

MICROSTRUCTURE ANALYSIS OF INTERNALLY OXIDIZED Cu-C COMPOSITE

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On the basis of experimentally obtained data, it was established that submicron-size bubbles are formed by the internal oxidation of Cu-C composite with fine dispersed graphite particles. They are homogeneously distributed in the Cu-matrix. This process starts with the dissolution of oxygen into the metal at the free surfaces, and continues with the diffusion of oxygen atoms into the volume of copper crystal lattice where they react with the graphite particles. The reactions of dissolved oxygen with carbon yield the gas products (CO_2 , CO), which cannot be dissolved in the crystal lattice of the matrix. The gas molecules, which are enclosed in the space previously occupied by the graphite, have a greater specific volume than the solid graphite. Consequently, compressive stresses arise in the copper matrix around the bubbles. The interaction of these stress fields with gliding dislocations during loading could improve the mechanical properties of the copper. The internal oxidation kinetic in Cu-C composite depends on the diffusion of oxygen in the copper matrix, and the penetration depth of the internal oxidation front indicates the parabolic nature of the process.

Key words: *microstructure, Cu-C composite, internal oxidation, bubbles*

Mikrostrukturalna analiza unutarnje oksidiranog Cu-C kompozita. Na osnovi eksperimentalnih rezultata utvrđeno je da pri unutrašnjoj oksidaciji Cu-C kompozita s finom disperzijom grafitnih djelića nastaju sub-mikronske pore. One su homogeno raspoređene u Cu-matici. Proces počinje otapljanjem kisika na slobodnoj površini metala i nastavlja s difuzijom kisika u kristalnu rešetku Cu-matrice gdje kisik reagira s grafitnim djelićima. Reakcija otopljenog kisika s grafitom daje plinske molekule (CO_2 , CO) koje se ne mogu rastopiti u kristalnoj rešetki matrice. Plinske molekule koje se nalaze u prostoru gdje je prije toga bio grafit, imaju veći specifični volumen od čvrstog grafita. Posljedično nastaju u matrici oko pora tlačne napetosti. Interakcija ovih napetosti s kliznim dislokacijama pod opterećenjem može poboljšati mehaničke karakteristike bakra. Zapaženo je da je kinetika unutarnje oksidacije u Cu-C kompozitu ovisna od difuzije kisika u Cu-matrici i da penetracijska dubina fronte unutrašnje oksidacije ukazuje na paraboličnu prirodu procesa.

Ključne riječi: *mikrostruktura, Cu-C kompoziti, unutrašnja oksidacija, pore*

INTRODUCTION

Materials with high electrical and thermal conductivity, respectively with microstructural stability and high temperature strength, are very attractive for the electric-electronic industry and special machine building industry (actively-cooled parts, rocket nozzles, magnet wire and cables, welding electrode tips). Copper is one of the most promising metals for these applications because it has the highest thermal and electrical conductivity among structural materials. In addition to its high thermal conductivity, cop-

per also has the advantage of low elastic modulus, which minimizes thermal stresses in actively-cooled structures. On the other hand, copper requires a considerable improvement in strength to be applicable at high temperatures.

Different strengthening mechanisms, such as solid-solution hardening, cold working, precipitation hardening and dispersion hardening can be used to improve the mechanical properties of metals [1, 2]. In all these cases the strengthening effect is a consequence of the interactions gliding dislocations with the barriers (solute atoms, precipitate, dispersoids - hereafter called simply inclusions), and with other dislocations. These interactions mean that these obstacles tend to pin dislocations and that dislocations can exert forces on them. According to many theoretical studies and some experimental results

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[3], the finely dispersed submicron-size gaseous bubbles are also potentially effective inclusions, which can serve to improve the mechanical properties of the metals. The bubbles exert their effect in two ways: (i) they are able to lock dislocations and (ii) by acting as barriers against grain boundary motion, they shift the recrystallization temperature of metals to higher values [4]. The strengthening effects depend on the distribution of bubbles, on their size and internal pressure, and on their interaction energy with single dislocations. The microstructure that develops during this process is related to manufacturing technology, and the alloying systems composition.

