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Embrittlement of Copper Wire Due to Oxygen

Krhkost bakra zaradi kisika

L. Kosec, V. Gontarev, B. Kosec, FNT, Odsek za metalurgijo in materiale, Ljubljana
N. Mlakar, Kolektor, Idrija

An example of the reversible oxygen embrittlement of copper is described in the paper. This phenomenon is combined with the drastic reduction of ductility and workability. It appeared at the low temperature annealing (500°C) of copper in the nitrogen atmosphere with a low oxygen concentration (5 ... 6 ppm), when diffusion of oxygen in copper took place preferentially on grain boundaries. During the cooling to the surroundings temperature oxygen precipitated from the saturated solution in the form of copper oxide (Cu_2O) on the grain boundaries, thus the conditions for the intergranular dimple fracture have been created.

Key words: oxygen, grain boundary diffusion, supersaturation, precipitation, intergranular dimple rupture, reversible embrittlement due to oxygen.

V prispevku je opisan primer reverzibilne krhkosti bakra zaradi kisika. Pojav je povezan z drastičnim zmanjšanjem duktilnosti in preoblikovalne sposobnosti bakra. Nastal je pri nizkotemperaturnem (500°C) žarenju bakra v dušiku z majhno koncentracijo kisika (5 ... 6 ppm), med katerimi je prišlo do prednostne difuzije kisika po kristalnih mejah bakra. Med ohlajanjem na temperaturo okolice je kisik iz nasičene raztopine precipitiral v obliki bakrovega oksida (Cu_2O) na kristalnih mejah in ustvaril pogoje za interkristalni prelom z jamicami.

Ključne besede: kisik, difuzija po kristalnih mejah, prenasičenje, izločanje, intergranularni jamičasti lom, krhkost zaradi kisika.

1. Introduction

Copper and some its alloys represent of high ductile and well cold workable materials. These properties can be usually obtained by annealing in the protective atmosphere. But there exist frequent exceptions. They are numerous since many products are made by advanced technology of the bulk shaping instead of machining. Limited ductility in the bulk shaping allowed only a certain amount of plastic deformation. Further plastic deformation initiated cracking till final fracture of material (**Fig.1**).

These problems are often caused by oxygen which concentration could be detected by the metallographic analyse of oxide inclusions or chemical[1,2]. The copper oxide inclusions well follow the deformation of metal if extreme degrees are not exceeded.

Oxygen in the solid solution which simultaneously hardens copper and reduces its ductility is harmful. In some cases the chemically measured differences in the oxygen concentration between ductile and brittle copper are very small, even within the measuring error. In such cases oxygen is expected to be concentrated on certain sites in the microstructure, for instance on the grain boundaries, but it could be detected only by an analitical in situ method.

Before rolling, the copper wire of 12.8 mm in diameter have been annealed for 1 hour at 500°C in the nitrogen atmosphere with 5 ... 6 ppm of oxygen. During the annealing proces the average concentration of oxygen in the copper increased from approximately 0.001% to approximately 0.002%.

Already after first or second pass through the grooved roll (round - square) the surface cracked. It was an obviously sign that further rolling was not possible any more. The cracks were approximately in the radial direction with characteristic changes of directions on the short sections. In single areas the surface damages were so intensive that even some small metalic particles split off. The wire with the limited ductility had the same strength and the yield stress as that which was be shaped into the demanding sections. The reduced ductility was explained by fracture surfaces and by the careful analysis of the microstructure. The contraction of the copper wire before annealing was approximately 90%, and it was reduced to less than 30% after the annealing process. Essential difference between the two wires was in the form of fracture. Not annealed copper wire exhibited ductile transgranular dimpled fracture with characteristic deep unidirected dimples (**Fig. 6**). On the fracture surface of the test bar broken in the air, the adsorbed carbon and oxygen have been measured (**Fig. 9**). After annealing the ductility was rapidly reduced while the fracture was completely intercrystalline. Intergranular fracture surface consisted of many fine and shallow dimples with inclusions of copper oxyde (**Fig. 2-5**).

High oxygen concentration on that fracture surface was proved by the AES analysis. Oxygen was distributed obviously deeper under the fracture surface when compared with the notannealed copper (**Fig. 10**).

