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THE MORPHOLOGY OF EUTECTIC COPPER OXIDES I (Cu_2O) IN THE PROCESSING OF WIRE ROD AND WIRES MADE FROM ETP GRADE COPPER

Eutectic copper oxides (Cu_2O) crystallize during the copper solidification process in the ETP grade copper which leads to high oxygen concentrations in interdendritic spaces. It has been experimentally found that they can be regular or elongated, and their size reaches several micrometres. During the multi-cage hot rolling process, homogenization of the oxide distribution in the entire volume of the wire rod occurs. This process is carried out in the soft copper matrix. Throughout the drawing process the fragmentation of oxides transpires along with changes in the shape from angular to more oval in a degree depending on the size of the deformation (wire diameter). Microcracks, fissures and local stress fields in the reinforced copper matrix arise around the oxide particles. The article presents the results of research on the evolution of copper oxides in ingots, wire rods and wires. The results of investigations of the wires properties and the limitations of the drawing process, especially of microwires, are presented.

Keywords: Cu-ETP, Eutectic copper oxides (Cu_2O), evolution of Cu_2O, fragmentation of oxides

1. Introduction

Electrolytic Tough Pitch (ETP) Copper is a grade of copper which typically contains between 150 and 200 ppm wt. of oxygen; thus making it a hypoeutectic copper-oxygen alloy. Cu_2O oxide crystallizes at 1066°C and considering the atomic properties of its components 1 g of oxygen forms 9 g of Cu_2O oxide, e.g. 1800 g of hypoeutectic Cu_2O oxide which crystallized during the solidification process involves 200 g of oxygen for one ton of liquid copper [1]. Current European standards that describe physicochemical properties of copper wire rod allow oxygen content up to 400 ppm. wt., and according to the American standards of ASTM, this content must not exceed 600 ppm. wt., which means there are several kilograms of Cu_2O oxide for every ton of ETP grade copper [2,3]. As the solidification proceeds Cu_2O oxide crystals segregate into interdendritic spaces and undergo evolution during the rolling and further wire drawing process in terms of shape and dimensional changes, constituting a permanent component of the internal copper structure [4]. In many research papers analysis of the formation and changes in the shape and dimensions of single crystals of Cu_2O during metallurgical synthesis may be found [5-10]. There is, however, no information on their evolution during rolling and drawing processes, which are indirect processes of producing wires intended for the production of a whole range of applications for electrical purposes. According to the literature analysis over 50% of copper wires ruptures in the drawing process are caused by the presence of inclusions, including the presence of Cu_2O [11-14]. Therefore, it is crucial to analyze the fragmentation and evolution of the shape of the brittled oxide which occurs in the copper rolling and wire drawing processes. H. Choa et al. have analyzed the state of the stresses around the inclusions, including around Cu_2O oxide during the deformation of the copper matrix and the effect of the strain value, particle size and distance between them on cracking of the wires during the drawing process [15]. A similar analysis of the oxide particle interaction with the copper matrix was executed with the use of the finite element method by calculating the state of stress around the particle [16]. It was also noted that during the drawing process, the copper oxide particles are the source for the nucleation of two voids on both sides of each particle along the axis of the wire and the length of these voids increases along the drawing direction as both the strain value and the reduction ratio accumulate. Taking the abovementioned analyses into consideration it should be assumed that copper with the oxygen content above 80 ppm wt. (maximum solubility in the solid state), i.e. with the chemical purity below 4N, is a two-phase material with a composite structure composed of a metallic copper matrix and single crystals of Cu_2O copper oxide [16,17].

The aim of this research work is to analyze the morphology of the shape and dimensions of Cu_2O single crystals in the wire rod and their evolution occurring during drawing process of wires and microwires along with the analysis of the wire microstructure depending on the degree of the applied strain.

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2. Materials and methods

The analysis of the morphology of the shape and dimensions of the eutectic Cu_2O oxide was carried out on the copper ingot from the continuous casting and rolling line, wire rods and wires of various diameters after the drawing process. Light microscope (Zeiss Axiocam) and scanning electron microscope (Hitachi S-3500N) were used for these analyses. In order to determine the effect of tensile and compressive forces on oxide fragmentation during metal forming processes, tensile and compression tests were carried out on wire rod and afterwards observations of longitudinal metallographic specimens of deformed samples in terms of quality, shape and dimensions of oxides were conducted. The macrostructure of the ingot and the place of sampling for testing is shown in Fig. 1.

