

## Article

# Microstructure and Mechanical Behavior of Cu-Al-Ni-B Alloys with Thermoelastic Martensitic Transformation

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**Abstract:** For the first time, using optical, scanning, and transmission electron microscopy and X-ray phase analysis in combination with measurements of tensile mechanical properties, we obtained data on the structural features of the polycrystalline shape-memory eutectoid Cu-Al-Ni-(B) alloys doped by aluminum (of 10 and 14 wt% Al in total amount), nickel (of 3, 4, and 4.5 wt% Ni), and boron (0.02–0.3 wt% B) in various compositions. The effect of boron on the grain sizes, structure, phase composition, and mechanical properties of shape memory (SM) alloys has been studied. The localization of aluminum borides in the structure was investigated and an effect of grain growth inhibition in the ( $\alpha + \beta$ ) and  $\beta$  Cu-Al-Ni-B alloys was established, both in the cast state of the alloys considered and after their heat treatment.

**Keywords:** copper alloys; boron alloying; microstructure; quenching; thermoelastic martensitic transformation; mechanical properties



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## 1. Introduction

The development of modern technology dictates the creation of new smart alloys that can be used in products, devices, and mechanisms for a wide range of appropriate thermal-power and other operating conditions. However, the critical disadvantage of most polycrystalline smart materials (with the exception of binary alloys of titanium nickelide) is their brittleness and low plasticity [1]. This does not allow one to introduce into practice the unique effects inherent to certain smart materials in both cyclic-multiple and single-application cases of their operation. The tasks of developing methods for obtaining, optimally alloying, and thermomechanically processing such polycrystalline materials in order to harden them, and at the same time plasticize them for subsequent various industrial applications, are becoming increasingly important. The class of economically promising smart materials consists of the copper ( $\alpha + \beta$ ) and  $\beta$  low-modulus alloys with thermoelastic martensitic transformations (TMTs) and shape memory effects (SMEs) of the Cu-Al-Ni system [2–4]. They are distinguished by low cost in production, favorable thermal and electrical conductivity, and manufacturability in processing. In the single-crystalline state, the alloys under consideration have excellent SME characteristics. At the same time, in the usual coarse-grained (CG) state, these polycrystalline alloys are distinguished by low characteristics of plasticity, crack resistance, and fatigue durability. Under conditions of high elastic anisotropy, the production of SM effects via the initiation of TMT is impossible due to the catastrophic brittleness generated as a result of TMT in the alloys. This phenomenon in polycrystalline CG alloys is due to the progressive accumulation of coherent elastic stresses arising in the course of TMT due to an increase in the volume effect value  $|\Delta V/V|$ , when grain boundaries of the general type become the only significant localization of elastic stresses. The problem in CG copper  $\beta$ -alloys is aggravated not only by the strong softening

of the elastic modulus  $C'$  and the growth of the elastic anisotropy in the pre-martensitic state, but also by grain boundary decomposition, increasing their grain-boundary component, brittleness. These reasons prevent the commercial use of these aging or eutectoid SM alloys. The development of technologies that ensure the size refinement of grains to increase their strength, plasticity, and to prevent brittleness is the only acceptable trend taking into account all three critical circumstances (grain size, elastic anisotropy, grain boundary decomposition). Intercrystalline brittleness is one of the key reasons preventing the practical use of copper alloys with an SME [5,6]. In eutectoid copper alloys, the decrease in plasticity is usually due to chemical liquation and heterogeneous—especially grain-boundary—decomposition, which primarily occur at temperatures below the eutectoid decomposition boundary ( $T_{ED}$ ), which is close—in the case of [6]—to 840 K. In addition, this phenomenon is worsened by the coarseness of grain inherent to copper alloys (the grain size reaches several millimeters) [1]. Finally, an important specific cause of intercrystalline fracture is the high anisotropy ( $A$ ) of elastic moduli,  $A = C_{44}/C'$  (namely, 12–13 unities of value), of copper alloys that are metastable with respect to a TMT [6–8]. The value of  $A$  for elastoisotropic low-modulus and ductile titanium nickelide alloys is 1–2 units [9]. A large elastic anisotropy at a TMT leads to significant elastic stresses at the junctions of martensitic packets, and, especially, at the grain boundaries; the level of these stresses and their localization at the boundaries are greater the larger the sizes of the alloy grains are. It is obvious that the above-listed features of these alloys prevent their application in practice. When such copper-based alloys after their melting preparation, quenching, hot deformation, and heat treatment acquire a fine-grained structure (of grain size down to 60 microns), this leads to an improvement in their mechanical properties, namely, elongation to fracture increases by 40–50%, strength properties by almost 30%, and fatigue failure resistance increases 10–100 times [1].

Nowadays, various methods of size refinement of a grain structure are known [10–16]. In order to suppress grain growth and increase the rate of formation of their nuclei during crystallization, methods such as complex microalloying, powder metallurgy [17–19], and rapid quenching from the melt (RQM) [20,21] are being tried out.

When implementing the modern method of targeted microalloying to obtain a fine-grained structure in bulk Cu-Al-Ni alloys, it is necessary to take into account that the additives introduced individually or in combination with other ones have a low solubility in the Cu-Al-Ni alloys undergoing alloying. In addition, some of these additives will form compounds with basic chemical elements in the form of disperse particles, which in turn inhibit grain growth, but their presence can lead to the embrittlement of alloys [1,4]. There are known attempts to refine (the sizes of) grains in Cu-Al-Ni alloys by alloying with Ti, V, and Mn [1,16,17]. For instance, the addition of Ti and V in cast alloys during crystallization entails the suppression of (i) the formation and growth of columnar crystallites—grains and thus (ii) the appearance of grain size diversity, which, conversely, initiates the formation of small (fine) equiaxed grains, preventing the nucleation and growth of cracks during crystallization and subsequent rolling. An additional effect of the influence of Ti and/or V when heating alloys after deformation treatment manifests itself in the containment of grain growth and the coarsening of the microstructure. Fine-grained alloys doped with Ti and/or V when being deformed by 20% during compression tests at  $T > 573$  K, and during tensile tests at 923 K, demonstrate an effect of superplasticity with an elongation of up to 300%. It is noted that with the introduction of titanium or vanadium, samples of the alloy during cold rolling or drawing attain the degree of deformation of about 10%, which cannot be realized in a Cu-Al-Ni ternary alloy. The reversible deformation at TMTs in fine-grained alloys produced/prepared in this way is equal to 5%, while pseudoelastic deformation is 5.5%, which is 1–1.5% higher than that in coarse-grained ternary alloys. Boron is one of the effective but poorly studied microadditions [1].

This work is devoted to the study of the structural-phase transformations and mechanical properties in the  $\alpha + \beta$  and  $\beta$  alloys of the Cu-Al-Ni system at the different contents of Al, Ni, and B in the cast state, as well as after their thermomechanical treatment.

