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Selected aspects of evolution properties of oxygen free copper for high-advanced electrotechnical application

Abstract. *The shaping of properties of metallic materials in the process of continuous casting takes place through changes in the parameters of the technological process, i.e., the temperature of liquid metal, casting rate, flow size and crystallizer cooling water temperature. In this work, characterization of the influence of parameters of the casting process has been carried out, especially that of the casting rate on formation of material structure in terms of the quantity, size and shape of grains. The properties of copper wires for highly advanced electro-technical applications (audio-video cables, fireproof cables, car bundles) have also been characterized.*

Streszczenie. *Kształtowanie własności materiałów metalicznych w procesie ciągłego odlewania odbywa się na drodze zmiany parametrów procesu technologicznego tj. temperatury ciekłego metalu, prędkości odlewania, wielkości przepływu i temperatury wody chłodzącej krystalizator. W pracy dokonano charakterystyki wpływu parametrów procesu odlewania, a w szczególności prędkości odlewania na kształtowanie się struktury materiału pod kątem ilości, wielkości oraz kształtu ziaren, a także własności drutów miedzianych przeznaczonych do wysokozaawansowanych aplikacji elektrotechnicznych (kable audio-video, kable ognioodporne, wiązki samochodowe).* ***(Wybrane zagadnienia oceny własności miedzi beztlenowej pod kątem jej zastosowania w wysokozaawansowanych konstrukcjach elektrotechnicznych).***

Keywords: oxygen free copper, continuous melting and casting line, wires, audio-video cables.
Słowa kluczowe: miedź beztlenowa, proces ciągłego topienia i odlewania, druty, kable audio-video.

Analysis of the problem

The rapid development of electronics and broadly understood electro-technology imposes a need for the search for new materials allowing for rapid lossless transmission of electric signals. The universality of use of electronic systems and electro-technical elements has caused the emergence of a new group of products with highly advanced properties, such as cables, conductors, microwires and connecting elements used in the electro-technical industry. Depending on the application, the ideal transmission cable should guarantee high sound and image quality (audio-video cables), optimal data transmission speed (cables for information technology applications), appropriate signal strength and minimization of attenuation and the risk of occurrence of interference. The above requirements create the need for use of a material allowing for an electron flow that is as lossless as possible.

Modern material solutions in this field of applications are mainly concentrated on copper. Although this functional material has been known to mankind for 10,000 years (and as an excellent conductor of electricity, since the XVIII century), the search for new possibilities of its utilization has not ceased. This is visible in the large amount of work and achievements in this field. The modern study of copper has two main directions of development: the first, still valid since the discovery of electricity, is the pursuit of a constant increase in electric conductivity, as well as deformability, for wires and microwires. The second direction is a new trend that has become visible over the last few years, i.e., studies on high strength copper alloys for electric purposes, with a strength reaching up to 1,200 MPa and electric conductivity at a level of 80 % IACS. This second group of work includes numerous worldwide studies carried out at institutions of higher learning and laboratories, especially in Japan and the United States.

The subject matter undertaken in this article regards the first of the above mentioned matters, that is, work on functionally perfect copper for the most sophisticated applications in the electronic and electro-technical industry. A standard for conductors of this type is Oxygen Free Electronic Copper (OFE) or Oxygen Free High Conductivity Copper with high chemical purity (OFHC). OFE copper with a purity grade of 4N (99.99 % Cu) contains about 1÷3 ppm. wt. of oxygen and total impurities in an amount of no more than 25 ppm wt. [1, 2]. Copper of this type is additionally characterized by excellent deformability, as well as resistance to atmospheric corrosion and hydrogen embrittlement [3÷6]. In electronic applications, a variant of oxygen free copper is used with specially shaped grains and, first and foremost, the smallest possible amount of grains per unit of length. Examples of such solutions are Long Grain Crystal Copper (LGC) and Long Crystal Copper (LCC). In the above mentioned grades of copper, the amount of grains is reduced to a level of 200 per meter of length, thanks to which the transmission of an electric signal in audio-video applications is not as lossy, and the elimination of drawbacks of connections has become possible. LGC and LCC surpass OFE copper, in which the amount of grains is equal to about 500/mb [7, 8].