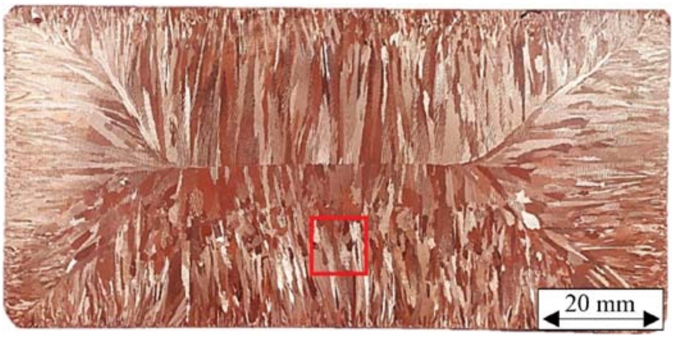

Fig. 1. Macrostructure of the ingot with the marked sampling place indicated for the testing of the oxide precipitations presence

3. Results and discussion

During solidification Cu_2O oxide is subjected to segregation in interdendritic spaces, as presented in the metallographic specimens of the copper ingots in Figures 2 and 3.

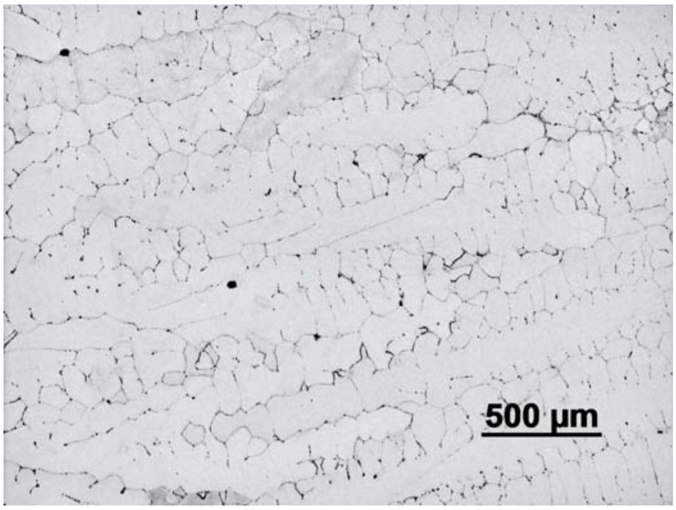

Fig. 2. Cross-section of the copper ingot, magnification 100×. Visible large clusters of oxides on cell boundaries

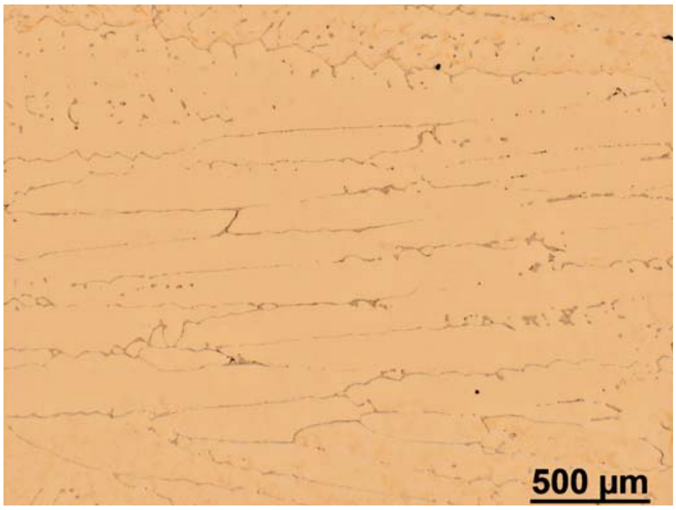

Fig. 3. Cross-section of the copper ingot, magnification 100×. Visible segregation of oxides on dendrite boundaries