## 2. Materials and Methods

Our Cu-Al-Ni-B alloys were melted from high-purity components (99.99% purity) with various concentrations of Cu, Al (10 and 14 wt%), Ni (3, 4, and 4.5 wt%), and powder-type B (0.02–0.3 wt%) in the Department of Precision Alloys of the Centre of Collective Access (CCA) of IMP of the Ural Branch of the Russian Academy of Sciences. Cast alloy ingots were subjected to homogenizing annealing at a temperature of 1173 K for 8 h to forging at 1223–1023 K and air cooling. The additional heat treatment (HT) of forged alloys was also carried out with heating at temperatures of 1223 K for 30 min and quenching in water. The structure, phase, and chemical composition of the samples were studied by X-ray diffractometry, optical microscopy (OM), transmission (TEM) and scanning electron microscopy (SEM), including the mode of image registration in backscattered electrons (BSE) and energy-dispersive spectroscopy (EDS) microanalysis. X-ray studies were carried out in monochromatized  $\text{CuK}\alpha$  radiation on a Bruker Advance D8 diffractometer (Bruker Corporation, Elmsford, NY, USA). OM was performed using an Altami MET 2C microscope (Saint-Petersburg, Russia). We also used the equipment of the CCA IMP UB RAS, namely TEM Tecnai G<sup>2</sup> 30 (accelerating voltage 300 kV), SEM Quanta 200, equipped with a Pegasus system and an EDS attachment (accelerating voltage 30 kV) (FEI Company, Hillsboro, OR, USA); SEM Tescan Mira (TESCAN, Brno, Czech Republic), equipped with an EDS attachment Ultim Max 100 (Oxford instruments, Abingdon, UK) (accelerating voltage 30 kV). The final (finishing) thinning of foils with a diameter of 3 mm for TEM studies was performed on the GATAN PIPS II installation (Gatan Inc., Pleasanton, CA, USA). Tensile tests and the determination of mechanical properties of cylindrical ( $\varnothing = 3$  mm) reference samples were carried out on a universal testing machine Instron 5982 (Buckinghamshire, UK).

## 3. Results

It is known that in alloys of the Cu-Al-Ni system at a temperature of 838 K ( $T_{\text{ED}}$ ) and below, under equilibrium conditions, the eutectoid decomposition  $\beta \rightarrow \alpha + \gamma_2$  occurs. The period  $a_\alpha$  of the crystal lattice of the  $\alpha$  phase is close to 0.361 nm, with its FCC lattice being of the type A1. The period  $a_{\gamma_2}$  of the crystal lattice of the  $\gamma_2$  phase (based on the intermetallic compound  $\text{Cu}_9\text{Al}_4$  with a cubic lattice of the D $8_3$  type) is close to 0.870 nm. In addition, precipitates are formed at temperatures below the  $T_{\text{ED}}$  of the  $\beta'_2$  phase with a BCC lattice of the type B2' based on NiAl ( $a_{\text{B2}'}$  is close to 0.289 nm) [1,8,16]. In previous studies, it was found that the quenching of alloys of the Cu-Al-Ni system from a single-phase  $\beta$  region of existence prevents eutectoid decomposition [10–16]. Additives 3, 4, and 4.5 wt% Ni reduce the diffusion mobility of copper and aluminum atoms, thereby restraining the eutectoid decomposition of the high-temperature  $\beta$  phase during quenching, whereas an increase in the content of aluminum leads to a decrease in the critical temperatures of the start ( $M_s$ ,  $A_s$ ) and finish ( $M_f$ ,  $A_f$ ) of the forward ( $M_s$ ,  $M_f$ ) and reverse ( $A_s$ ,  $A_f$ ) TMTs [16]. At the same time, it is important that in the process of cooling or heat treatment at temperatures above  $M_s$ , along with decomposition, the atomic ordering occurs by the sequence  $\text{A2}(\beta) \rightarrow \text{B2}(\beta_2) \rightarrow \text{D0}_3(\beta_1)$ . The long-range atomic order of the austenitic atomically ordered  $\beta_1$  phase is inherited by martensite, which, as a consequence, ensures the thermoelasticity of the latter [1,7]. As our cooling in air of the Cu-Al-Ni alloys after forging did not allow us to prevent its eutectoid decomposition, we performed the procedure of quenching in water from the temperature 1223 K, with preliminary holding exposure for 10 min. According to X-ray studies, it was found in forged quenched alloys with an aluminum content of 10 and 14 wt% Al, due to a TMT with the formation of twinned martensitic phases according to the schemes  $\beta_1(\text{D0}_3) \rightarrow \beta'_1(18\text{R})$  (with the parameters of the long-period monoclinic lattice 18R close to  $a = 0.4450$  nm,  $b = 0.5227$  nm,  $c = 3.8050$  nm,  $\beta = 91.0^\circ$ ) and  $\beta_1(\text{D0}_3) \rightarrow \gamma'_1(2\text{H})$  (with the parameters of the orthorhombic lattice 2H close to  $a = 0.4390$  nm,  $b = 0.5190$  nm,  $c = 0.4330$  nm) (Figure 1a).