The internal oxidation (IO) of the Cu-C composite with dispersion of nano-sized graphite particles can lead to the formation of sub-micron sized compressed bubbles. The Cu-C phase diagram is characterized by a highly restricted mutual solubility of the elements in the solid state. It was found, however, in our previous research work [5, 6] that a discontinuous copper-graphite composite with nano-sized graphite particles can be obtained with a new processing approach consisting of rapid solidification and internal carbonisation. In this process rapid solidification is the source for obtaining a high concentration of defects in the copper crystal lattice, which act as nucleation sites in the subsequent internal carbonisation process. By internal oxidation, the reaction of oxygen atoms - dissolved in the copper - with graphite particles yields the gas products (CO_2 , CO), which cannot be dissolved in the crystal lattice of the copper. The gas products are enclosed in the space previously occupied by the graphite and they have a greater specific volume than solid graphite ($V_{(s)}^{\text{C}} = 5,298 \text{ cm}^3 \ll V_{(g)}^{\text{CO, CO}_2} = 24789,2 \text{ cm}^3$) [7], thus establishing compressive stresses in the matrix and, consequently, causing the strengthening effect. Namely, the obtained stress fields in the Cu matrix [8] around the bubbles can react with dislocations during loading and this interaction improves the mechanical properties of the copper. The phenomenon of internal oxidation is known in literature [9, 10] and is also used in practice to improve the mechanical properties.

In this paper we present some results of our experimental studies of oxygen behaviour in the composite Cu-C. We examined the required conditions for the internal oxidation of nano-sized graphite particles dispersed in the copper matrix, and we verified the occurrence of this process by microstructural characterization.

EXPERIMENTAL WORK

Rapidly solidified Cu ribbons (Cu - 99,99 %) had been prepared using the Chill-Block Melt Spinning Technique. The process was performed under Ar atmosphere using a quartz crucible 48 mm of inner diameter and nozzle with an orifice diameter of 1,5 mm [11]. The melt was ejected by argon overpressure of 0,02 to 0,03 MPa onto the sur-

face of a copper-beryllium wheel, rotating at a speed of about 21 m/s. Continuous ribbons were produced 3 to 5 mm in width and 60 to 80 mm in thickness [12]. The microstructure of the attained rapidly-solidified ribbons consists of a zone with columnar grains extending from the wheel surface to the free surface of the ribbon (Figure 1.). Rapid solidification served for obtaining ribbons with a high concentration of defects in the copper crystal lattice, which would act as graphite nucleation sites in the subsequent internal carbonisation (IC) process.

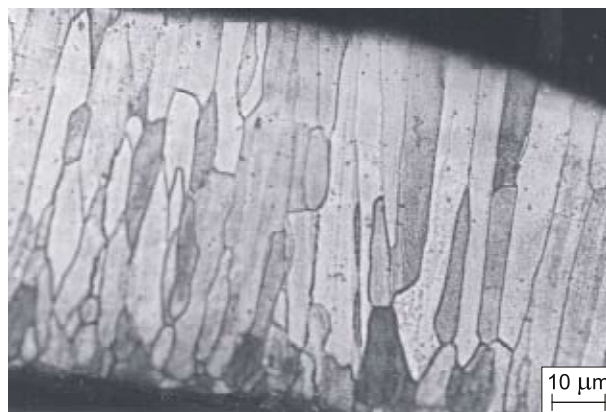


Figure 1. Microstructure of transverse cross-section of RS copper
Slika 1. Mikrostruktura poprečnog presjeka RS bakra

Short pieces of Cu-ribbons were packed in amorphous carbon powder, isostatically pressed into 3 cm long tablets and enclosed in a quartz ampoule. The heat treatments were carried out in a tube furnace at a temperature of 873 K for 2 hours. The microstructure of the attained ribbons consists of Cu-matrix and very fine graphite sub-micron particles that are homogeneously distributed through the volume of the grains (Figure 2.). The nature of the particles was determined by Auger Electron Spectroscopy, as well as