Properties similar to those of LGC and LCC copper are possessed by OCC copper obtained according to Ohno Continuous Casting Technology, the main purpose of which is the decrease of the amount of crystals in the conductor. In highly specialized applications, such as electron technology (elements of particle accelerators, cryogenics), 6N grade copper with a purity of 99.99997 % is used. The highest grade of purity for copper obtained industrially is currently 8N grade purity (99.999999 %). High quality cables are often made from copper with a purity grade of 6-7N. The traditionally used ETP copper, in which oxygen content is at a level within 200÷600 ppm. wt., does not guarantee such properties [9, 10]. The assortment of oxygen free copper products is very broad and is concentrated mainly on highly advanced products. According to the data included in Table 1., oxygen free copper of the highest quality (according to JISH 2123 grade C1011) is mainly used in electron technology (accelerator elements and electron tubes), vacuum apparatus, cryogenics (elements operating at low temperatures), superconduction, cable technology (connecting elements, microwires, enamelled conductors, transmission conductors, conductors for applications in information technology, audio-video conductors).

Interest in the dynamically developing oxygen free copper electro-technical industry, its production technology, as well as its physical and mechanical properties, is a result of the wide applications of this material. One application of oxygen free copper is the production of wires and microwires with diameters of less than 0.1 mm. Such capacity for use of oxygen free copper in the drawing process is related to the limited potential of the traditionally used ETP grade copper for electric applications, characterized by its content of hard copper oxides (Cu_2O) with sizes of 5÷10 µm, which, for very small wire diameters, significantly decrease their ductility.

Table 1. Classification of oxygen free copper according to international standards

Country		Japan	USA	Germany
Standard		JISH 2123	ASTM B170	DINI 787
Designation		Grade1 C1011	Grade 1 C10100	OF-Cu 2.0040
Chemical composition	Cu min. %	99.99	99.99	99.95
	O_2 ppm. wt.	10 max.	5 max.	-
Standards applying to products		JIS H3510	ASTM F68	DIN 40500
Products		elements of electron tubes microwires, audio-video cables, tapes, tubes	system elements in electron technology, microwires, cables,	conductive material for electric applications

The dynamic evolution of electronics and broadly understood electro-technics taking place these last few years is determined by the most recent technical and technological solutions in the field of metallurgy and processing of metallic materials, especially copper. Super-standard requirements expected of wires for the most sophisticated current applications are transferable to the high technological regime of perfect control over the entire production system, from control of the type and chemical composition of the concentrate and quality of anodes and cathodes through processes of casting and hot rolling, to multi-stage drawing combined with heat treatment, up to obtaining of the final product. The presence and improper quantitative proportions of foreign atoms in the cathode, being the feedstock in the wire production process, play a negative role in shaping the properties of copper in the processes mentioned above. It is the assortment and quality of feedstock used for production of electronic products that determine their construction and the production technology used in a significant way and therefore, also properties of use, including durability and reliability of products. However, taking into account the fact that the feedstock in the production process of ETP and OFE grade copper is a high purity Cu-CATH-1 grade cathode with the same chemical composition, obtaining oxygen free copper in a way that secures it a place in the centre of interest of modern electronics requires the utilization of highly advanced production techniques. Techniques making it possible to produce a material that not only possesses high chemical purity, but also a beneficial structure, in terms of electro-technical applications, characterized by a minimal amount of defects, including the property of grain boundaries being places where conducted electrons are scattered.

Methods of constant melting and casting of oxygen free copper

One of the most modern methods making possible the production of feedstock from oxygen free copper for direct processing through the method of drawing wires and microwires is the Upcast® technology of the Outokumpu company, which is based on constant melting of the high purity cathode, oxygen reduction and constant casting of OFE oxygen free copper in the form of a rod wound in circles.

The feedstock are high purity Cu-CATH-1 grade (LME Grade A) copper cathodes that are subjected to constant melting in an induction furnace. According to the ASTMB 170 standard, Cu-CATH-1 grade copper cathodes should not have a total impurity content of more than 25 ppm. Next, the liquid copper is subjected to the deoxidation process. The role of the deoxidizer is fulfilled by charcoal with a decreased Fe and S content, a layer of which covers the liquid copper. Metal solidification takes place in a special vertical crystallizer immersed in liquid copper. The solidified ingot is pulled up with a given speed by means of drawing rollers and subsequently wound into circles by means of a system of winders. The above method makes it possible to produce oxygen free copper wire of high conductivity and plasticity with diameters ranging from 8-24 mm and with a speed of 4 m/min (for a diameter of 8 mm), which allows for the achievement of an average yearly output of about 15,000 tons.