The oxygen concentration on the surface corresponded to the composition Cu_2O and was rapidly reduced away from the grain boundaries. The initiation of cracks in the annealed copper is

Figure 1: Cracks on copper wire surface after cold rolling (first step of reduction); 100x

Slika 1: Površina bakrene žice z razpokami po prvi redukciji pri hladnem valjanju; 100x

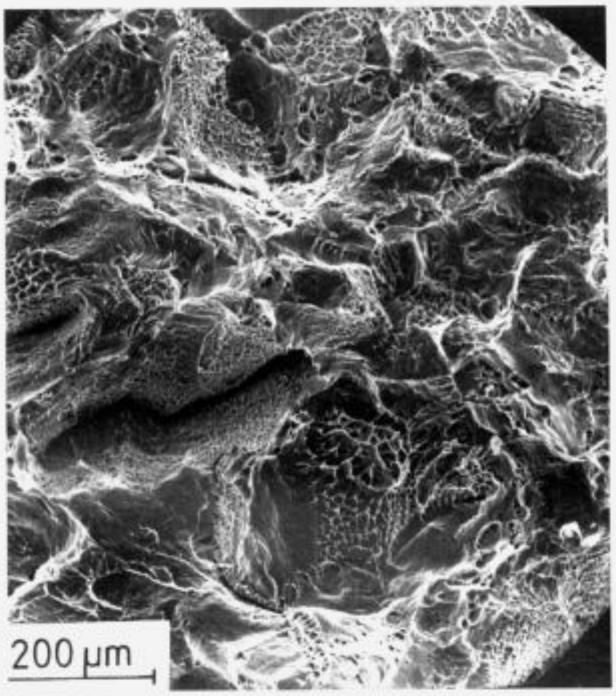

Figure 2: Intergranular dimple rupture in copper wire resulting from microvoids coalescence at grain boundaries; 100x

Slika 2: Intergranularna jamničasta površina preloma valjane bakrene žice; 100x

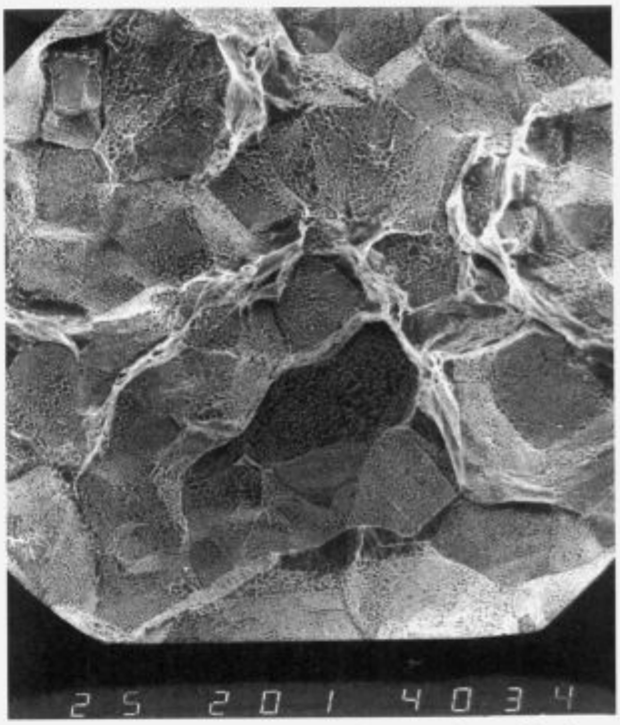

Figure 3: Intergranular dimple rupture in copper wire resulting from microvoids coalescence at grain boundaries (Z = 25%); 200x

Slika 3: Intergranularna jamničasta površina preloma bakrene žice (Z = 25%); 200x

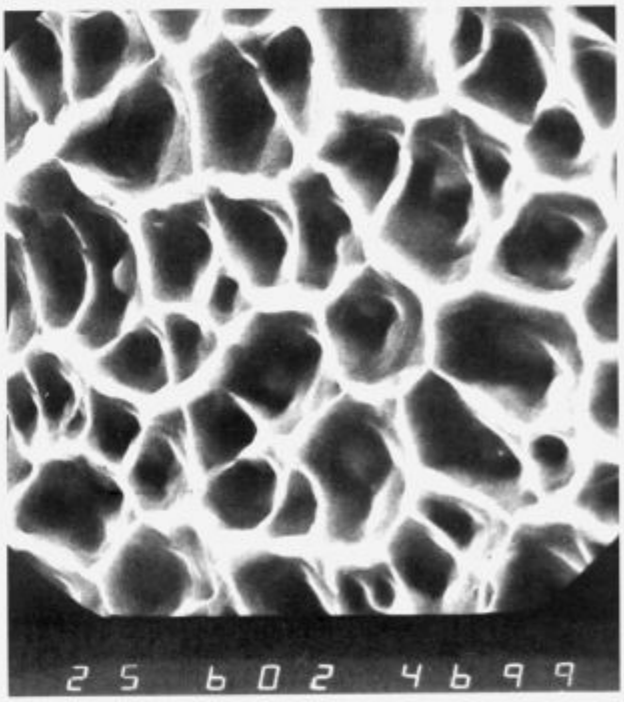

Figure 4: Detail of intergranular rupture surface with copper oxyde inclusions in dimples (**fig.3**); 6000x