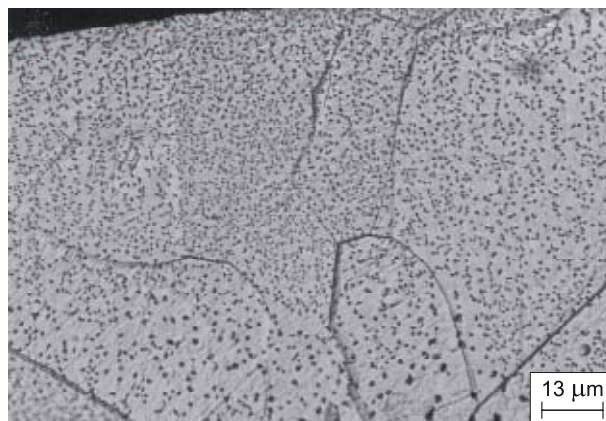


Figure 2. Microstructure of transverse cross-section of ribbons with graphite particles in Cu matrix
Slika 2. Mikrostruktura poprečnog presjeka traka s grafitnim česticama u Cu matici

by chemical microanalysis and a selected area diffraction pattern taken from the coarser particles in thin foils. These investigations revealed that the particles contain only the carbon atoms bound in the graphite.

Afterwards the short pieces of Cu-C ribbons were annealed at 1173 K in oxygen partial pressure equal to the decomposition pressure of the cuprous oxide. In order to accomplish this, short pieces of ribbons were packed in a mixture of equal parts cuprous oxide and copper metal powder and enclosed in a quartz ampoule (Rhines packet). The heat treatments were carried out in a tube furnace over various periods of time.

Modelling samples consisting of copper matrix and graphite filament were produced (Figure 3.), for confirming the proposed mechanism for internal oxidation of Cu-C composite. This then enabled determination of the kinetics of graphite oxidation in the Cu matrix and an estimation of the occurred pressure during this reaction.

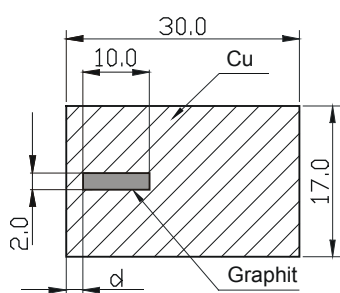


Figure 3. Schematic presentation of modelling samples Cu-C
Slika 3. Shematski prikaz modelnog uzorka Cu-C

Microstructural characterisation of the internally oxidized samples was carried out using optical microscopy (OM), scanning electron microscopy (SEM-Jeol JSM 849 A), as well as EDX microanalysis (Link analytical AN 1000). In addition, Auger Electron Spectroscopy (AES-Microlab 310-F equipped with SEM and X-ray Photoelectron Spectrometer-XPS) was used to determine the elemental compositions of precipitated particles after internal carbonisation. The surfaces of the particles were cleaned and etched with Ar^+ ions ($E = 2 \text{ keV}$, $r = 12 \text{ mAcm}^{-2}$; $Q = 47^\circ$) to remove surface contaminants and to obtain compositional depth profiles. Specimens of internally-oxidized ribbons for optical and scanning electron microscopy were prepared using standard metallographic methods and etched in $\text{FeCl}_3\text{-H}_2\text{O-HCl-C}_2\text{H}_5\text{OH}$ solution.