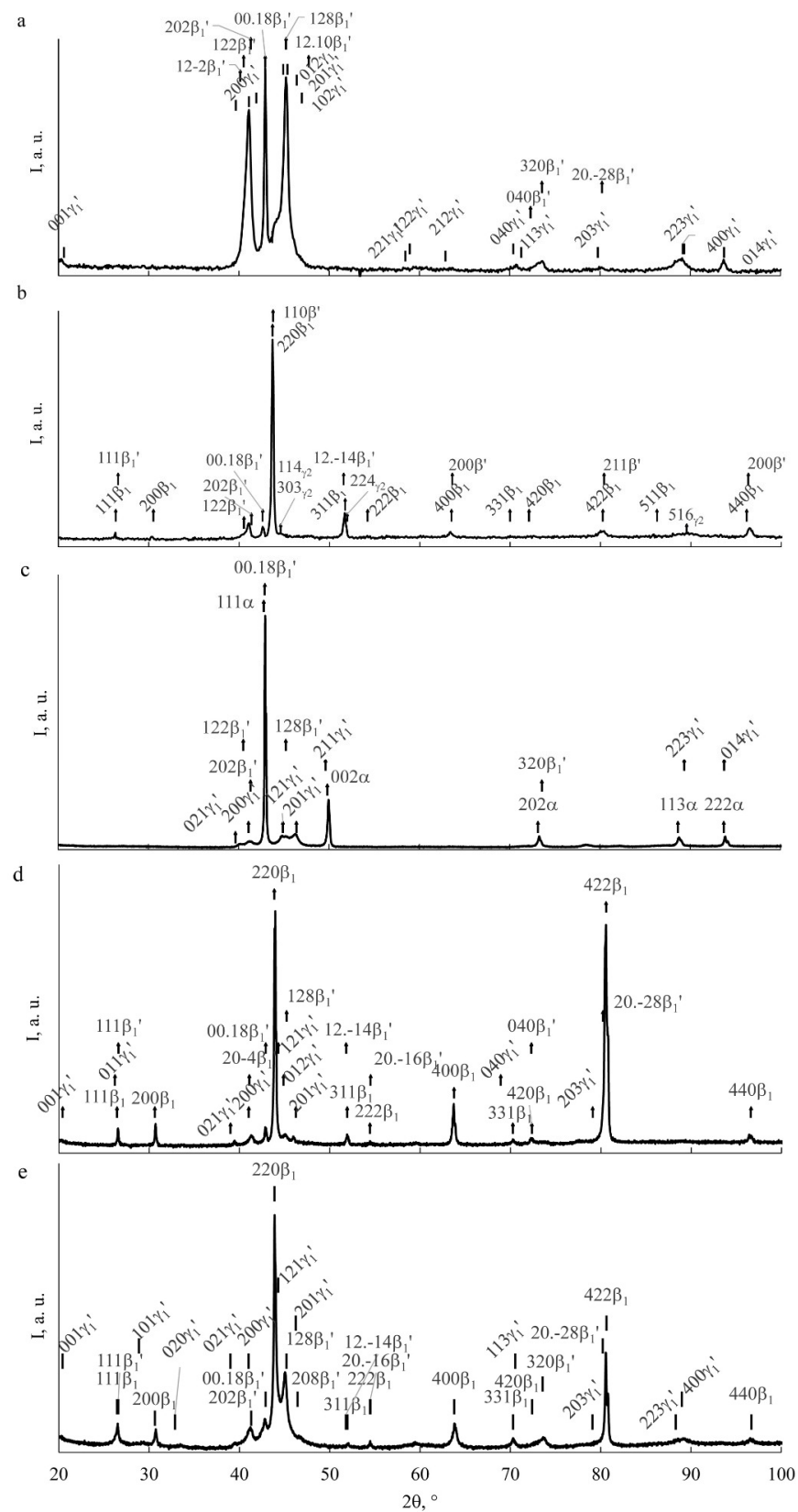


**Figure 1.** X-ray diffractograms typical (a) of the Cu-14Al-3Ni alloy after forging and quenching from 1223 K, (b) of the Cu-14Al-3Ni-0.05B in the cast state; and of the following alloys after forging and quenching from 1223 K for 30 min: (c) Cu-10Al-4.5Ni-0.1B, (d) Cu-14Al-3Ni-0.2B, (e) Cu-14Al-4Ni-0.3B.

Formation of the  $\beta_1$  ordered state in Cu-14Al-3Ni-0.05B, Cu-14Al-3Ni-0.2B and Cu-14Al-4Ni-0.3B alloys both in the cast state (Figure 1b) and after forging and quenching at a temperature of 1223 K (Figure 1d,e) occurred during heating or quick cooling. At the same time, boron doping does not affect the change in the phase composition. However, the main phase in the Cu-10Al-4.5Ni-0.1B alloy is the martensitic phase 18R (Figure 1b), and the ordered phase  $\beta_1$  has not been detected. Obviously, the temperature  $M_f$  is much higher than room temperature. It should be emphasized that the embrittlement  $\gamma_2$  phase was not identified in the interpretation of X-ray diffraction patterns for the alloys under study.

In the Cu-10Al-4.5Ni alloy from the set we studied, martensite that had been formed during abrupt cooling was characterized by a large saw-tooth and lamellar packet morphology of alternating pairs of mutually-twinned crystals. The sizes of the grains of the former austenitic phase preceding the TMT reached 0.5–1 mm (Figure 2a,b).

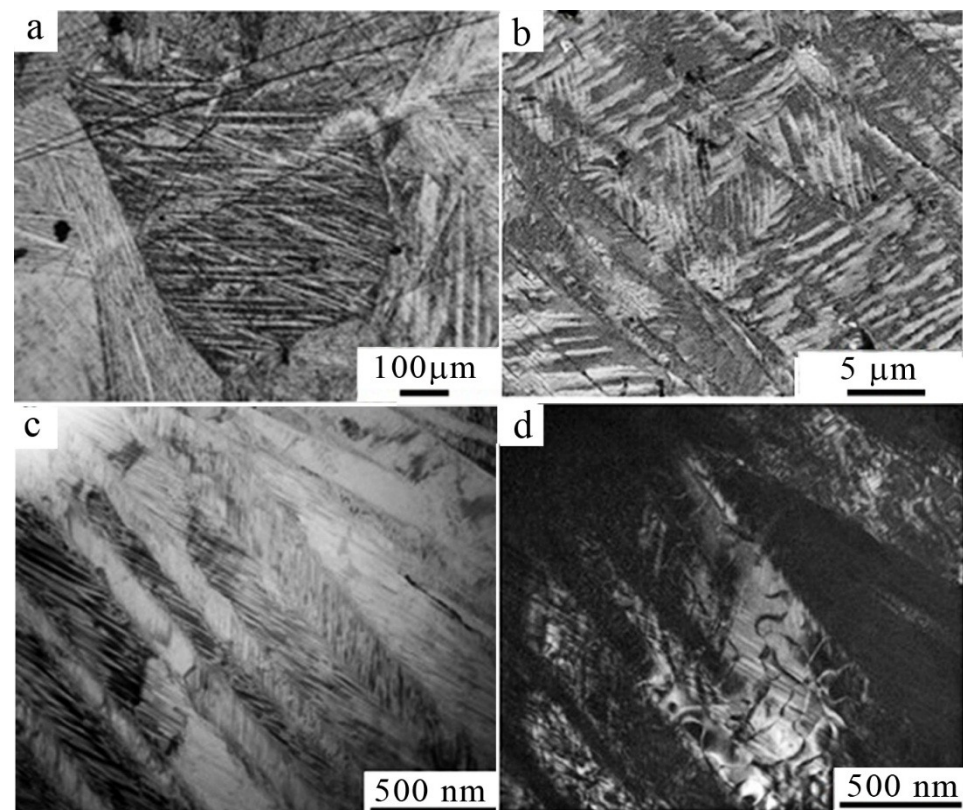


**Figure 2.** OM (a), SEM (b) and TEM (c,d) images of the martensitic microstructure of Cu-10Al-4.5Ni alloy after hot forging and quenching from 1223 K.

In the TEM images (Figure 2c,d), thin secondary nanotwins (Figure 2c) and antiphase boundaries (APBs) in martensite lamellae were clearly observed (Figure 2d). Inherited from  $\beta_1$  austenite, APBs are a consequence of the multi-site nucleation mechanism of the atomic ordering of the  $\beta$ (A2) structure into the B2 and D0<sub>3</sub> superstructure.

