X-ray analysis of the Cu-Zn alloys system subjected to ECAP and subsequent rolling

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Abstract. The results of X-ray diffraction analysis aimed to reveal the features of the evolution of microstructure parameters as a result of equal-channel-angular pressing and subsequent flat rolling of the Cu-Zn alloys system with different Zn (10 and 30 wt. %) contents and, as a result, different stacking fault energies are presented.

1. Introduction
The method of severe plastic deformation (SPD) makes it possible to form bulk ultrafine-grained (UFG) nanostructured states in various metallic materials, characterized by attractive structural and functional properties. Flat rolling is a method of deformation processing that allows one to continue improving the microstructure of these materials and to give blanks the geometric dimensions and shape required for the manufacture of various products [1]. Bulk UFG nanostructured alloys with a lower stacking fault energies (SFE) than that characteristic for the corresponding pure metals are characterized by even smaller grain sizes [2].

The results of microstructure investigations performed by transmission electron microscopy (TEM) as applied to the Cu-10 wt.% Zn and Cu-30 wt.% Zn alloys subjected to ECAP and subsequent flat rolling also indicate the formation of UFG states with nanosized grains and nanotwins [3]. SFE of these alloys differs by 2.5 times. X-ray structural analysis is a powerful tool for investigation of UFG nanostructured metallic materials, which makes it possible to estimate a number of important additional parameters in relation to those established by the TEM method [3].

The purpose of the investigations, the results of which are presented in this paper, is the application of the X-ray structural analysis method for the comparative characterization of the microstructure of Cu-10 wt.% Zn and Cu-30 wt.% Zn alloys subjected to ECAP and subsequent flat rolling.

2. Experimental
The Cu-Zn alloys with a content of 10 and 30 wt% Zn were selected as the material for research in this work. The SFE values of these alloys were ~ 35 mJ·m⁻² and ~ 14 mJ·m⁻², respectively. The prepared samples of Cu-10 wt.% Zn and Cu-30 wt.% Zn alloys were subjected to two passes of ECAP at T = 150, 300 °C, respectively, in a tool with an angle of intersection of the channels φ = 90 ° along the Bc route. Further, the obtained billets, heated to the temperatures selected for the corresponding alloys, were repeatedly passed between the rotating rolls of the rolling mill until a reduction degree of 95% was reached. The choice of different temperatures of deformation processing is associated with the requirement to preserve the integrity of the samples.
X-ray diffraction analysis was performed using a Rigaku Ultima IV diffractometer (the "Bragg-Brentano" scheme at an accelerating voltage of 40 kV and a current of 40 mA at room temperature). The X-ray tube anode was copper, and the corresponding characteristic radiation length was $K_{\alpha 1} = 0.15406$ nm. X-ray measurements were carried out from a longitudinal horizontal section of the workpieces in the initial states and states after ECAP, and from the plane of the rolled samples.

Before measurements, the surface of the workpieces was polished with diamond suspensions. The MAUD software was used to calculate the crystal lattice parameter ($a$), the size of the coherent scattering domains ($d_{XRD}$), elastic microdistortions ($\langle\varepsilon^2\rangle^{1/2}$) of the crystal lattice, and the dislocation density ($\rho$) [4]. The concentration of twins (the twins probability) $\beta$ was estimated by determining the displacement of the diffraction peaks (111) and (200) on the X-ray diffraction patterns of the material under study relative to the initial state [5].

3. Results and analysis

Figure 1 a, b shows the X-ray diffraction patterns of the investigated states of the alloys. All X-ray patterns are characterized by a set of diffraction peaks characteristic of single-phase copper alloys with an FCC lattice. The relative intensity of the peaks changes as a result of broadening and displacement of the peaks due to changes in the microstructure depending on the nature of the deformation treatment.

Figure 1a shows the diffraction patterns of the Cu-10 wt% Zn alloy in the initial state, and states after two passes of ECAP and ECAP with subsequent flat rolling to a maximum reduction degree of 95%. Figure 1b shows the diffraction patterns of the Cu-30 wt% Zn alloy of similar states. As the degree of applied deformation increases, the intensity of the peaks changes. During SPD, the tendency of the change in the peaks (111), (200), and (220) is different for the alloys. In the Cu-10 wt% Zn alloy, the intensity of the (111) peak decreases in the ECAP state with flat rolling with reduction degree of 95%, while in the Cu-30 wt% Zn alloy it increases. The intensity of the (200) peak in both alloys during ECAP with flat rolling with a reduction degree of 95% decreases in comparison with the initial state. There is also a sharp increase in the intensity of the (220) peak in the alloys in comparison with the initial state. This is explained by possible changes in the crystallographic texture of the samples, apparently, the grains acquire preferential orientations.