RESULTS AND DISCUSSION

Metallographic examinations of the internally-oxidized experimental samples of Cu-C ribbons reveal that the microstructure contains two different zones after partial internal oxidation: the internal oxidation zone and the unoxidized two-phase zone. A typical cross-section of the partially oxidized ribbons used to measure the penetration depth of the internal oxidation front is shown in Figure 4. The oxidation front is hardly visible as a border between the lighter outer region and the darker unoxidized zone containing

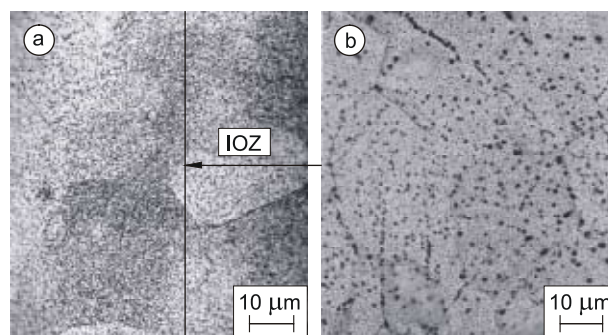


Figure 4. Microstructure of the Cu-C ribbons after partial (a) and complete (b) internal oxidation at 1173 K (IOZ - internal oxidation zone)

Slika 4. Mikrostruktura Cu-C traka poslije djelomične (a) i ukupne unutarnje oksidacije pri temperaturi 1173 K (IOZ - zona unutarnje oksidacije)

the graphite particles. The internal-oxidation zone consists of Cu matrix and coarser oxide particles - bubbles. Their distribution mostly corresponds to those of the graphite particles in the unoxidized two-phase zone. These bubbles are bigger than graphite particles and their number in unit volume is a little lower. These facts show that they probably had to be formed by direct graphite oxidation. Chemical microanalysis was also performed in order to determine the nature of the rounded bubbles. In the particle region we didn't detect carbon or any other element, with the exception of copper. Additionally, numerous bubbles can also be seen on the free surfaces of the ribbons.

The mechanism and kinetic of the internal oxidation process in Cu-C ribbons were studied by microstructural examination of ribbons exposed to internal oxidation over different periods of time and at a chosen temperature (1173 K). The penetration depth of the internal oxidation front was measured, as an indicator of the kinetic of IO process, and the parabolic function of time was confirmed.

The internal oxidation in Cu-C composite starts with the adsorption of oxygen on the sample's surface, its dissolution into the lattice of the copper matrix, continues with diffusion of the dissolved oxidant in the matrix interior, and the reaction at the advancing reaction front with the graphite particles (Figure 5.). At the interface of the copper/graphite, reaction of carbon with the oxygen dissolved in the copper matrix takes place according to the following reactions:



The oxidation products are gaseous molecules CO and CO_2 , which cannot solve in the Cu-lattice and they are meshed in the space previously occupied by graphite. The gas products have a greater specific volume than solid

graphite, thus establishing compressive stresses in the metallic Cu-matrix around the bubbles and, consequently, causing a strengthening effect. On the other hand, such stress fields can react with sliding dislocation, whereby they impede dislocation motion. The growth of bubbles