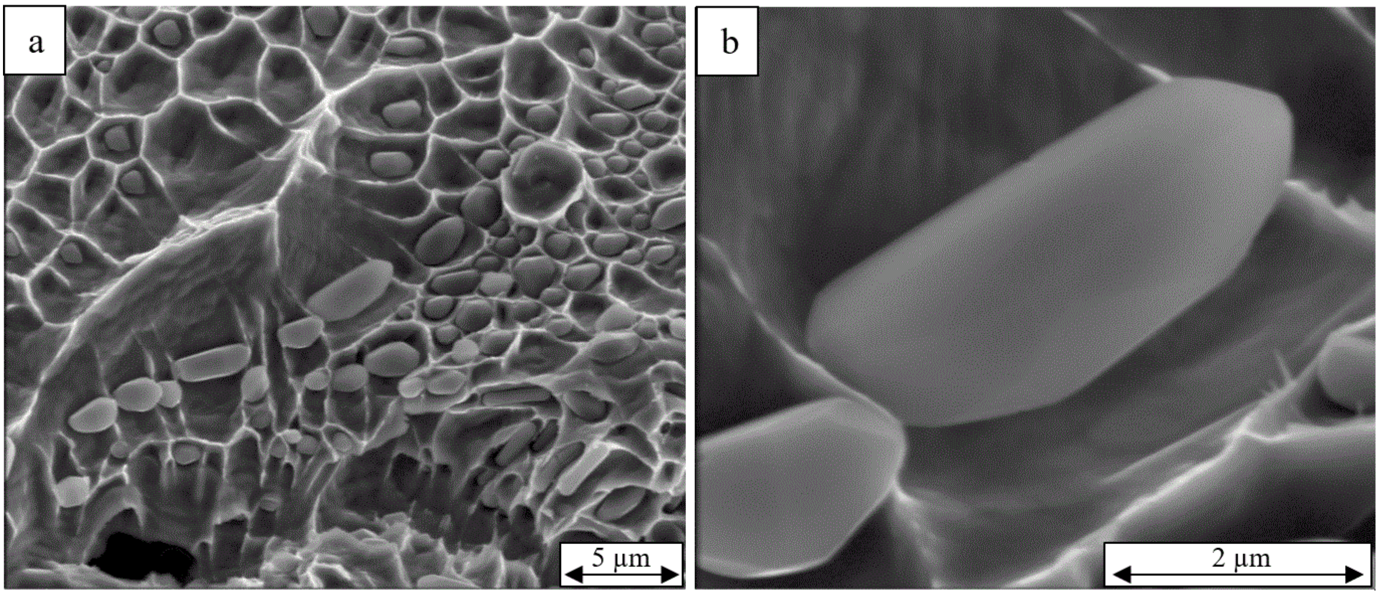

Fig. 4. Longitudinal sections of the copper ingot; a) magnification 10000×, b) magnification 20000× with visible crystals of Cu_2O oxide

Thus, a discrete distribution of Cu_2O single crystals that are found in the spaces between cells and dendrites occurs in the ingots. Microstructural analysis of the ingot shows that they have a generally regular shape with a main dimension of 2-3 µm, however, they may also have an elongated shape (up to 10 µm). Their size depends on the thermodynamic conditions of the solidification process. Figure 4 presents scanning electron microscope images of Cu_2O crystals found on the surface of the fracture of the ingot.

The analysis of the image presented in Fig. 4 shows that Cu_2O oxide is not wettable by copper, which results in the fact that the interface is characterized by low mechanical strength. During the rolling process, the oxide particles are not subjected to fragmentation, as illustrated by the selected microstructure images shown in Fig. 5. Fig. 5a shows the microstructure of the longitudinal section of the wire rod and Fig. 5b presents the microstructure of the cross-section of the ingot out of which the wire rod is manufactured. The lack of fragmentation can be explained with the high compressive strength of Cu_2O oxide and the compressive component in the triaxial state of stress of the hot-rolled soft copper matrix that does not exceed the Cu_2O oxide cracking stresses. An additional reason for the lack of fragmentation of Cu_2O oxide is the fact that there is no coherence between the oxide and the copper matrix.

The dimensions of the Cu_2O oxide single crystals in the ingot and in the wire rod are in the range of between 2 and 3 µm, and their shapes are regular with no sharp edges characteristic for cracked ceramics, which may mean that oxides do not subject to fragmentation during the rolling process, which is conducted in several rolling stands calibrated in an oval-circle configuration. Such observation is in accordance with the fact that during the rolling process the material is in a triaxial state of compression, and its temperature varies from about 830°C in the first rolling stand to about 400°C in the last one which creates favorable conditions for hydrostatic compression (negative stress tensor) which results in oxides being compressed by a very soft copper matrix.