The microstructure of the forging-quenched Cu-14Al-3Ni alloy was characterized by the presence of large polyhedral grains ranging in size from 0.5 to 1.5 mm. Obviously, due to chemical liquation during the crystallization process, the regions of different contrast observed in the OM and SEM images (Figure 3a,b) had different elemental composition: they either had an increased Cu content or were enriched in Al and Ni [10]. According to structural TEM studies, the alloy, when cooled to room temperature, underwent TMT with the formation of two martensitic phases  $\beta'_1$  and  $\gamma'_1$  (Figure 3).

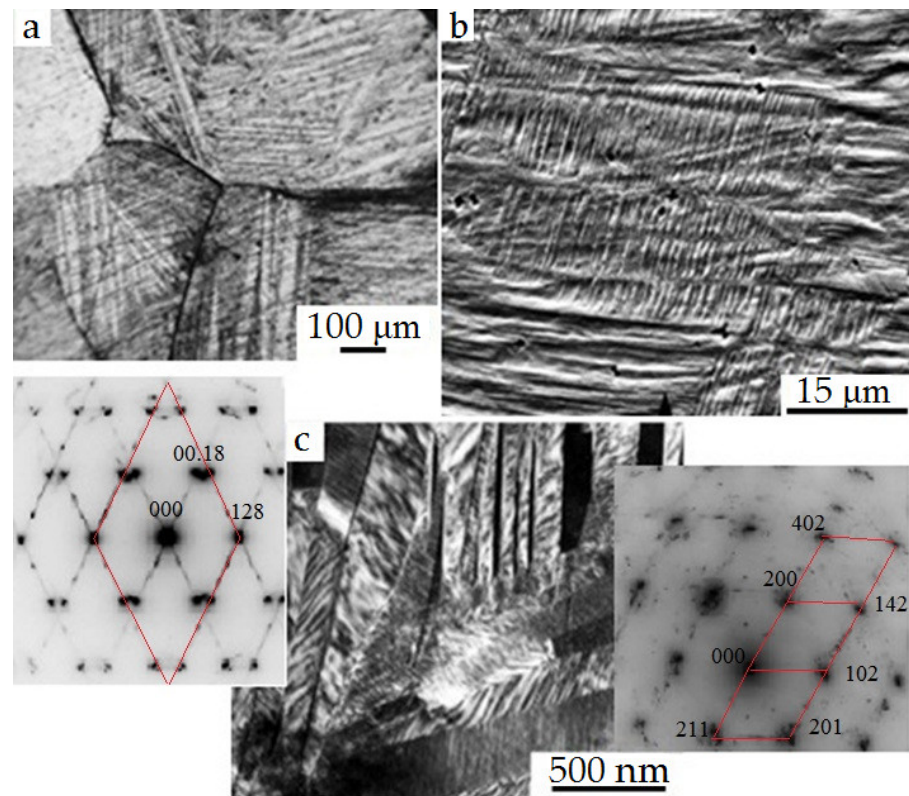


**Figure 3.** The (a) OM, (b) SEM, and (c) TEM images of the martensitic microstructure of the Cu-14Al-3Ni alloy after forging and quenching from 1223 K. The selected area electron diffraction (SAED) patterns (in the insert) correspond to different types of martensite phases (on the left— $\beta'_1$ , on the right— $\gamma'_1$ ). The red lines show the layout of reflections.

To reduce grain sizes in the alloys of the Cu-Al-Ni system, the test on the effect of boron alloying of various concentrations was carried out and comprehensively investigated. The cooling of the cast alloys Cu-10Al-(3, 4.5)Ni-(0.02–0.3)B, as well as Cu-14Al-(3, 4)Ni-(0.02–0.3)B, in air was accompanied simultaneously by (i) eutectoid decomposition according to the reaction  $\beta \rightarrow \alpha + \beta'_2 + \gamma_2$  and (ii) the formation of  $\beta'_1$  martensite. Figure 4 shows an example of an SEM image of a microstructure together with the mapping over chemical elements of the Cu-10Al-3Ni-0.3B cast alloy in the characteristic radiation. In particular, image analysis has shown that the Ni-Al and Al-B particles are present in the alloy.

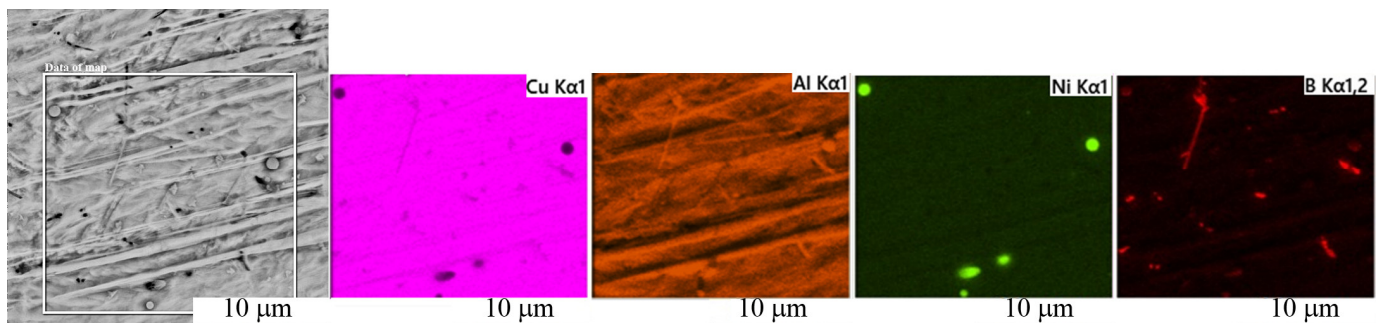


**Figure 4.** Shown are the SEM imaging of microstructure and mapping over chemical elements in characteristic radiation during energy dispersive microanalysis of Cu-10Al-3Ni-0.3B cast alloy.

At the same time, the formation of the microcrystalline structure of alloys with grain sizes of 300–450 microns was observed (Figure 5). Boron particles with sizes of 150–400 nm, localized both at the boundaries and in the volume of grains, are clearly distinguished by

contrast (see Figure 5d). The Ni–Al-based disperse  $\beta'_2$  phase precipitates had dimensions not exceeding 1 micron (see Figure 4). The  $\beta'_2$ -phase particles were previously detected by us in direct resolution by the TEM method in the Cu–14Al–4Ni alloy after its equiaxial compression at 1223 K. It has been established that this phase is precipitated at temperatures below the  $T_{ED}$ , mainly heterogeneously along the boundaries, and with prolonged cooling of the alloy in air, this takes place also in the volume of  $\alpha$  grains [12].