Slika 4: Detalj intergranularne prelomne površine z vključki Cu_2O v jamicah (**sl.3**); 6000x

Figure 5: Small cracks on grain boundaries and copper oxyde precipitates; 200x

Slika 5: Kratke razpoke na kristalnih mejah s precipitati bakrovega oksida; 200x

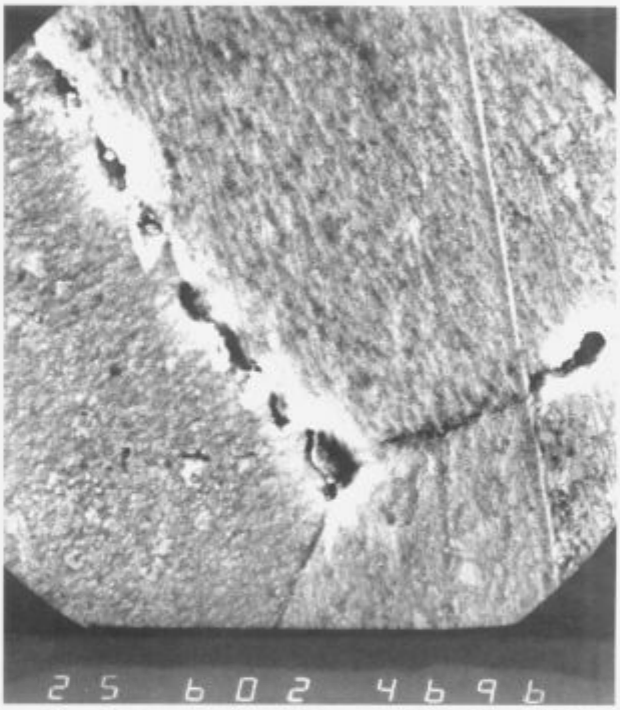

Figure 6: Copper oxyde precipitates on grain boundary; 6000x

Slika 6: Precipitati bakrovega oksida na kristalni meji; 6000x

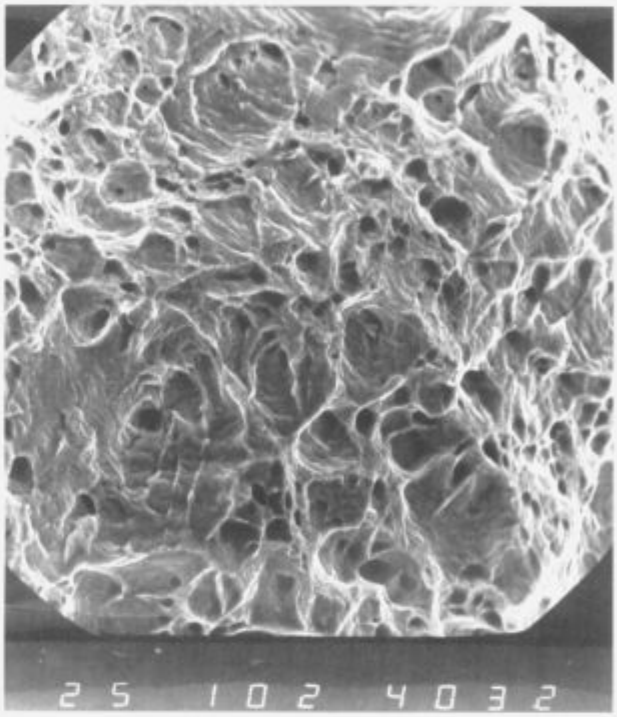

Figure 7: Ductile fracture of copper wire (Z = 90%); 1000x

Slika 7: Duktilni prelom bakrene žice (Z = 90%); 1000x

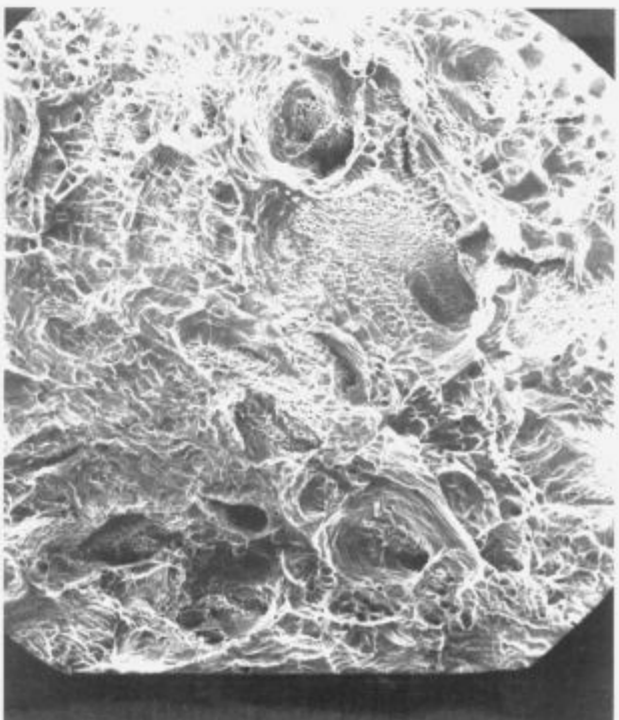

Figure 8: Fracture surface of copper wire after vacuum annealing (Z = 90%); 200x

Slika 8: Prelomna površina žice po žarenju v vakuumu (Z = 75%); 200x

connected with the inclusions of copper oxide on the grain boundaries (**Fig. 3,5**). As reference, also the surface of copper wire which has been covered with thin layer of corrosive products during storing has been analysed. The composition was not the same on the whole surface. On one section of the surface the chemical composition of the corrosive products corresponded to the CuO copper oxide (**Fig. 13**). The layer is thin and it adheres to the unchanged metal at