A similar analysis of the evolution of the shape and dimensions of Cu_2O oxide was carried out for the wires obtained in the drawing process. Figure 6 presents selected images of evolution and fragmentation of oxides in wires with a diameter from 6 to 0.2 mm. Fig. 7-10 presents selected examples of longitudinal metallographic specimens of wires with a diameter of 0.5 mm (total coefficient of elongation $l = 256$) and a diameter of 0.2 mm (total coefficient of elongation $l = 1600$) magnified in order to show distinct material voids in accordance with the direction of the plastic flow of material around the oxide.

During the drawing process, the Cu_2O single crystals fragmentation proceeds especially in the first stage of deformation. Cu_2O oxide is crushed and has an irregular shape at this stage of processing. Fragmentation of the oxide occurs during the drawing process, however, it has been found that below a certain diameter (in the analyzed case below approx. 2 mm) no further cracking is observed, while with the strengthening of the copper matrix there are empty voids around the oxide in accordance with the direction of the plastic flow. It may be therefore assumed that during the low diameter wire drawing process, the drawing forces (and thus the tensile forces in the deformation zone) are lower than the tensile strength of the oxide. There are material voids in such wires which resemble “the comet tail”. Too low unit pressure values and high yield strength of the strengthened matrix are the main cause of their presence on the front and rear part of the precipitation. The lack of further fragmentation of the oxide during the wire drawing process is, however, unfavorable, because their fraction in the cross-section of the wire, in particular the microwire, becomes dominant and may lead to its rupture.

In order to answer the question why no further fragmentation of the oxide in wires with smaller diameters occur, uniaxial tensile test and compression test of the wire have been carried out. Figure 11 shows the characteristics of the uniaxial tensile test of the wire rod to the 30% elongation value and the image of Cu_2O oxide visible in the longitudinal section of the tensioned material. The tensile strength during the uniaxial tensile test of

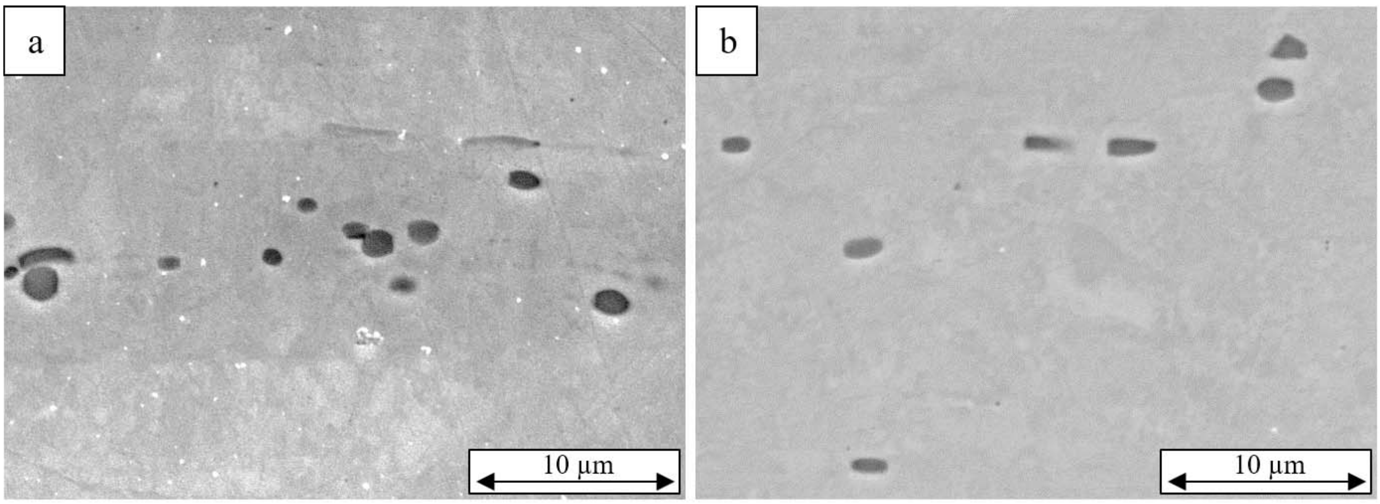

Fig. 5. Longitudinal section of the ETP grade copper wire rod with a diameter of 8 mm (a) and cross-section of the ETP grade copper ingot (b); magnification 4000×