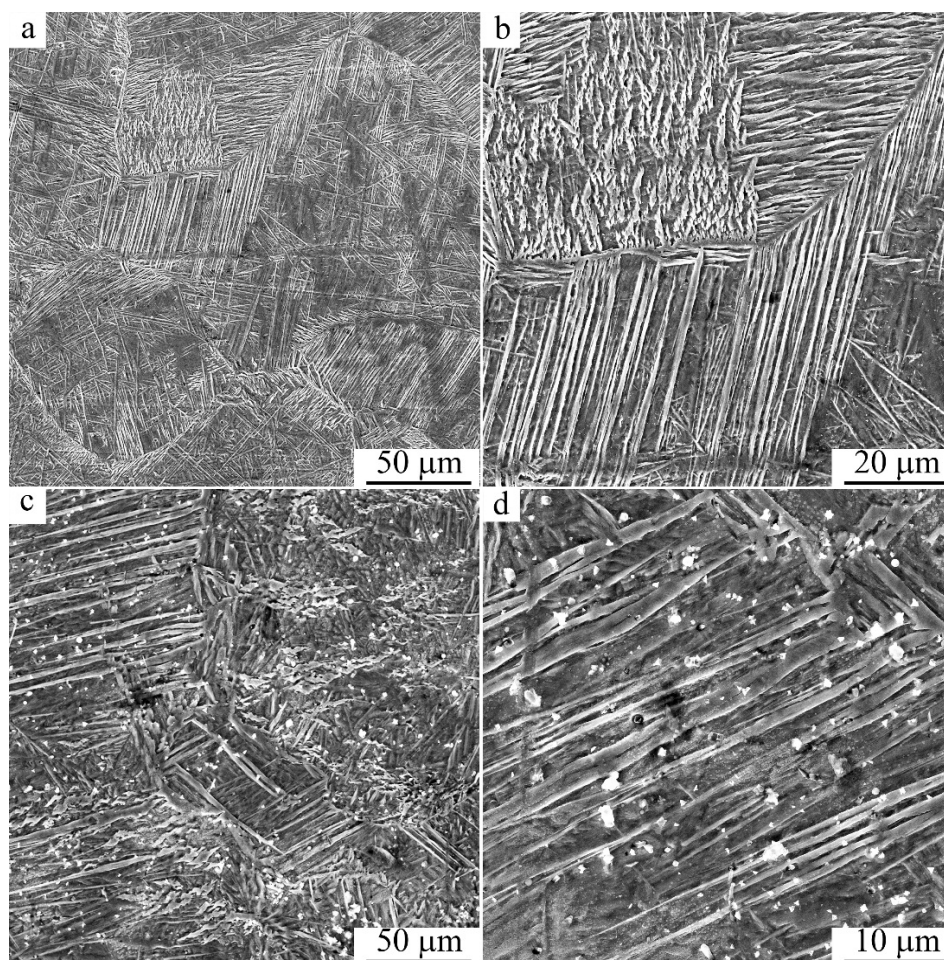


**Figure 5.** (a–d) SEM images of the microstructure of the cast alloys (a,b) Cu–10Al–4.5Ni–0.1B and (c,d) Cu–10Al–3Ni–0.2B.

It should be noted that during cooling, simultaneously with the decomposition, a TMT occurred with the formation of martensite of packet-needle morphology (Figures 4–6). It is known that Cu–Al–Ni alloys with a content of 10 wt% Al experience TMT at high temperatures  $M_s$  and  $M_f$  (850 and 870 K, respectively) [14]. The dependence of the critical temperature of the direct thermoelastic martensitic transformation on the concentration of Al correlates with the microstructure of the alloys in the martensitic state (see Figure 5).

With an increase in the aluminum content of more than 10 wt%, it is possible to almost completely avoid the formation of the  $\alpha$  phase in alloys during crystallization, as is evidenced by X-ray and microstructural studies (Figures 1d,e and 6). Thus, for instance, using the SEM method at different magnifications, in the BSE mode, the  $\gamma_2$  phase with a “clover” morphology (the shape in the form of a clover list) was observed, as well as the same for “rare” packets of martensite formed during the TMT process during cooling at relatively low temperatures (Figure 6).

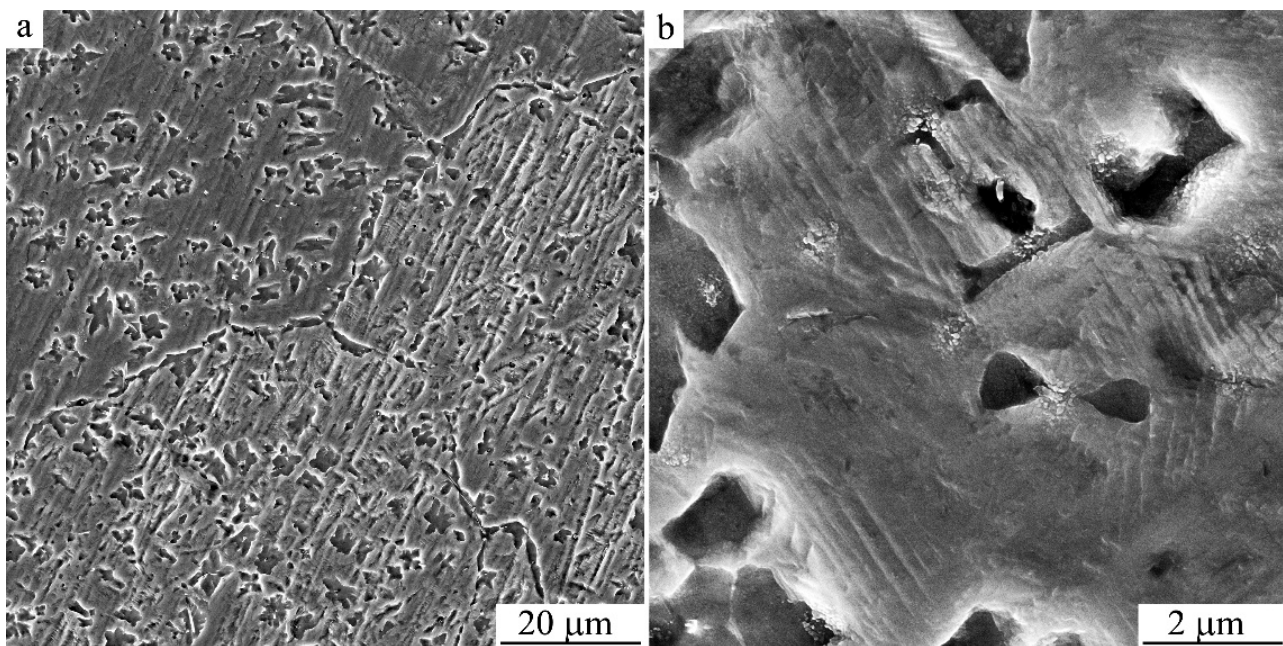


**Figure 6.** (a,b) The SEM images of the microstructure of the cast alloys (a) Cu-14Al-3Ni-0.2B and (b) Cu-14Al-4Ni-0.02B taken in the BSE (backscattered electrons) mode.