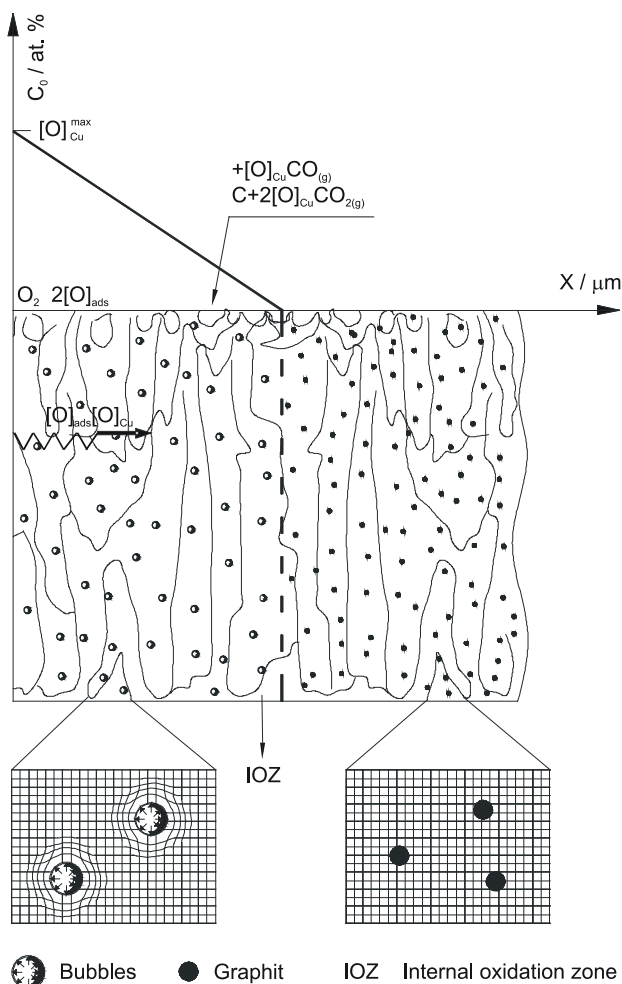


Figure 5. Schematic presentation of internal oxidation of graphite particles in Cu matrix
Slika 5. Shematski prikaz unutarnje oksidacije grafitnih čestica u Cu matrici

is stimulated by pressure from the gaseous products, which deforms the copper matrix during high temperature oxidation. Open-pores are formed on the sample's surface in places previously occupied by graphite particles and shear bands occur through local inhomogeneous deformation of the copper matrix during internal oxidation of the graphite particles, which were enough close to the free surfaces of the ribbons (Figure 6). Thermodynamically both reactions at the Cu/C boundary proceed as the oxygen concentration in the solid copper solution is higher than the equilibrium value for reactions (1) and (2). Taking into account the oxygen activity in the copper matrix γ_0 , the Gibb's energy for the formation of gaseous products ΔG° , their equilib-

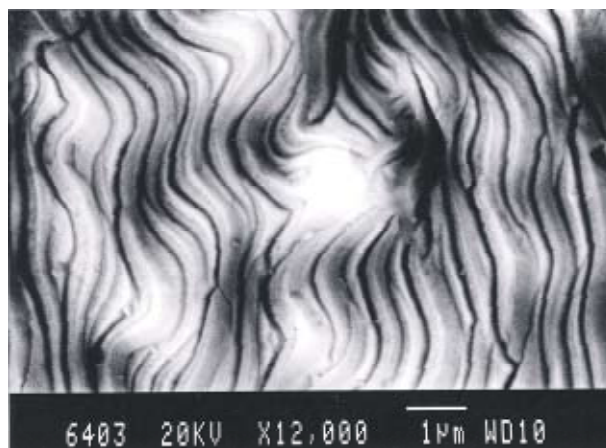


Figure 6. Topography on the free surface of internally oxidized ribbons of Cu-C composite
Slika 6. Topografija vanjske površine unutarnje oksidirane Cu-C trake

rium pressure in the pores (p_{CO}, p_{CO_2}) and, by considering that $a_C = 1$, the equilibrium oxygen concentration can be calculated for the reactions (1) and (2) from the equilibrium conditions ($\Delta G = 0$):

$$[C_0]_{Cu}^{eq} = \frac{\exp(\Delta G_f^0 / RT)}{p_g \cdot \gamma_0} \quad (3)$$

According to the equilibrium of the reaction, $2Cu + [O]_{Cu} \rightarrow Cu_2O$, γ_0 was calculated from the equation:

$$\gamma_0 = \frac{\exp(\Delta G_f^0)}{C_0^{max}} \quad (4)$$

where the ΔG_f^0 is the Gibb's energy formation for the oxide Cu_2O [7], and C_0^{max} is the maximum solubility of the oxygen in the copper at 1173 K.

The estimated equilibrium oxygen concentrations for both reactions were much lower than the maximum oxygen solubility in the copper matrix. This confirms that the activity of oxygen atoms in the copper matrix is high enough for internal oxidation of the graphite in the copper matrix.