a high oxygen concentration gradient. In the other surface area, there was found a layer with high carbon concentration and it was thicker than that rich in oxygen (**Fig. 14**). The oxygen embrittlement of copper exhibited reversibility. Annealing in the vacuum (5.10^{-6}mbar, 850°C, 10 hours) essentialy increased (Z = 75%) the copper ductility. The fracture surface of that annealed copper was predominantly transgranular dimpled ductile fractured with a very small amount of residual intergranular dimpled fracture (**Fig. 8**). The chosen annealing conditions in the vacuum were obviously not so favourable enough to remove all the oxygen accumulated in the copper during the annealing in the nitrogen atmosphere. The not uniform removal of oxygen was proved also by the AES analy-

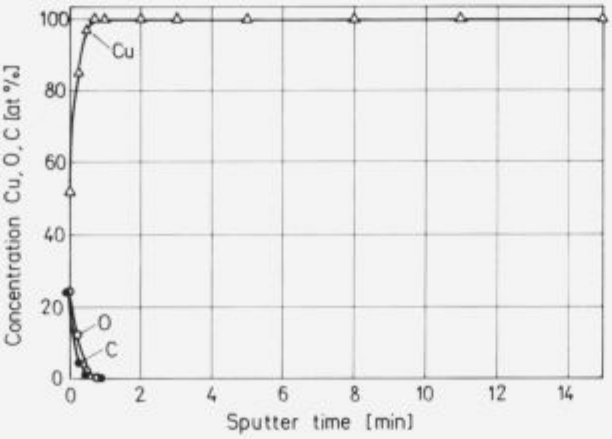

Figure 9: Copper, oxygen and carbon concentration distribution on fracture surfaces of high ductility copper (Z = 90%)

Slika 9: Profil koncentracij bakra, kisika in ogljika na prelomu bakra z veliko duktilnostjo (Z = 90%)

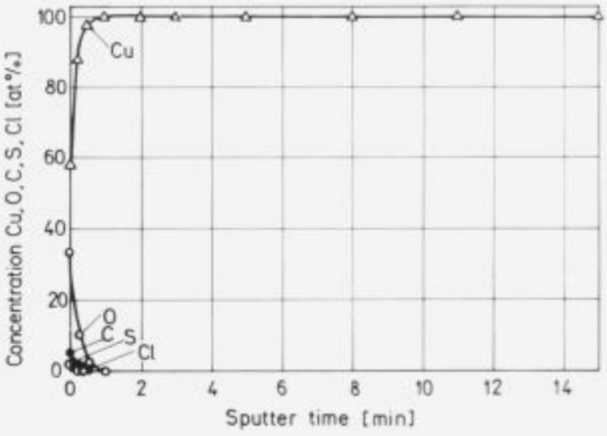

Figure 11: Copper, oxygen and other elements concentration distribution on fracture surface of copper after vacuum annealing (fracture after annealing)