Oxygen free copper is also produced using other methods, e.g.: Rautomead®, which is based on a principle similar to that of the Upcast® method, which is constant melting and upward casting, with which the processes of melting, oxygen reduction and casting are carried out, in contrast to the Upcast® method, in the same furnace [11,12].

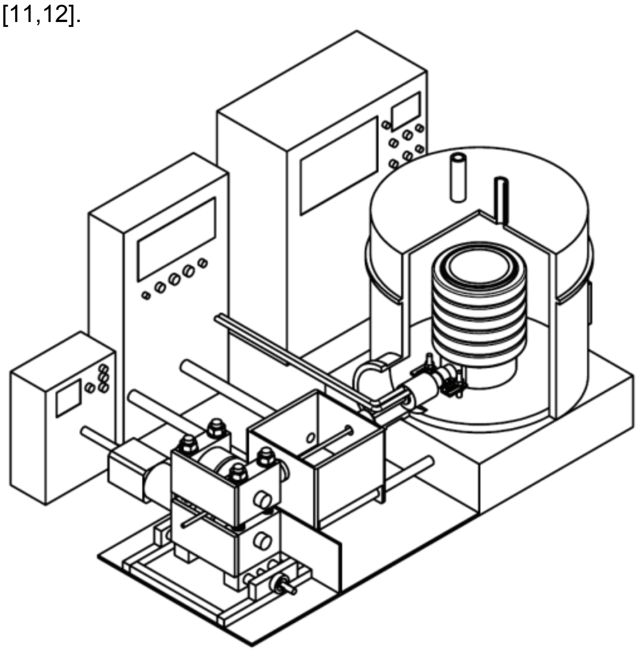


Fig. 1. Apparatus for continuous casting in schematic perspective view – own design DCC-AGH® [13]

Dynamic scientific studies of a laboratory method of obtaining copper with increasing chemical purity, being carried out simultaneously worldwide, have led to the development and start-up of an installation for production of feedstock of Cu-OFE grade with an oriented structure characterized by grain size being as small as possible [13, 14]. The unique DCC-AGH® casting station designed for this purpose, and made based on international standards at the AGH University of Science and Technology in Cracow, facilitates the complete study and analysis of the effect of the structure as well as chemical purity of the material on the properties of the wire, analysed from the angle of loss of transmission of an electric signal. Figure 1. presents a scheme of the device shown in perspective. The process of constant casting of oxygen free copper realized on the above mentioned station is based on introduction of the copper starting element through its passing through an isolated crystallizer to a melting furnace until the moment of its contact with the liquid metal. Next, its movement is facilitated by means of an automatic supply system, and Cu-OFE grade copper is cast. In the initial stage of the casting process, the liquid copper is subjected to a cooling process by means of a cooling medium located in a metal sleeve which tightly closes off the isolated crystallizer, after which the circulation of the primary cooling system zone is closed with the exit of the material from the crystallizer, and the subsequently cast copper is subjected to cooling by means of the secondary cooling system zone. This zone is located at the crystallizer output near the surface of the cast material. After the cast product passes through the secondary cooling system zone, it is directed towards a drawing unit made from pressure and guide rolls, the pressing force of which, on the surface of the finished cast product, is regulated by screws.

A significant characteristic of the station is the use of a high-output, isolated crystallizer with a simple and uncomplicated construction and a secondary cooling system using, among others, cooling gases such as liquid nitrogen, which makes it possible to shape the structure of copper with a limited amount of grains and to control the direction of grain development. This results from the characteristics of the solidification process, and more precisely from the process of conduction of heat (offtake) by the crystallizer and the distribution of the vector of the temperature gradient on the front of metal crystallization, changing from a radial direction to an axial direction (flat crystallization front). The designed casting system makes it possible to fulfil the dependency so that the difference of temperatures between the liquid copper in the crystallizer and the walls of the isolated crystallizer (ΔT_1) is smaller than the difference of temperature between the liquid copper in the crystallizer and the already solidified part of the material (ΔT_2). Therefore, the following dependency is fulfilled: $\Delta T_1 < \Delta T_2$. The special construction of the device makes it possible to achieve this goal through skilful control of casting speed as well as cooling conditions. Change in casting speed, as well as introduction of a controlled heat conduction (offtake) zone in the crystallizer, makes it possible to obtain consistency of the direction of heat conduction with the direction of the axis of the cast product.