In the next step, the boundary layer on the graphite particles burned down and the contact between the reactans was lost. Namely, a gap is formed between the copper matrix and the graphite, so the direct oxidation process can only flow further by moving the internal oxidation front to a new place, where contact between the copper matrix and the graphite particles still exists. Additionally, in the non-contact region internal oxidation probably continues indirectly by the following reactions:



Reaction (5) takes place at the interface gas/copper matrix and reaction (6) at the interface gas/graphite. During this indirect oxidation process, the oxygen atoms are transported to the reaction surface of the graphite by oxygen dioxide. Such a proposed mechanism for internal oxidation of Cu-C composite was also confirmed in those experiments with the modelling samples (Figure 7.). The reaction of the dissolved oxygen with graphite yielded the gas products CO, CO₂, which established compressive stress in the Cu-matrix. The experiments have shown that the oxidation rate of graphite particles in the Cu-matrix is

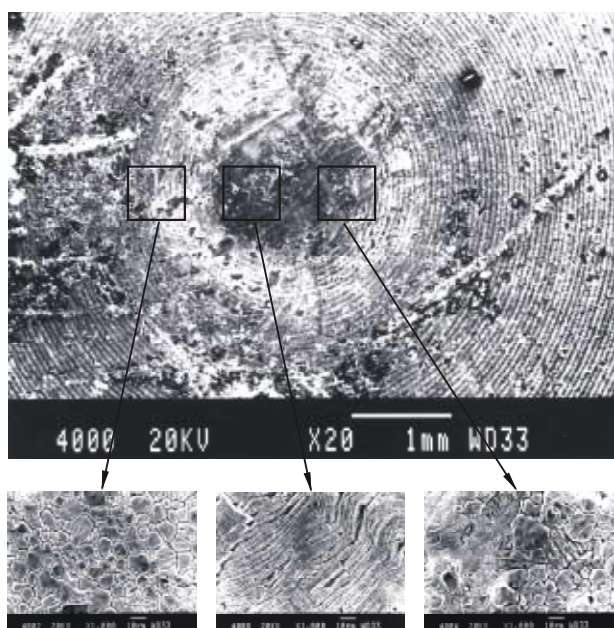


Figure 7. Cu-C modelling samples after partly oxidized region at the top of graphite filament

Slika 7. Cu-C modelni uzorci poslije djelomične oksidacije u području vanjske površine iznad grafitnih vlakana

the parabolic time function. This kinetics is a consequence of the gas products increasing pressure and oxidation transition to indirect CO₂ phase graphite combustion. The chamber, clearly visible at the top of the graphite filament, can be attained only by the indirect oxidation process (Figure 7). Furthermore force was required, for deformation of the outer Cu-wall, which could be calculated from the proposed model (Figure 8.). Taking into account that the outer Cu-wall is plate, the thickness of the Cu-wall remains constant, and by considering metal forming utilizing working media [13], the required force (*F*) for Cu-wall deformation can be calculated from equation:

$$F = p \times h \times s \times R_m \times c_v \quad (7)$$

where:

h is the deformation of the Cu-wall, measured as the rise in [mm],

R_m as the tensile strength of the copper at 1173 K and

c_v as the coefficient of force [14].

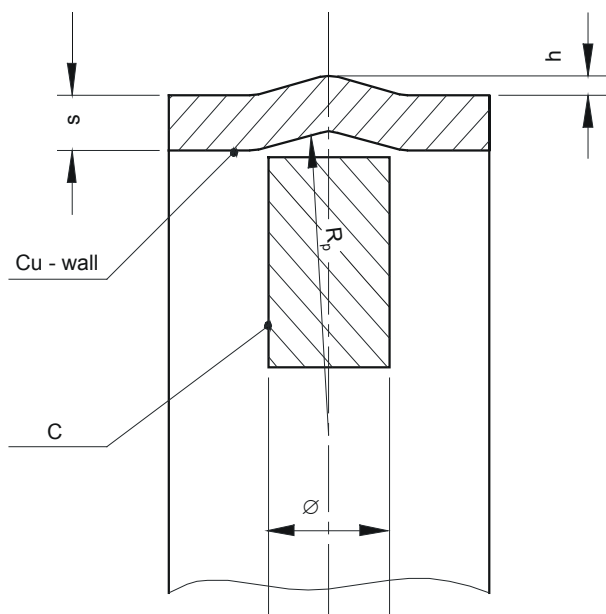


Figure 8. Schematic presentation of model for determination of required force for deformation