To achieve an ordered state and the formation of austenite grains in boron-doped alloys, high-temperature thermomechanical treatment was also carried out, which included hot forging and additional heating for quenching from a single-phase high-temperature  $\beta$  region (of existence of the  $\beta$  phase). Alloys with an Al content of 14 wt% after this treatment, on the one hand, had an ordered state  $D0_3(\beta_1)$  of a superstructure with a doubled period of the unit cell (see Figure 1d,e), which was capable of experiencing TMT during rapid cooling. On the other hand, it was able to prevent decomposition, eliminate chemical heterogeneity in composition, and completely realize the TMT (see Figure 1c–e). In addition, equiaxed coarsened grains up to 150 microns in size were observed, which is almost 10 times smaller than in forged prototype alloys without boron. Boron particulates, when localized at the boundaries and in the volume of grains, restrained the movement of the boundaries, exerting a “barrier” effect during heating for quenching, without affecting the change in phase composition.

The micro addition of boron (0.02 wt%) in the alloys of the Cu-Al-Ni system has also affected the reduction in grain size (Figure 7). After the heating and quenching, the grain sizes were two times smaller (400–500 microns) than in the boron-free alloys, corresponding to the base (boron-free) composition (Figure 7a).

In the SEM image (Figure 8a), the grain structure of the Cu-10Al-4Ni-0.2B-alloy after thermomechanical treatment was illustrated. It was found that the average grain size was 20  $\mu\text{m}$ . In the TEM images of the fine structure of the alloy (Figure 8b,c), the martensitic phases  $\beta'1$  and  $\gamma'1$  were observed in mainly single-packet morphology within the initial austenitic grains. The SAED pattern (Figure 8d) contains extra reflexes characteristic of martensitic phases. Boron particulates of a rectangular shape and in the form of cuboids localized in the volume of the microstructure did not exert a “barrier” effect to TMT.

The mechanical properties of the studied alloys are shown in Table 1 and Figure 9 in comparison with composition-corresponding alloys without boron additives. As can be seen, the best properties in terms of strength and ductility in uniaxial tension were demonstrated by alloys alloyed with boron. The most durable and ductile were ( $\alpha + \beta$ ) alloys, with an aluminum concentration of 10 wt%. For example, the Cu-10Al-4.5Ni-0.1B alloy after HTMT was mainly in the austenitic state and demonstrated a relatively high strain hardening (630 MPa), and, at the same time, a significant accumulated relative

elongation, which amounted to 9%. However,  $\beta$ -alloys (14 wt% Al) did not show improved mechanical properties. First of all, this is due to the coarse-grained state of the alloys and the presence of large-sized martensite packets. Obviously, the accumulated internal stresses were concentrated at the grain boundaries and the joints of the martensite packets. Microstructure studies and the analysis of the obtained data of mechanical tests on the uniaxial tension showed that boron alloying and quenching leads to a size refinement of the grain structure alloys, and, as a consequence, to an increase in tensile strength ( $\sigma_u$ ), yield strength ( $\sigma_{0.2}$ ), and elongation to fracture ( $\delta$ ) necessary for the implementation of SME.

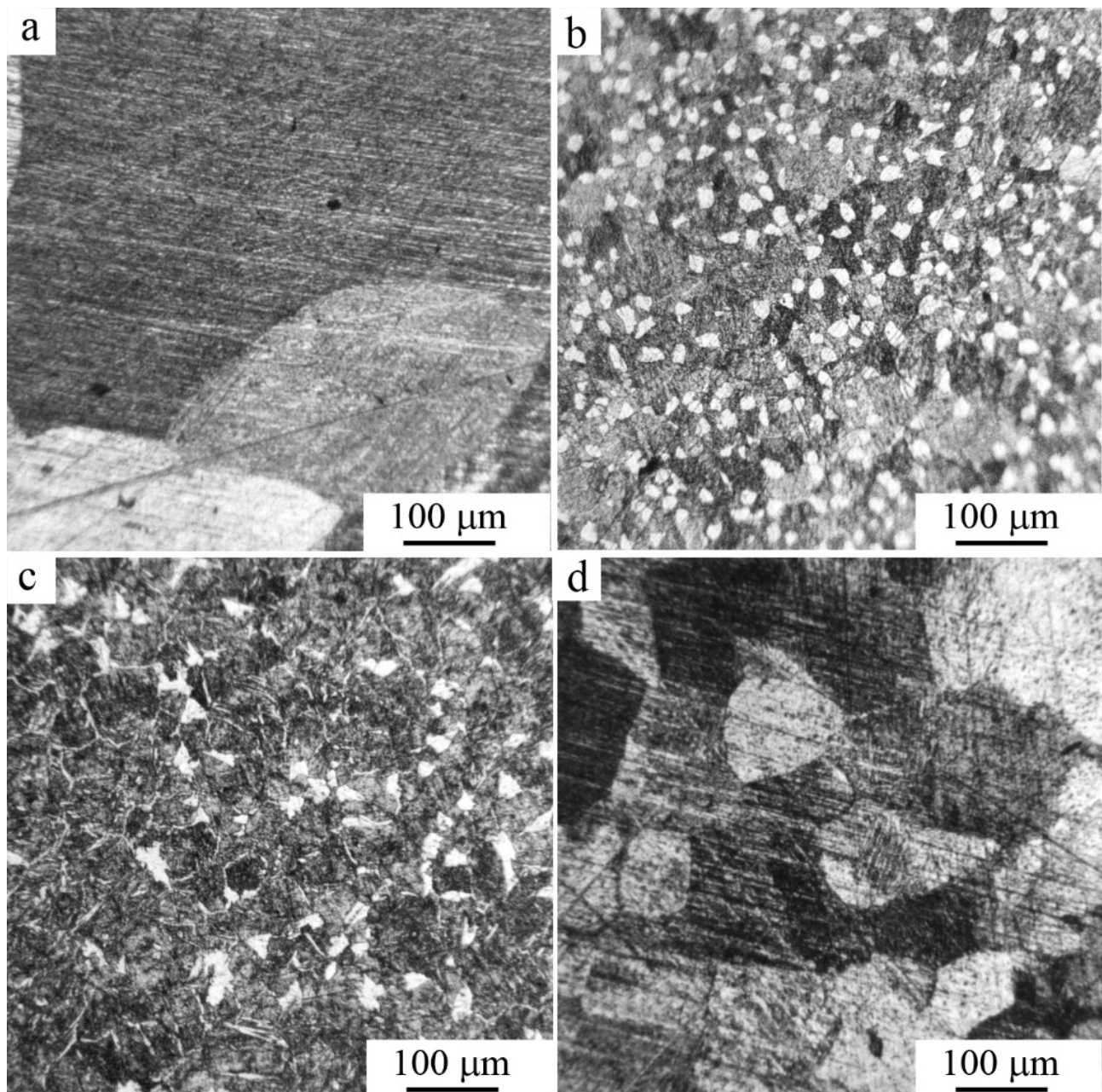


**Figure 7.** (a–d) OM images of fine-grained microstructure of the (a) Cu-10Al-4.5Ni-0.02B, (b) Cu-10Al-4.5Ni-0.1B, (c) Cu-10Al-4Ni-0.2B, and (d) Cu-14Al-3Ni-0.2B alloys after their forging and quenching in water from 1223 K.