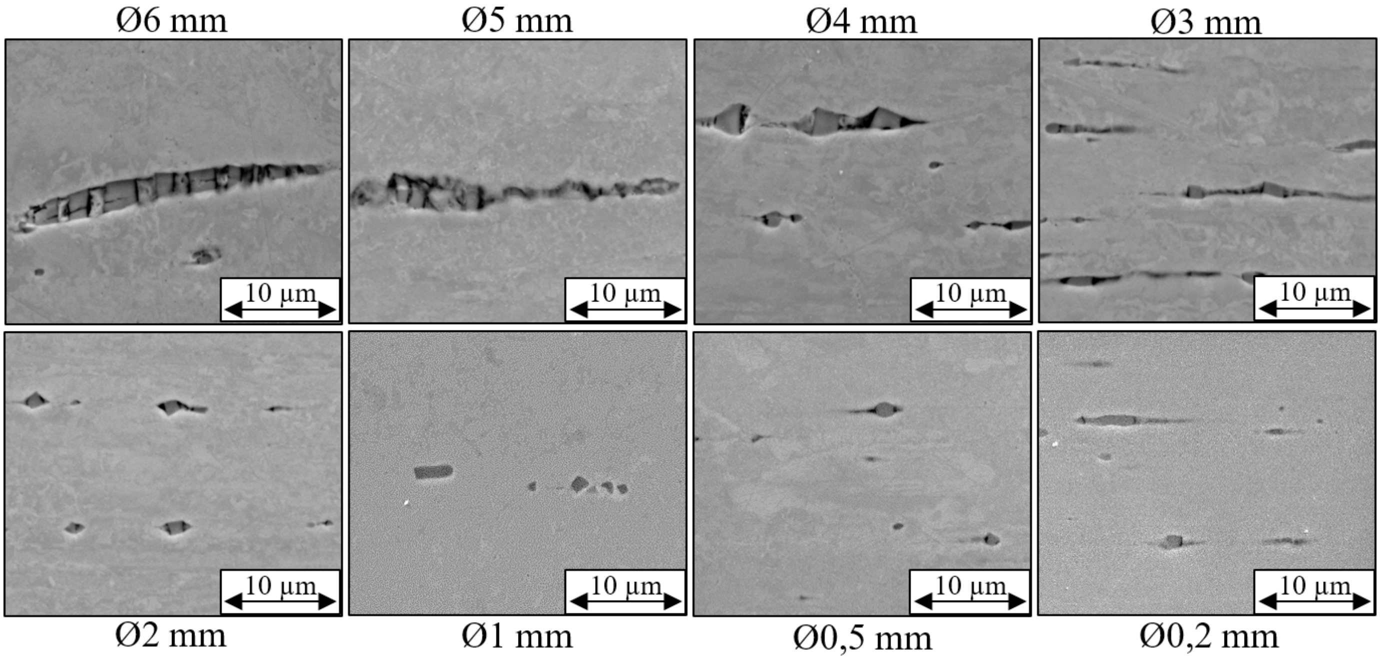

Fig. 6. Selected images of evolution and fragmentation of oxides in wires of various diameters, scanning electron microscope, magnification 4000×

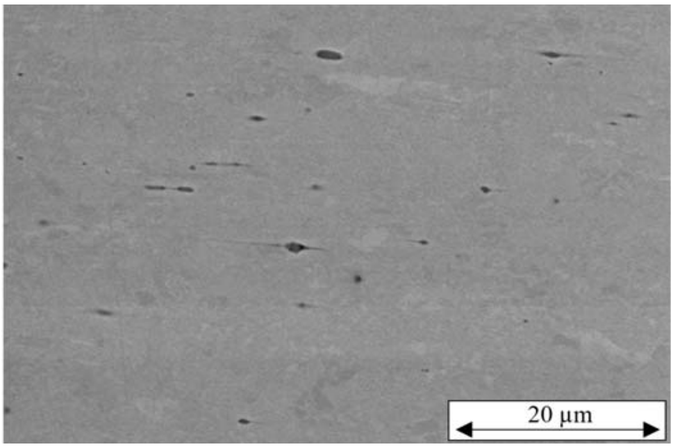

Fig. 7. Material voids behind and ahead of the oxide in accordance with the direction of the plastic flow, longitudinal section, diameter 0.5 mm, total coefficient of elongation *l* = 256, 2000× magnification