Slika 8. Shematski prikaz modela za izračun potrebne sile za deformaciju

Furthermore, according to the stress equation:

$$p = \frac{F}{A_p} \quad (8)$$

where *A_p* is the common deformed surface, the size of this stress was estimated to be 3×10⁶ Pa.

CONCLUSIONS

The results of this experimental work clearly confirm that submicron-size bubbles are formed by the internal oxidation of Cu-C composite with finely-dispersed graphite particles.

The other principal conclusions of this study are:

1. Gaseous products (CO, CO₂) are enclosed in the space previously occupied by the graphite.
2. The bubbles are larger than the C-particles, and mainly of spherical shape.
3. The specific volumes of the gaseous molecules are much greater than solid graphite, so strong compressive stresses

arise in the copper matrix. The size of this stress was estimated to be 3×10^6 Pa.

4. In the first step, the reaction between the graphite and dissolved oxygen atoms in the Cu matrix proceeds as direct internal oxidation and, in the second step, the internal oxidation transition to indirect CO₂ phase graphite combustion.
5. The oxidation rate of the graphite particles in the Cu-matrix is the parabolic time function. This kinetics is a consequence of the increasing pressure of the gas products and the oxidation transition to indirect CO₂ phase graphite combustion.
6. The internal oxidation kinetic was controlled by the diffusion of oxygen in the copper.

REFERENCES

- [1] E. Arzt, D.S. Wilkinson, Acta Metallurgica, 34 (1986) 10, 1863 - 1898.
- [2] E. Arzt, P. Grahle, Zeitschrift für Metallkunde, 87 (1996) 5, 874 - 883.
- [3] R. W. Weeks, S. R. Pati, M. F. Ashby, P. Barrand, Acta Metallurgica, 17 (1969) 5, 1403 - 1415.
- [4] D. J. Srolovitz, M.J. Luton, R. Petkovic-Luton, D.M. Barnett, W. D. Nix, Acta Metallurgica, 32 (1984) 7, 1079 - 1088.
- [5] I. Anžel, R. Rudolf, A. Križman, A. C. Kneissl, Praktische Metallographie, 41 (2004) 4, 516 - 527.
- [6] R. Rudolf, L. Kosec, I. Anžel, A. Križman, Materiali in tehnologije, 38 (2004) 6, 317 - 324.
- [7] E. A. Brandes, G. B. Brook, Smithell's Metals Reference Handbook, London, 1992.
- [8] B. Kosec, Euroteh, 3 (2004) 5, 32 - 33.
- [9] F. N. Rhines, Transactions AIME, 137 (1940), 246 - 290.
- [10] C. Wagner, Zeitschrift für Electrochemie, 63 (1959) 7, 772 - 782.
- [11] G. Lojen, I. Anžel, A. C. Kneissl, A. Križman, E. Unterweger, B. Kosec, M. Bizjak, Journal of Materials Processing Technology. (in Print)
- [12] B. Kosec, L. Kosec, F. Kosel, M. Bizjak, Metall, 54 (2000) 4, 186 - 188.
- [13] H. Elsasser, Betriebserfahrungen und Wirtschaftlichkeit beim Hydromechanischen Tiefziehen von Blechen, Blech Rohre Profile, 29 (1982) 2, 348 - 352.
- [14] B. Musafija: Obrada metala plastičnom deformacijom, Svjetlost, Sarajevo, 1988.

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