It should be noted that, in both alloys, the peaks in the diffraction patterns with an increase in the deformation degree are shifted towards small values of the angles 2$\theta$ in comparison with the peaks for pure copper, which indicates an increase in the crystal lattice parameter (the lattice parameter of pure copper 0.36150 nm) due to the complete dissolution of Zn atoms in a copper matrix (table 1). 

![Figure 1. General view of diffraction patterns of Cu-10 wt% Zn alloy (a) and Cu-30 wt% Zn alloy (b) in different structural states.](image)
The results of the following parameters such as $a$, $d_{XRD}$, $<\varepsilon^2>^{1/2}$, $\rho$ and $\beta$ for all realized deformation values are presented in tables 1 and 2.

In the initial coarse-grained state, the lattice parameter of the Cu-10 wt.% Zn alloy was 0.36395±0.00003 nm (table 1). Carrying out ECAP and then subsequent flat rolling results in changes in the values of the lattice parameters almost within the measurement error. In this case, ECAP and subsequent flat rolling lead to a significant increase in the dislocation density. As the degree of deformation increases, the $d_{XRD}$ values decrease, the obtained XRD results do not contradict the TEM results ($d_{TEM}$). There is also a decrease in the $<\varepsilon^2>^{1/2}$ values, which indicates the recovery processes. In [3], the TEM method revealed the formation of nanotwins in the structure as a result of SPD. X-ray diffraction data also indicate the formation of deformation twins in this alloy in various structural states (table 1).

Table 1. Lists of the XRD-measured lattice parameters ($a$), crystallite size ($d_{XRD}$), dislocation density ($\rho$), elastic microdistortion level ($<\varepsilon^2>^{1/2}$), twin probability ($\beta$) and average size of the structural elements ($d_{TEM}$) of the ECAP + flat rolling Cu–10 wt.% Zn sample.

|                | $a$, nm  | $d_{XRD}$, nm | $\rho$, $10^{14}$ m$^{-2}$ | $<\varepsilon^2>^{1/2}$, % | $\beta$, $10^{-4}$ | $d_{TEM}$, nm [3] |
|----------------|----------|---------------|-----------------------------|------------------------|-------------------|-------------------|
| Non rolled     | 0.36395±0.00003 | -             | 0.142                       | 0.031                  | 46.5              | 117·10$^3$±5·10$^3$ |
| ECAP – 2 p     | 0.36372±0.00007 | 180±5         | 1.0                         | 0.13                   | 41.5              | 800±66            |
| + roll 30%     | 0.36354±0.00012 | 142±5         | 1.7                         | 0.18                   | 37.8              | -                |
| ECAP – 2 p     | 0.36368±0.00010 | 79±2          | 2.9                         | 0.17                   | 40.7              | -                |
| + roll 40%     | 0.36346±0.00011 | 73±1          | 3.6                         | 0.19                   | 36.2              | -                |
| ECAP – 2 p     | 0.36388±0.00012 | 54±1          | 3.9                         | 0.15                   | 45.0              | 375±49            |
| + roll 80%     | 0.36401±0.00009 | 50±1          | 3.4                         | 0.13                   | 47.5              | 292±21            |
| ECAP – 2 p     | 0.36389±0.00007 | 45±1          | 3.6                         | 0.12                   | 45.1              | 220±30            |
| + roll 95%     |           |               |                             |                        |                   |                   |

The strength of the alloy in the initial state is 240 ± 30 MPa, after ECAP it is 413 ± 78 MPa, and after ECAP with subsequent flat rolling with reduction degree of 95%, the strength increases up to 670 ± 120 MPa [3]. Thus, the reason for the increase in the strength of the alloy can be grain refinement, increase of dislocation density, concentration of deformation twins, and the evolution of crystallographic texture with an increase in the strain during SPD.

In the Cu-30 wt.% Zn alloy the lattice parameter is higher than in the Cu-10 wt.% Zn alloy, which is apparently associated with an increased content of alloying atoms in the solid solution. With an increase in the reduction degree during rolling in general, the $a$ value in the Cu-30 wt.% Zn alloy increases (table 2). Apparently, this may be due to the peculiarities of the forming microstructures, in which the $d_{XRD}$ sizes have significantly decreased. The dislocation density increases with the applied strain. In the case of the Cu-30 wt% Zn alloy with a lower SFE after SPD, the twins probability is 2.8 times higher than that of the Cu-10 wt% Zn alloy.