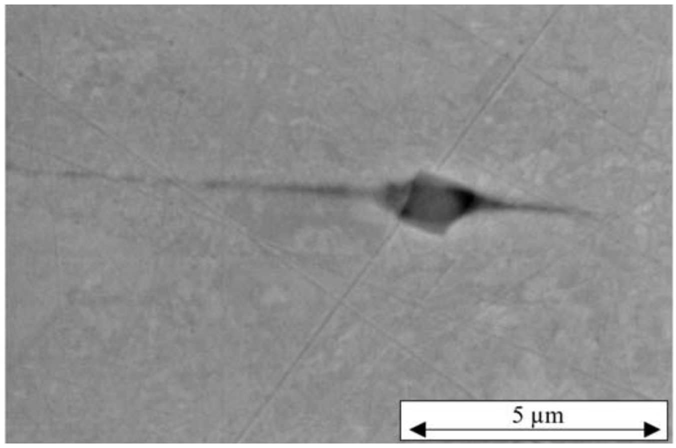

Fig. 8. Material voids behind and ahead of the oxide in accordance with the direction of the plastic flow, longitudinal section, diameter 0.5 mm, total coefficient of elongation *l* = 256, 10000× magnification

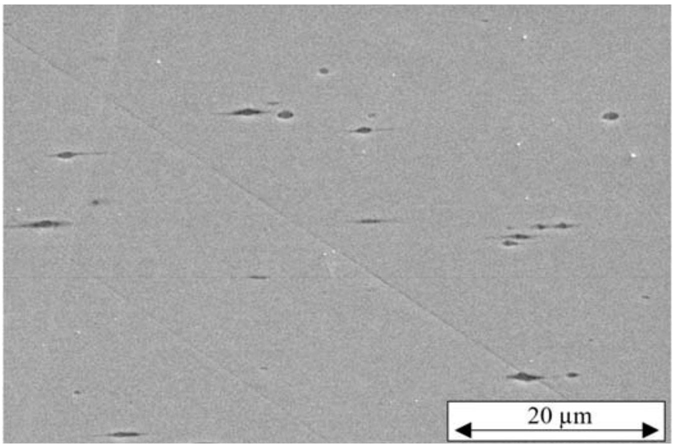

Fig. 9. Material voids behind and ahead of the oxide in accordance with the direction of the plastic flow, longitudinal section, diameter 0.2 mm, total coefficient of elongation *l* = 1600, 2000× magnification

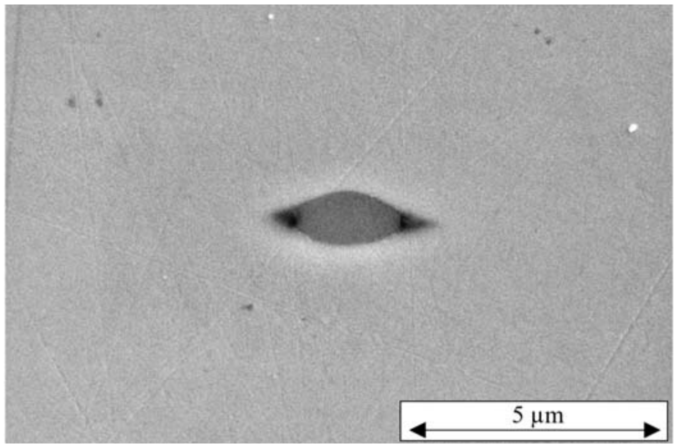

Fig. 10. Material voids behind and ahead of the oxide in accordance with the direction of the plastic flow, longitudinal section, diameter 0.2 mm, total coefficient of elongation *l* = 1600, 10000× magnification

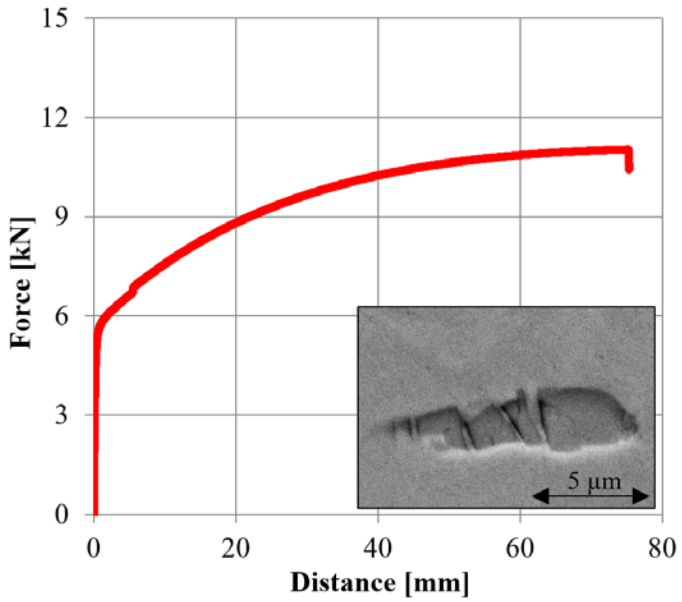

Fig. 11. Characteristics of the uniaxial tensile test of the wire rod up to 30% elongation value and the image of Cu_2O, scanning electron microscope, magnification 10000×

the wire rod was about 11 kN. It is clearly visible that the oxide has cracked, in this case into 5 parts.

