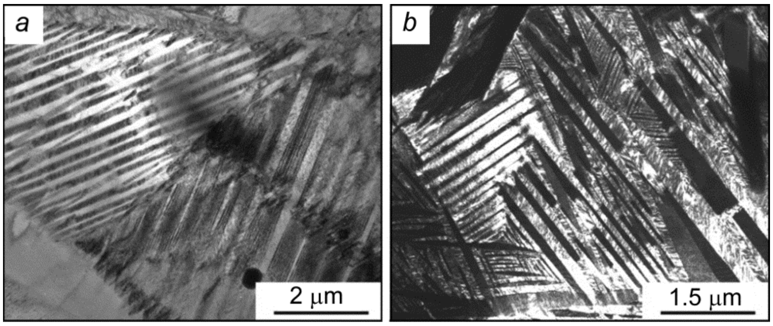

Fig. 4. Bright- (*a*) and dark-field (*b*) electron microscopy images of the martensite in the Cu – 9.5 wt% Al – 3 wt% Ni (*a*) and Cu – 14 wt% Al – 3 wt% Ni (*b*) alloys after their thermomechanical treatment.

data of an integral spectral analysis and an X-ray energy dispersive microanalysis with the lateral localization of the latter within 0.5 μm for three adjacent areas of the alloy metallographic sections. Table 1 implies a segregation of the chemical composition of the alloy with respect to all three alloying elements, which started as early as in the course of their crystallization.

In order to ensure a more homogeneous grain size distribution and grain refinement in the alloys, as well as to rule out the segregation effect after melting, we used a thermomechanical treatment of the ingots including two stages: hot forging to form bars and subsequent recrystallization annealing for 10 min at 1223 K with quenching into water. It turned out that, depending on the compositions of the alloys subjected to thermomechanical treatment, their initial coarse-grained structure changed in a different fashion: it became fine-grained with the average grain size on the order of 60–80 μm in the case of the aluminum concentration 9.2–10 wt%, medium-grained with the grain sizes from 100 to 350 μm for the aluminum concentration from 10.5 to 12 wt%, or remained coarse-grained, though becoming equiaxed, with the grain dimensions from 0.5 to 1 mm for the aluminum concentration 12.5–14 wt%.

As a result of quenching of the alloys, completing their thermomechanical treatment, they underwent a TMT. The X-ray phase analysis performed at room temperature revealed two martensitic phases in the alloys: β'_1-18R (whose parameters of the long-period monoclinic lattice were close to $a = 0.443$ nm, $b = 0.533$ nm, $c = 3.819$ nm, $\beta = 89.0$–$89.5°$) and γ'_1-2H (with the parameters of the orthorhombic lattice close to $a = 0.439$ nm, $b = 0.534$ nm, $c = 0.422$ nm). The data obtained on the phase composition are consistent with the microstructure examination by the methods of optical, scanning and transmission microscopy (Figs. 3 and 4). An analysis of the experimental alloys demonstrated that their martensitic structure is primarily characterized by the package morphology of plate crystals of the γ'_1-martensite

TABLE 2. Mechanical Properties (Ultimate Tensile Strength σ_{UTS}, Yield Strength σ_M, Relative Elongation δ, Contraction ψ) and Average Grain Size $\langle d \rangle$ of the Cu – Al (x, wt%) – Ni (3 wt%) after their Thermomechanical Treatment

x, wt%	σ_{UTS}, MPa	σ_M, MPa	δ, %	ψ, %	$\langle d \rangle$, μm
9.2	780	280	14.5	0.5	60
9.5	600	270	10.0	0.5	70
10.0	520	260	5.0	0.5	80
10.5	500	250	4.0	0.5	100
11.0	490	260	5.0	0.5	130
11.5	460	260	4.0	0.5	200
12.0	450	260	4.0	0.5	350
12.5	420	240	5.0	0.5	500
13.0	390	200	5.0	0.5	750
13.5	330	150	5.0	0.5	900
14.0	250	120	3.5	0.5	1000