The results of the performed investigations of alloys in UFG states, obtained by ECAP and subsequent flat rolling, indicate an increased probability of twins in an alloy with a high Zn content. This observation correlates with the known results obtained for coarse-grained Cu-Zn alloys with different SFE. At the same time, it is known that twinning processes play an important role in the deformation of coarse-grained Cu-Zn alloys with a lower SFE [6]. In our case, it was found that
rolling of alloys in the UFG state does not lead to an increase in the probability of twins (tables 1 and 2). This phenomenon can be explained by the activation of detwinning processes. A similar process, which consists in the transformation of atomically flat coherent twin boundaries into incoherent ones, and then, as the applied strain increases, the transformation of incoherent boundaries into high-angle grain boundaries was previously observed as a result of investigation a Cu-Zn alloy subjected to SPD by high pressure torsion [7]. More solid conclusions on this issue will be made based on the results of planned studies of the evolution of the crystallographic texture in these alloys in the UFG states during flat rolling.

The \( \langle \varepsilon^2 \rangle^{1/2} \) values for a given alloy increase with an increase in the deformation degree and remain higher than for a Cu-10 wt% Zn alloy.

The sizes of structural elements \( d_{\text{TEM}} \) estimated by TEM decrease during SPD in comparison with the initial state. However, the difference in the data obtained by TEM and XRD is very significant. This is due to the fact that the X-ray diffraction analysis method determines the \( d_{\text{XRD}} \) values associated with the inner regions of grains with a slightly distorted crystal lattice, while the TEM method measures the total grain size, which includes highly distorted near-boundary regions [8]. Also, the anisotropy of the grain shape can significantly affect the results obtained by TEM and XRD. The TEM method is used to measure the grain size in a plane parallel to the surface of the sample, and by XRD, the grain size is measured in the direction perpendicular to this plane.

### Table 2.

| Sample Description                  | \( a \), nm | \( d_{\text{XRD}} \), nm | \( \rho \), \(10^{14} \) m\(^{-2}\) | \( \langle \varepsilon^2 \rangle^{1/2} \), % | \( \beta \), \(10^{-4}\) | \( d_{\text{TEM}} \), nm [3] |
|------------------------------------|-------------|--------------------------|------------------|------------------|------------------|------------------|
| Non rolled                         | 0.36770±0.00008 | -                        | 0.052            | 0.003            | 121.1            | 93·10\(^3\)±3·10\(^3\) |
| ECAP – 2 p + roll 30%              | 0.36762±0.00019 | 111±6                    | 2.4              | 0.19             | 122.7            | 290±55           |
| ECAP – 2 p + roll 40%              | 0.36810±0.00015 | 79±2                     | 4.3              | 0.25             | 132.8            | -                |
| ECAP – 2 p + roll 60%              | 0.36775±0.00014 | 85±1                     | 2.7              | 0.17             | 125.4            | -                |
| ECAP – 2 p + roll 90%              | 0.36782±0.00018 | 66±2                     | 5.9              | 0.29             | 126.8            | -                |
| ECAP – 2 p + roll 95%              | 0.36783±0.00017 | 38±1                     | 10.3             | 0.29             | 127.0            | 161±7            |
| ECAP – 2 p + roll 95%              | 0.36793±0.00014 | 33±1                     | 10.3             | 0.25             | 129.2            | 130±10           |

The revealed structural changes lead to an increase in strength properties of the Cu-30 wt.% Zn alloy from 320 ± 40 MPa in the initial state to 590 ± 89 MPa after ECAP and 812 ± 130 MPa after ECAP and flat rolling with reduction degree of 95% [3].

### 4. Conclusions

As a result of the application of X-ray diffraction analysis, the features of the microstructure of the Cu-10 wt% Zn and Cu-30 wt% Zn alloys subjected to ECAP and subsequent flat rolling and having different SFE are revealed.

With an increase in the applied deformation degree, the lattice parameter \( a \) of the Cu-10 wt% Zn alloy does not change, while the lattice parameter \( a \) of the Cu-30 wt% Zn alloy increases insignificantly. At the same time, the \( d_{\text{XRD}} \) values in both alloys decrease, while in the Cu-30 wt% Zn
alloy the values remain lower. The dislocation density $\rho$ values during ECAP and ECAP with subsequent flat rolling increase for both alloys. The dislocation density in all structured states of Cu-30 wt% Zn alloy is higher. Values $\langle \varepsilon^2 \rangle^{1/2}$ during ECAP increase for Cu-10 wt% Zn and Cu-30 wt% Zn alloys. Subsequent flat rolling changes the data only slightly. However, the values are higher for Cu-30 wt% Zn alloy. These differences can be associated with the temperature conditions during deformation and the SFE values. The values of twin probabilities $\beta$ of the alloys differ by about 3 times. The data correspond to the previously obtained results of TEM investigations and practically do not depend on the deformation degree. It can be concluded that in the process of SPD and subsequent flat rolling, the processes of twinning and detwinning take place in parallel.

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