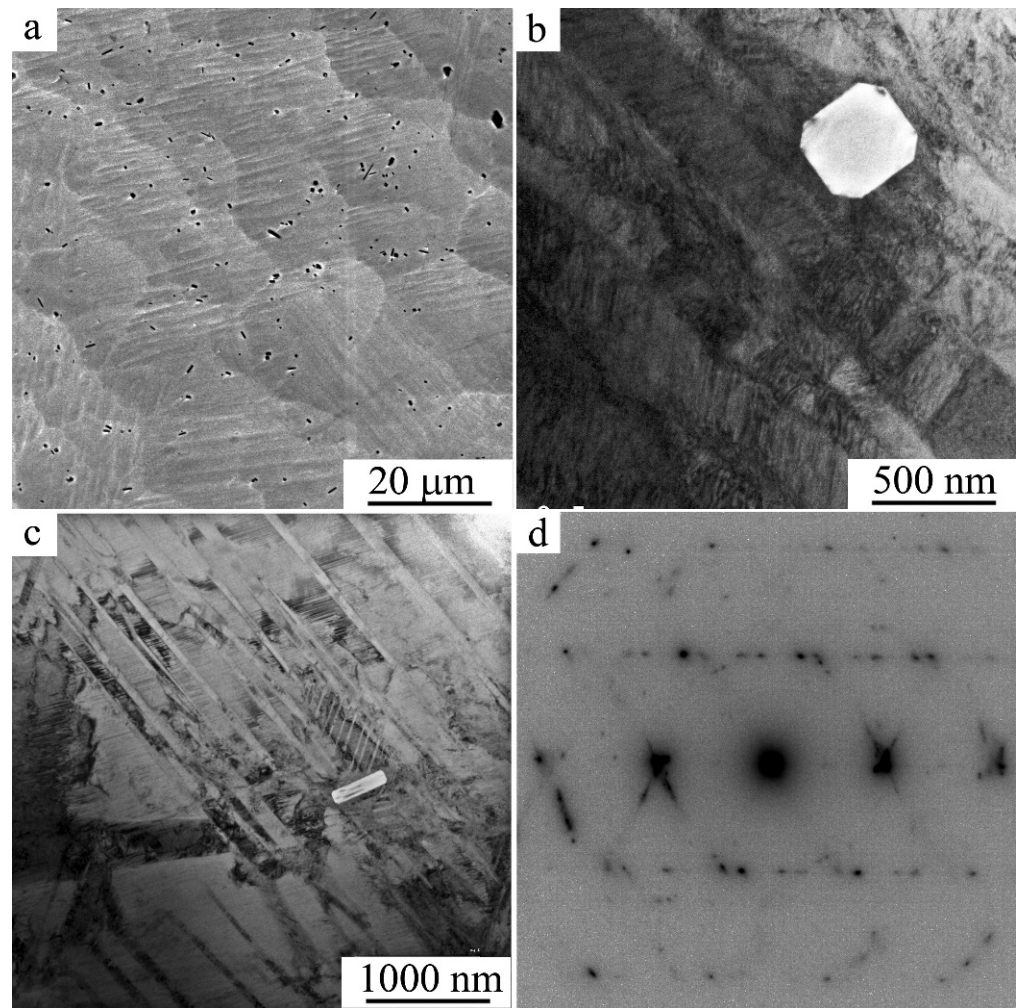


**Figure 8.** The (a) SEM and (b,c) TEM images of the microstructure and (d) the corresponding SAED pattern of the Cu-10Al-4Ni-0.2B-alloy martensite after forging and quenching in water from 1223 K.