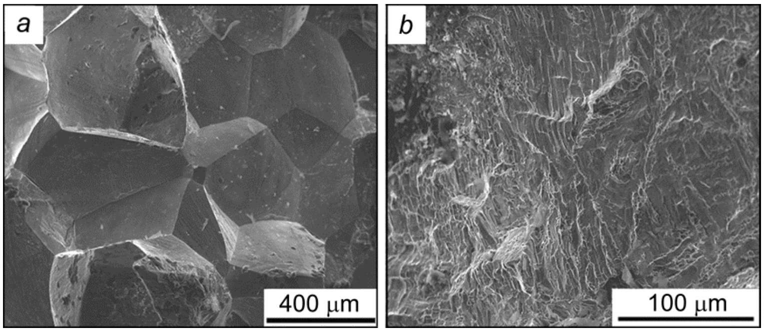

Fig. 5. Fractography of the alloys: Cu – 14 wt% Al – 3 wt% Ni (*a*) and Cu – 9.5 wt% Al – 3 wt% Ni (*b*) subjected to forging and quenching.

and by the package framework morphology of lens-like crystals of the β'_1-martensite (Fig. 3*b*). In the case of a decrease in the content of copper and, respectively, increase in the that of aluminum in the alloys, the critical temperatures of TMTs decrease from 873 K to room temperature, and along with the β'_1-martensite there is a gradual increase in the content of the γ'_1-martensite. Inside the crystals of the pairwise twinned package substructure, similarly to the situation inside the lens-like crystals, there are thin secondary twins (Fig. 4*b*).

The main crystal structure characteristics of the package morphology of martensite are the planar boundaries of the primary pair- and twin-wise oriented crystals, whose crystallographic habiti are close to $\{110\}\beta$ and the orientation relationships are of the Bain type. The observed package–framework morphology of the martensite is on the whole also typical for that in single-crystal alloys of the same compositions [1].

The results of the room-temperature mechanical tensile testing of the manufactured polycrystalline alloys, subjected to thermomechanical treatment, are presented in Table 2. Their analysis implies that the formation of a more homogeneous fine-disperse equiaxed grain structure in the alloys has a favorable influence on their mechanical properties: ultimate tensile strength σ_{UTS}, yield strength σ_M and relative elongation δ, which stabilize at a comparatively good level after this treatment in the alloys with a lower content 9–10 wt% of aluminum (see Table 2).

The fracture of the specimens of coarse-grained alloys with an increased content of Al (14 wt %) under tensile conditions has an intergranular brittle character (Fig. 5*a*), while in the fine-grained alloys with a reduced content of Al (9–10 wt %) it becomes ductile (Fig. 5*b*). In the alloys with a medium content of Al (within 10–12 wt %) it was of a mixed type – ductile-brittle fracture.

CONCLUSIONS

The following regular features of the structural and phase transformations taking place in the Cu–Al– Ni (3 wt%) alloys with a varying content of Al (9–14 wt%) have been determined at different heat and thermomechanical treatments:

1. The microstructure and phase composition of all alloys in the initial as-cast states is characterized by the presence of coarse grains and grains of varying sizes, chemical segregation, and partial disintegration followed by precipitation of the α, β_2, and γ_2-phases. Homogenization followed by quenching of as-cast alloys does not eliminate the chemical segregation.

2. A thermomechanical treatment, involving hot forging and subsequent heating at 1223 K for 10 min followed by quenching in water makes it possible to eliminate segregation of the chemical composition and phase inhomogeneity; note that as a result of recrystallization the average grain size in the alloys decreases and so does the grain-size difference.

3. The average size of equiaxed grains in the alloys subjected to thermomechanical treatment, with the content of aluminum decreasing from 14 to 9 wt%, is reduced from 1.0 mm to 60 μm, respectively. This change is well correlated with the improving mechanical properties, in particular: ultimate tensile strength increases from 250 to 780 MPa, yield strength (or critical resolved stress of the martensitic shear) increases from 120 to 280 MPa, and relative elongation – from 3.5 to 14.5%.

4. The alloy fracture is a typical brittle intercrystalline process occurring along the boundaries of the ‘former’ comparatively coarse austenitic grains and those of the large austenitic laths, when the content of Al increases (to 14 wt%). The mechanism of predominantly ductile transcrystalline fracture is observed in the alloys with a lower content of Al (9.2– 10 wt%), which correlates with the considerably smaller average grain size.

5. In all of the alloys investigated in this work, quenching in water after thermomechanical treatment is accompanied by thermoelastic martensitic transformations to form two martensite phases, β_1 and γ_1, prevailingly of the package and framework morphology, which ensures a possibility of implementing a shape memory effect in them.

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