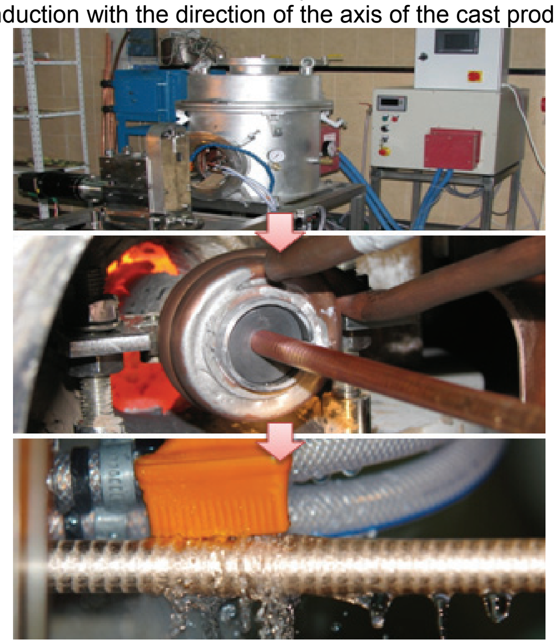


Fig. 2. Vacuum induction melting and casting furnace – own design DCC-AGH® [13]

Figure 2 presents a general view of the entire installation, as well as a close-up of the crystallization system and finished rods for special applications cast with non-industrial speeds.

A very important aspect of study is the problem of shaping structure during the casting process. As mentioned before, this can be done by skilfully controlling casting speed as well as cooling conditions. During studies, through changing casting speed and introducing a controlled heat conduction zone in the crystallizer, conformity of the direction of heat conduction with the direction of the axis of the cast product is aimed for. Such a method of casting leads to visible changes in the structure of copper, which is shown in Figure 3.

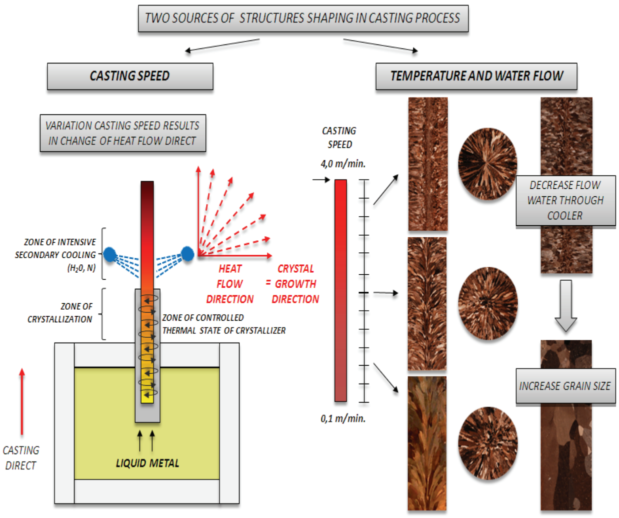


Fig. 3. Shaping of copper structure in the continuous casting process

Cel i zakres pracy. Program badań. Materiał

The purpose of experimental studies is to determine the influence of changes in metal crystallization conditions in the process of constant casting of oxygen free copper, using the Upcast method under industrial conditions as well as using a laboratory method using the DCC-AGH® casting station, on shaping the structure of the material, which in turn determines the physical and technological properties of the wires. The specificity of constant casting allows for the utilization of variable parameters of casting speed and flow size of cooling water in the primary system as well as in the secondary system. Both of these parameters play a significant role during the course of the process of crystallization of liquid metal. Therefore, identification of materials for study has the purpose of making differences in structure and the properties of materials obtained using different parameters during the casting process (casting speed, expenditure of cooling water) apparent, which will in turn indicate possible differences resulting from variations in structure during processes of plastic working and annealing. For comparative purposes, in order to determine a point of reference, the same course of study was carried out for Cu-ETP grade copper from the Contirod® line, which is traditionally used for electric purposes. The basis for such methodology is the fact that OFE and ETP grade copper are feedstock for the drawing process for obtaining wires and microwires that have completely different structures, which is a result of different methods of production.