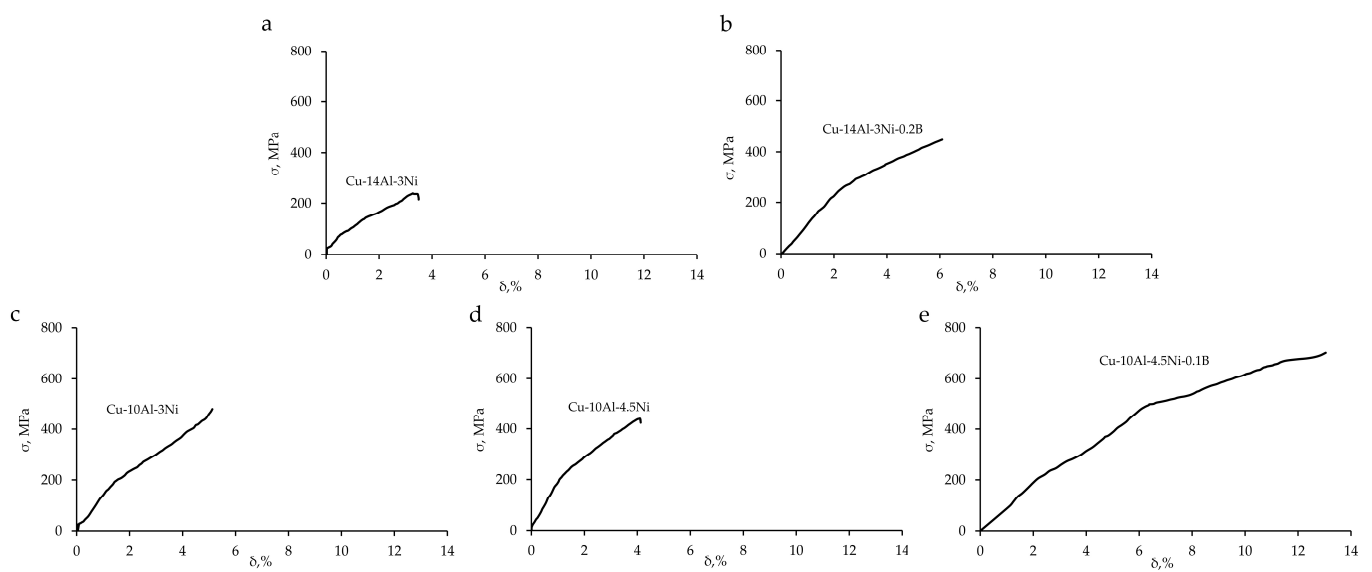


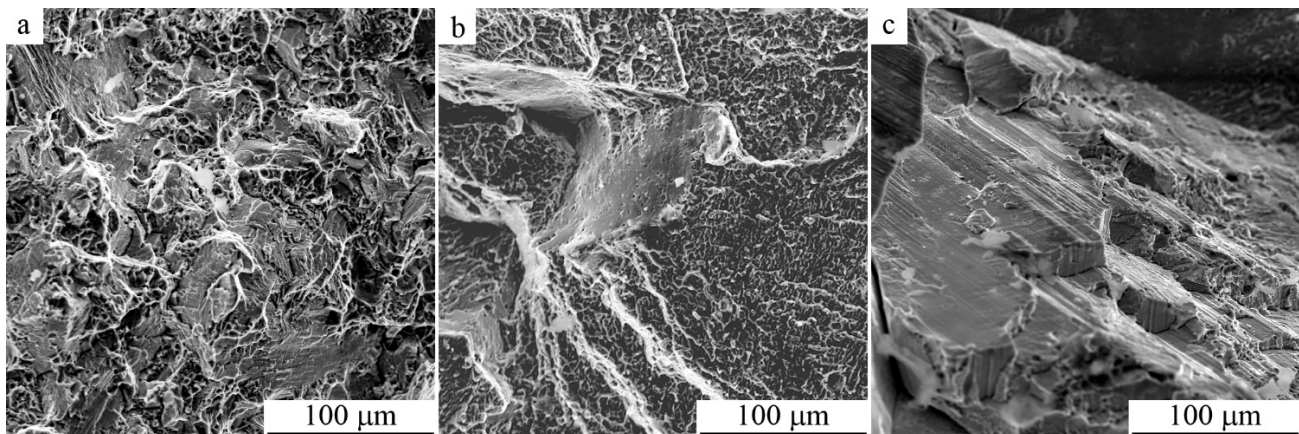
**Figure 9.** Tensile  $\sigma$ - $\delta$  (stress-strain) curves of the (a) Cu-14Al-3Ni; (b) Cu-14Al-3Ni-0.2B; (c) Cu-10Al-3Ni; (d) Cu-10Al-4.5Ni, (e) Cu-10Al-4.5Ni-0.1B alloys after their forging and quenching from 1223 K.

**Table 1.** Mechanical properties and average grain size (d) of the Cu-Al-Ni-(B) alloys after their forging and quenching from 1223 K.

| Composition        | $\sigma_u$ , MPa | $\sigma_{0.2}$ , MPa | $\delta$ , % | d, $\mu\text{m}$ |
|--------------------|------------------|----------------------|--------------|------------------|
| Cu-10Al-3Ni        | 520              | 200                  | 5            |                  |
| Cu-10Al-4.5Ni      | 400              | 230                  | 4            | 900              |
| Cu-10Al-4.5Ni-0.1B | 630              | 220                  | 9            | 100              |
| Cu-10Al-4.5Ni-0.2B | 820              | 200                  | 6            | 150              |
| Cu-14Al-3Ni        | 250              | 120                  | 3            | 1000             |
| Cu-14Al-3Ni-0.2B   | 640              | 270                  | 6            | 150              |
| Cu-14Al-4Ni-0.02B  | 490              | 100                  | 5.5          | 500              |

It is necessary to emphasize that the addition of boron provided a “barrier” effect to grain growth, which led to reduced grain sizes in prototype alloys, and, consequently, to increased strength and ductility characteristics being required for practical applications.

The fractographic analysis of Cu-Al-Ni alloys with boron addition after tensile tests showed that the fractures have a quasi-tough character, unlike the alloys without boron. Figure 10a,b clearly shows areas of both the river (brook) and shallow-dimple character of the fracture, as well as the smooth zones of intragrain cleavage. Localized boron particles in the body of a grain and along the grain boundaries, apparently, provided an increased deformability of alloys with the appearance of a tough fracture mechanism. The alloy with the lowest boron content (0.02 wt%) was characterized by a brittle intercrystalline fracture, which occurred along the grain boundaries and martensite packets (Figure 10c). Such a concentration of boron, apparently, did not provide high tensile plasticity, but, nevertheless, allowed us to achieve increased values of the tensile strength  $\sigma_u$  and elongation to fracture  $\delta$ .

**Figure 10.** SEM images of surface of the (a) Cu-10Al-4Ni-0.1B, Cu-14Al-3Ni-0.2B (b) and Cu-14Al-4Ni-0.02B (c) alloys after their forging and quenching in water from 1223 K.

#### 4. Conclusions

1. X-ray and phase analysis data showed that after forging and subsequent quenching from a single-phase  $\beta$  region, the  $A2(\beta) \rightarrow B2(\beta_2) \rightarrow D0_3(\beta_1)$  ordering occurs in the alloys with an increased content of aluminum, and with the appearance of the superstructure of a higher rank. This, in turn, ensures the passing of TMT, with the formation of the martensitic phases 2H and 18R in the alloys.
2. Via analyzing the data of microstructural studies, it was established that in boron-doped alloys, the Al-B and Al-Ni-B particles, for which the dimensions do not exceed 400 nm, are uniformly distributed over the volume of the alloys. The localization of boron particles along grain boundaries is also established. In this case, there is a chemical separation over boron.

3. It has been found that microalloying with boron, in concentrations from 0.02 to 0.2 wt%, provides grain size refinement up to 500–100 microns in the cast  $\alpha + \beta$  and  $\beta$  Cu-Al-Ni-B alloys, whereas in the corresponding cast alloys without boron, grain sizes attain even a 1.5 mm size.
4. Boron-doped alloys have also demonstrated, during uniaxial tensile mechanical tests, the effect of the strengthening and plasticity increase. Thus, for instance, the initially coarse-grained prototype alloy Cu-14Al-3Ni has exhibited the values of the ultimate tensile strength  $\sigma_u$  (250 MPa), the yield strength  $\sigma_{0.2}$  (120 MPa), and elongation to fracture  $\delta$  (3%), which are almost 2.5 times less than those for the alloy with the addition of 0.2 wt% B.
5. The alloys with the lowest content of boron, i.e., 0.02 wt% B, did not exhibit any size refinement of the grain structure, but, nevertheless, their mechanical characteristics turned out to have been higher in comparison with the boron-free alloys. In addition, changing the character of the alloy's fracture, namely from quasi-tough, in the case of boron content from 0.1 to 0.2 wt% B, to inter-crystalline, in the case of boron content from 0 to 0.02 wt% B, was established.

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