Slika 11: Profil koncentracij bakra, kisika in drugih elementov na prelomu bakra z majhno duktilnostjo po žarjenju v vakuumu (prelomljeno po žarjenju v vakuumu)

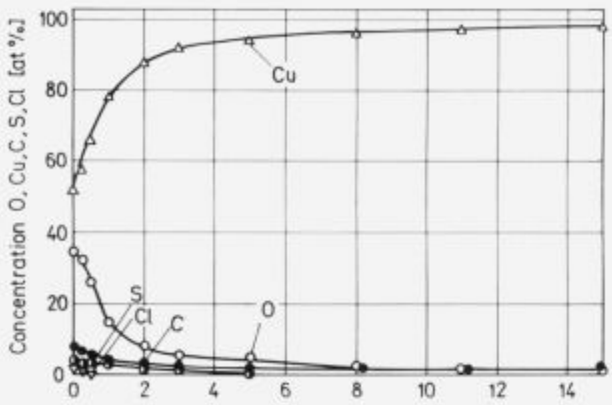

Figure 10: Copper and oxygen concentration distribution on fracture surface of copper after annealing in nitrogen (5 ... 6 ppm O2)

Slika 10: Profil koncentracij kisika in bakra na prelomu bakra z majhno duktilnostjo po žarjenju v vakuumu (5 ... 6 ppm O2) na temperaturi 500°C

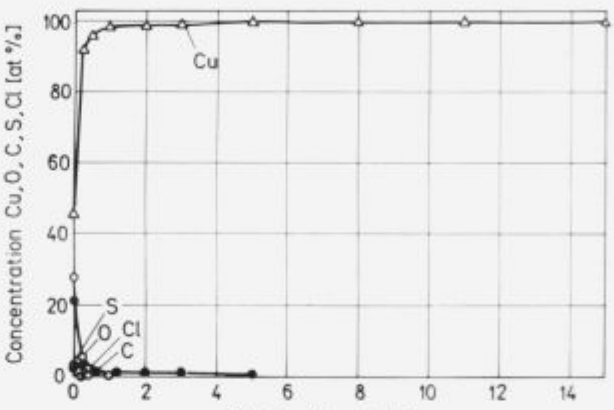

Figure 12: Cooper, oxygen and other elements distribution on fracture surface after vacuum annealing (fracture before annealing)

Slika 12: Profil koncentracij bakra, kisika in drugih elementov na prelomu bakra z majhno duktilnostjo po žarjenju v vakuumu; (prelomljeno pred žarjenjem v vakuumu)

sis of oxygen and of other elements on the fracture surface. The effect of the oxygen removal by the annealing in vacuum has been estimated by the comparison of the oxygen concentration on the fracture of the vacuum annealed copper wire and those when the fracture surface of the brittle copper was annealed in vacuum (**Fig. 12,13**). During the vacuum annealing much more oxygen has been removed from the fracture surface than from the bulk wire sample.

2. The Mechanism of the Copper Embrittlement

At 500°C, the grain boundary diffusion in the copper is preferential to the diffusion inside grains[3].

The solubility of oxygen in copper is about 10 ppm[3] at 500°C. At the annealing temperature of 500°C the grain boundary diffusion rate of oxygen is higher for few orders of magnitude to the bulk diffusion rate inside grains. Thus mainly grain boundaries become enriched with oxygen. After completed annealing the temperature of copper droped to the surroundings temperature. Major amount of oxygen was precipitated in form of the copper oxide Cu_2O on the grain boundaries. The precipitation from solid solution is characterized by the formation of many fine particles distributed on the grain boundaries. At suitable stresses or deformation, pores appear on the boundary between the precipitates of the copper oxide and the metal matrix along the grain boundaries. Since precipitates are numerous the dimples are small and shallow. The oxygen embrittlement is a reversible phenomenon if oxygen enriched copper is annealed under the conditions which enables the oxygen removal below the solubility limit at the surroundings temperature.