The objects used for this article are oxygen free copper rods with a nominal diameter of 8 mm, obtained under industrial conditions using the Upcast® method and under laboratory conditions at the DCC-AGH® casting station. The specificity of both technologies allows for changes of crystallization conditions through the regulation of two technological parameters: casting speed and the size and manner of flow of cooling water. For studies, ten materials were obtained: five Upcast rods obtained with different casting speeds under industrial conditions, i.e.: 0.5 m/min., 1.0 m/min., 2.0 m/min., 3.0 m/min., 4.0 m/min., with a crystallizer cooling water flow of 60 l/min, and also five rods from oxygen free copper cast under laboratory conditions using the above mentioned DCC-AGH® station using the following casting speeds: 0.006 m/min., 0.03 m/min., 0.06 m/min., 0.15m/min., 0.2 m/min. with cooling water flow at a level of 0.1÷0.4 l/min. in the primary system and 0.2÷1.0 l/min. in the secondary system. In both cases, the cooling water temperature was equal to 20 °C. In comparison, the results of the study for Cu-ETP rods with an output diameter of 8 mm obtained from the Contirod line are also presented. In this way, eleven types of materials obtained using different technological processes were selected for study (industrial conditions – installations: Upcast®, Contirod®, laboratory conditions – DCC-AGH® installation), as well as for different casting conditions (Upcast®, DCC-AGH®). Table 2 illustrates a comparison of the studied materials.

Table 3. Materials for research

Material	Casting process parameters		
	Casting speed m/min.	Water flow l/min.	
		Primary cooling	Secondary cooling
Cu-OFE (DCC-AGH®)	0.006	0.1 ÷ 0.4	0.2 ÷ 1.0
	0.03		
	0.06		
	0.15		
	0.20		
Cu-OFE (Upcast®)	0.50	60	
	1.00		
	2.00		
	3.00		
	4.00		
Cu-ETP (Contirod®) - rolling speed 25 m/s			

The material was subjected to testing during each stage of the drawing process. In this way, experimental research was commenced by the identification of macrostructures and mechanical and electric properties of the listed feedstock with diameters of 8.0 mm. Macrostructural photographs of cross-sections and longitudinal sections of materials were taken. Static tensile and torsion testing of ETP and OFE grade copper was carried out, and electric properties of materials were determined.

Results and analysis of experimental research

The first results of testing, i.e., identification of the structure of feedstock, have been presented in Fig. 4. Identification of makrostructures was carried out using longitudinal and cross sections of Cu-OFE grade rods cast at ten different speeds. The materials exhibit a structure that is typical for classic castings, i.e., for copper cast with high speeds in a range from 0.5÷4.0 m/min., a clear structure of equiaxial grains and a zone of column crystals perpendicular to the axis of the cast material are distinguishable. Furthermore, analysis of longitudinal sections indicates that the lower the casting speed, the larger the grains found in the castings. Special attention should be paid to the fact that these grains change their orientation from perpendicular to the rod axis, for materials cast at high speeds, to parallel to the rod axis for materials cast at low speeds. It was observed that the material, for which the lowest casting speed was used, exhibits a two to three grain structure of arbitrary length, since this a process of constant casting. In the lower part of Fig. 4.9, changes in the directions of grain orientation on the cross–section, as well as the forecast change in shape of the crystallization front, were marked. On the left side, the structure of the ETP rod as a product after 99.99 % hot deformational strengthening (elongation factor 144) is presented and is characterized by a homogeneous, fine-grain structure that is susceptible to the deformation process. Crystals have a size of about 10÷20 μm and are characterized by equal orientation in all directions. In structural terms, the rod is an isotropic material.