In Fig. 12 the characteristics of the compression process of the wire rod and the image of the Cu_2O oxide in the longitudinal section have been shown.

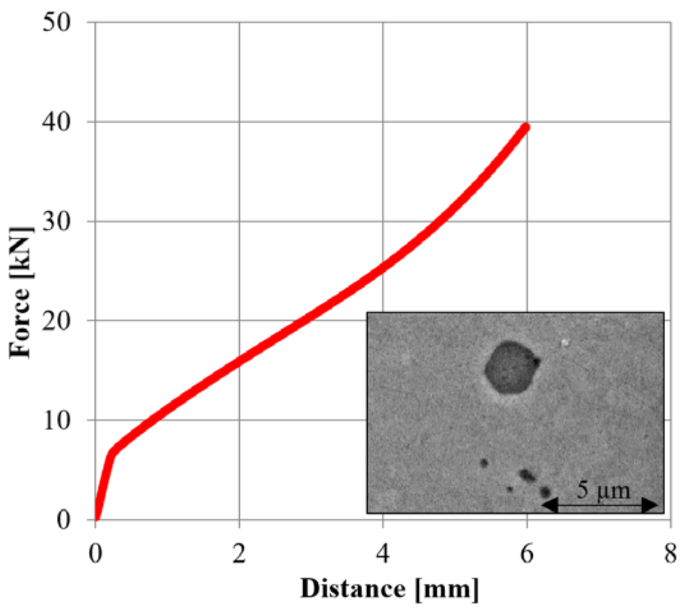

Fig. 12. The characteristics of the compression processes of the wire rod and the image of the Cu_2O, scanning electron microscope, magnification 10000×

Taking the compression process into consideration, the oxide did not undergo fragmentation, with the applied compression force of 40 kN, which is almost four times higher than in the case of tensile testing. The conducted research confirms the high compressive strength of the oxide as a ceramic material and its low ultimate tensile strength. The stress state in the die reduction angle in the circular-symmetric drawing process is characterized by two compression components (radial and peripheral) in the cross-sectional area of the drawn wire and one tension component in the direction parallel to the axis of the drawn wire. Such state of stress leads to the fragmentation of the oxide with the tensile forces occurring in the plastic zone of the drawn material (in the deformation zone). The analysis of the estimated size of the single crystals (see Fig. 6) and its mass density (Cu_2O density is 6.0 g/cm^3) shows that with the oxygen content of 200 ppm. wt. in the material found in the die reduction angle, from several hundred thousand to tens of millions of crushed Cu_2O oxide particles can be formed and disturb the continuity of the copper structure. This leads to a reduction in its ductility and electrical conductivity and affects the instability of the wire recrystallization process in the drawing lines, due to the very high drawing speeds and microsecond recrystallization time intervals.

4. Conclusions

Taking everything into account, Cu_2O oxides are characterized by high compressive strength and low ultimate tensile strength. The size of the Cu_2O oxide single crystals in the ingot manufactured in the continuous casting and rolling line is from 2 to 3 µm, the oxide is not subjected to fragmentation during the rolling process due to the compressive state of stress that occurs during the rolling process. However, during the drawing process, the oxide fragmentation occurs, which results from the stress state scheme (the occurrence of the tensile component in the drawing direction). Considering wires of low diameter, which are characterized by a strengthened copper matrix, there are difficulties in radial flow of the material around the oxide, which causes the discontinuity of the material observed in accordance with the direction of the plastic flow both behind and ahead of the oxide. The occurrence of these types of internal defects in the wire leads to a decrease in its quality (lower electrical conductivity, lower density, locally inhomogeneous state of the macro-stress around the oxide, reduced ultimate tensile strength, which jeopardizes the risk of wire rupture, especially on sliding drawing machines that are characterized by dynamic binary work rhythm).

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