3. Conclusions

In annealing copper in the atmosphere with a very low partial pressure of oxygen at a temperature favourable for the grain boundary diffusion, higher oxygen concentrations has been detected only on grain boundaries. During the cooling to the surroundings temperature oxygen precipitated from the metal in the form of the copper oxide (Cu_2O). Such a formation of the copper oxide favours the formation of a great number of fine precipitates. On the boundary between the precipitates and the metal matrix pores appear at a suitable high deformation, and they

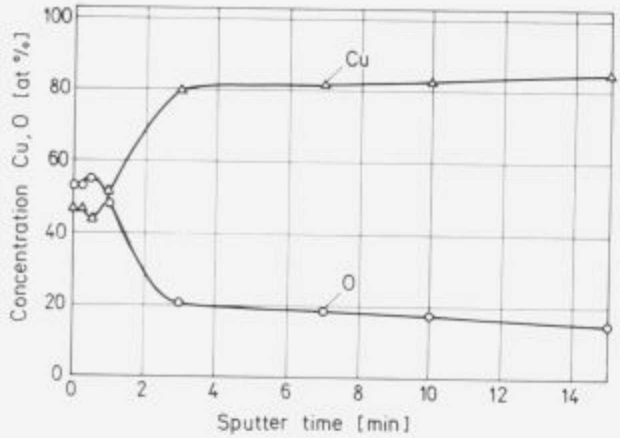

Figure 13: Copper and oxygen distribution on wire surface before annealing in nitrogen

Slika 13: Profil koncentracij kisika in bakra na površini bakrene žice pred žarjenjem v dušiku

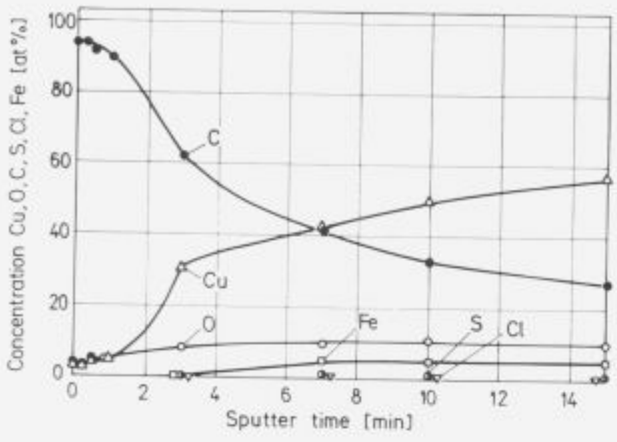

Figure 14: Oxygen, copper and other elements concentration distribution on wire surface before annealing in nitrogen

Slika 14: Profil koncentracij kisika, bakra in drugih elementov na površini bakrene žice pred žarjenjem v dušiku

propagate into a intergranular fracture with the small microscopic and macroscopic degree of deformation. The phenomenon of the oxygen embrittlement of copper is reversible. If the oxygen is removed from the metal below the solubility limit at

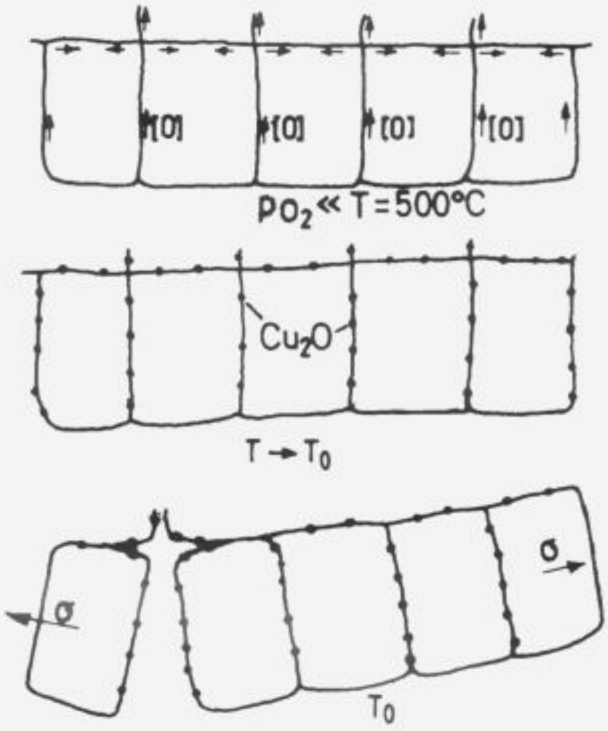

Figure 15: Mechanism sequences of copper wire embrittlement

Slika 15: Mehanizem krhkosti bakrene žice

the surroundings temperature, there exist conditions for the formation of the intergranular dimpled fracture. In the analyzed case the oxygen was found to be distributed unevenly in the metal and predominantly on the grain boundaries. Thus it is essential the reduced oxygen concentration on the grain boundaries and not the average oxygen concentration in the bulk metal.

4. Literature

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