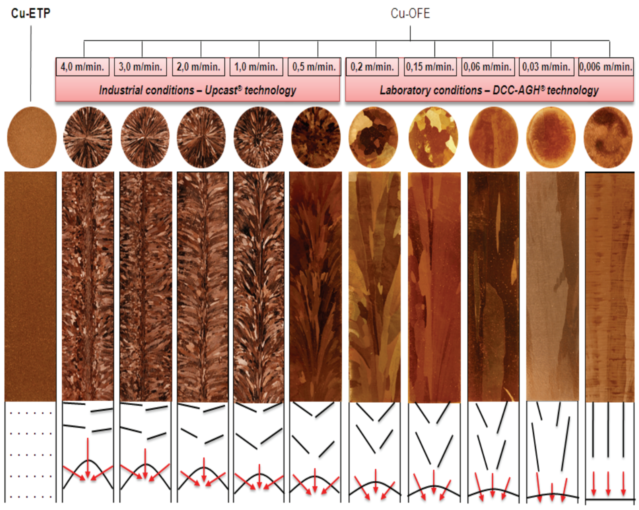


Fig. 4. Identification of structure of feedstock

Further test results apply to the mechanical properties of feedstock for the process of drawing wires and microwires. The prepared samples, with a base length of 100 mm, were subjected to tensile tests on a testing machine made by the Instron company with a traverse speed of 70 mm/min. and a reading frequency of 5 pts./s. Furthermore, torsion tests were carried out. The prepared segments were loaded at their endings with two counterbalanced torques acting in planes perpendicular to the sample axis. The test was concluded at the moment of breakage of the rod. Both mechanical tests differ from one another by the direction of application of the vector of force. The purpose of carrying out these two different mechanical tests was to test if the apparent structural differences are reflected in material properties when the material is subjected to different deformation schemes.

Figure 5. presents comparative results from tensile testing of the materials being studied. Through analysis of the tensile curves, a significant difference in the process of strengthening of Cu-OFE and Cu-ETP copper was observed. The rods are materials obtained from the process of hot rolling and possess a fine-grain structure typical for copper subjected to dynamic recrystallization. It is characterized by high tensile strength and a relatively low yield point. Oxygen free copper rods are, however, obtained from the process of constant casting and exhibit a structure typical for castings, which, in a way, determines the fact that their mechanical properties, for a similar yield point value, are lower than for the rolled rods. Differences in the chemical compositions of materials also have an effect on these properties.

Furthermore, three groups of materials with different courses of tensile curves can be observed: the first group includes materials cast at industrial speeds using the Upcast installation, the second group consists of materials obtained in laboratory conditions using the DCC-AGH® method, and the third group is comprised of material obtained using the lowest casting speed in laboratory conditions using the DCC-AGH® technique.

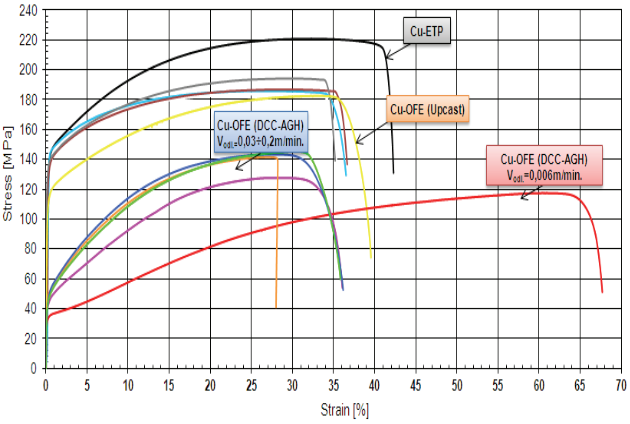


Fig. 5. Tensile curves of Cu-ETP rod and Cu-OFE rods

On the basis of analysis of data on the strength properties of the studied materials, it was stated that the level of strength obtained by the ETP rod equal to approx. 220 MPa, which is significantly higher than that for oxygen free OFE copper, which oscillates in the range of 120÷195 MPa. However, the fundamental structural difference between the discussed grades of copper should be taken into account.

For oxygen free copper obtained under industrial conditions using the Upcast installation, a monotonic increase in tensile strength was observed with a decrease of casting speed. For the material obtained at a casting speed of 1.0 m/min., the value of tensile strength is equal to approx. 195 MPa; however, for the oxygen free copper sample cast at a higher speed of 4.0 m/min., tensile strength was at a lower level of 180÷185 MPa. This is a significant difference taking into account the change of only casting speed with no difference in the chemical composition of the material as well as the general method of production.

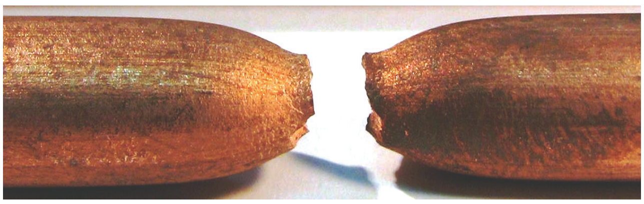


Fig. 6. Cu-ETP rod after tensile test

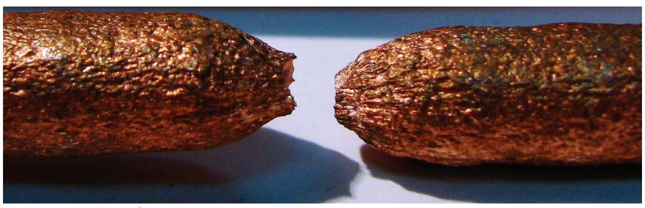
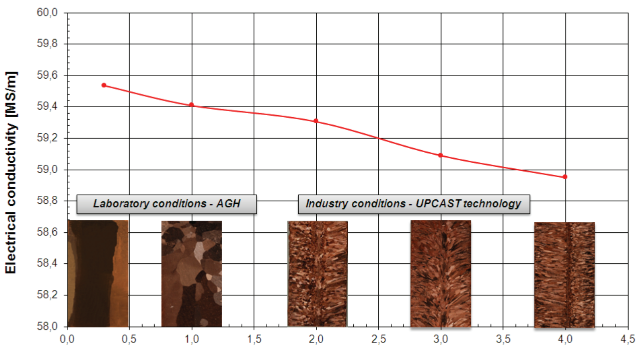


Fig. 7. Upcast® wire rod after tensile test


Fig. 8. DCC-AGH® wire rod after tensile test

Figures 6 and 7 present material surfaces after tensile tests. On the basis of analysis of the photographs, it was observed that insofar as no significant changes in the surface of the rod after tensile testing are present in Cu-ETP grade copper, in the case of the oxygen free copper rod (Figs. 7., 8.), the surface is uneven, which is a result of deformation of large crystallites.

Another very important group of tests is in regard to electric properties, which have been illustrated in Fig. 10. as a chart of the dependency of electric conductivity as a function of casting speed. It was observed that lowering casting speed results in an increase in material conductivity. Furthermore, attention must be paid to the fact of how significant the influence of casting speed on the increase of electric conductivity is relative to the difference between the electric conductivity of Cu-ETP grade copper, for which a value equal to 58.67 MS/m was recorded during measurements, and Cu-OFC grade oxygen free copper rods cast at different speeds. Furthermore, on the basis of analysis of the presented chart, it was observed that the lower the casting speed, the more coarse-grained the material's structure was. The photograph on the left shows the structure of the cast rod, which possesses only three grains on its axial section. In turn, the photograph on the right also shows the macrostructure of a rod cast with a speed that is 50 times greater. It is visible that the casting possesses a large amount of radial grains oriented perpendicularly to the surface. Such distribution is dependent upon the method of casting.



Rys. 9. Wpływ prędkości odlewania na własności elektryczne miedzi beztlenowej

Conclusions and final statements

1. A significant influence of casting process parameters and cooling conditions (amount and temperature of water at the input/output of the crystallizer) on shaping material structure in terms of grain amount and morphology was stated.
2. A change in the direction of grain orientation from a direction perpendicular relative to the rod axis, for materials cast at high speeds, to parallel to the rod axis, for materials cast with lower speeds and with a special direction of the vector of the temperature gradient in the crystallizer. This conclusion applies to the casting

process in laboratory conditions and well as industrial conditions.

3. A change in the temperature gradient on the crystallization front makes it possible to shape material structure during the casting process.
4. Decreasing casting speed leads to a change in the direction of heat conduction, which, in consequence, results in the creation of a flat crystallization front, making it possible to obtain a structure with grains parallel to the axis of the cast material.
5. Conductivity of oxygen free copper wires is a function of casting speed. Conductivity decreases with the increase of casting speed.
6. The benefits of oxygen free copper with a casting structure shown here, based on simultaneous high conductivity and heat resistance without metallurgic intervention, allow for its use in a variety of applications in modern energy and electric industries.

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