Comparison of the electrochemical behavior of cast and sintered CuAg 4 at. % alloy during thermomechanical treatment

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Abstract: The paper presents a comparison of the electrochemical behavior of samples of CuAg 4 at. % alloy obtained by the powder metallurgy method and the same alloy obtained by melting and casting during oxidation in an alkaline medium. The investigated alloys exhibited the anneal hardening effect. Hence, they were examined in each stage of thermomechanical treatment resulting in this effect. Cyclic voltammetry investigations showed that both the sintered and cast samples after cold rolling to a final reduction of 60 % behaved as completely homogenous phases. In this stage of thermomechanical treatment, peaks corresponding to reactions on silver did not appear and the currents on the cyclic voltammograms were the lowest. After annealing below the recrystallization temperature, both samples exhibited anneal hardening; in this stage, the sintered alloy retained its corrosion stability, whereas the current densities for the cast alloy increased and peaks characteristic for silver appeared again. Further annealing above the recrystallization temperature led increasing current density on voltammograms for samples obtained by both methods and all characteristic current peaks for silver reappeared.

Keywords: copper; silver; anodic oxidation; anneal hardening; recrystallization.

INTRODUCTION

Copper–silver alloys can be obtained by the so-called ingot metallurgy (IM) method, *i.e.*, by melting and casting, as well as by the powder metallurgy (PM) method.[1–3] The Ag–Cu binary alloy is a characteristic example of a eutectic system, with full solubility in the liquid state and mutually restricted solubility in the solid state.[4] The maximum solubility of silver in copper at the eutectic temperature is 4.9 at. % and it decreases with decreasing temperature. Cu–Ag alloys have wide range of electrical applications because of good combinations of high

mechanical properties and high electrical conductivity. Tensile strengths up to 1 GPa and electrical conductivities of about 60–70 % of the International Annealed Copper Standard (IACS) make them particularly suitable for applications such as pulsed high-field solenoids and conductor materials for Bitter type magnets.[5,6] Additional improvements in properties such as electrical conductivity, corrosion resistance, strength and maintenance of strength at high temperatures can be achieved by application of proper thermomechanical treatments. Anneal hardening is a genuine hardening mechanism that occurs in some copper-based alloys, including Cu–Ag alloys, where alloying elements segregate on dislocation after cold deformation and annealing below the recrystallization temperature. Anneal hardening of Cu–Ag alloys was observed in the annealing temperature range from 140 to 400 °C, the hardness increasing with the degree of pre-deformation.[2,3] The phenomenon was observed in alloys synthesized by both the IM and the PM method.

Oxidation and passivity of pure copper and silver have been widely investigated in the electrochemical literature.[7–13] Cu–Ag alloys have been less examined, but some recent papers deal with electrochemical characteristics of this binary alloy.[14–21] Taking into account that the method of synthesis of an alloy may influence its corrosion stability, the goal of the current work was to compare the electrochemical behavior of CuAg 4 at. % alloy obtained by the PM method with the same alloy obtained by the IM method. The samples obtained by the two different methods were compared in the corresponding stages of thermo-mechanical treatment that results in anneal hardening.

EXPERIMENTAL

Electrochemical characterization was performed using a standard three-electrode system consisting of a saturated calomel electrode (SCE) as the reference electrode, platinum as the counter electrode and CuAg 4 at. % alloy, as the working electrode material. The active surface area of the working electrodes was 0.25 cm^2 and that of the counter electrode was 2 cm^2. The investigations were performed in a 0.1 M NaOH solution (pH 12.7) by cyclic voltammetry and open-circuit potential measurement under the following conditions: temperature, 25 °C and scan rates of 10, 20, 50, 75 and 100 mV s^{-1}.

The CuAg 4 at. % alloy for the working electrodes was obtained by both the PM and IM methods. The sample marked as IM1 (pre-saturated solid solution) was prepared in the following usual metallurgical way: metallic silver and electrolytic copper wire with a purity of 99.99 % were weighed in the required ratio, melted in a laboratory electric furnace and cast in a sand clay mould; the obtained ingots were subjected to homogenization annealing at 800 °C for 34 h, pre-final cold rolling, solution annealing and quenching in ice water.

Electrolytic copper powder and silver powder with purities of 99.7 and 99.9 %, respectively (the silver powder content in the mixture was 4 at. %) were used to prepare the samples marked as PM. Powder mixture compacts measuring 6–7 mm in height, 30 mm in length and 12 mm in width were prepared by the method of one sided pressing at a pressure of 300 MPa on a hydraulic press (sample PM1 for electrochemical investigations). The compacts were sintered at 790 °C in a horizontal tube furnace under an atmosphere of high purity dry

hydrogen for 1 h to obtain the sample marked as PM1. Detailed synthesis and thermomechanical treatment to obtain starting samples are described in previous works.[2,3,18,19] The samples for testing are chosen in corresponding different stages of thermomechanical treatment that resulted in anneal hardening for both the IM and PM samples. This treatment included final cold rolling and annealing at different temperatures below the recrystallization temperature. Finally, the samples were subjected to annealing above the recrystallization temperature. The sample assignments and descriptions of preparation are given in Table I.

TABLE I. Sample abbreviations and descriptions of preparation

Abbreviation	Description of preparation
IM1	Pre-saturated α solid solution obtained by melting, casting, annealing at 700 °C for 1 h and quenching in ice water (the treatment is fully described in ref. 16)
IM2	Cold rolled sample IM1 after a final reduction of 60 %
IM3	Sample IM2 annealed at 260 °C for 90 min (exhibited anneal hardening)
IM4	Sample IM3 annealed at 600 °C for 60 min
PM1	Powder mixture pressed at a pressure of 300 MPa and sintered at 790 °C for 1 h with a two-phases structure
PM2	Cold rolled PM1 after a final reduction of 60 %
PM3	Sample PM2 annealed at 260 °C for 150 min (exhibited anneal hardening)
PM4	Sample PM3 annealed at 600 °C for 60 min

Five measurements of hardness and electrical conductivity were performed on each chosen sample. The hardness measurements were realized using a Vickers hardness tester VEB Leipzig with a load of 5 kg and a dwell time of 15 s. Electrical conductivity was measured using a "Sigmatest" conductometer.

For electrochemical measurements, all the investigated samples were prepared in the form of electrodes. Electrical contact between the copper wire and the electrode material was achieved using conducting silver glue IM-P3014 (Iritel, Belgrade) and then mounted in cold polymerized SIMGAL mass (Galenika, Belgrade). For each set of experiments, working electrodes were ground with the finest grinding paper, polished with alumina (0.05 μm), washed with distilled water and alcohol, dried, and finally drowned into electrolyte. Before each experiment, the working electrode was polished with alumina.

The system for electrochemical measurements consisted of hardware (PC, AD–DA converter NI-6251 produced by National Instruments and an analog interface) and software for excitation and measurement (LabView 8.2 platform, National Instruments, Austin, TX, and application software) both fully developed by the Technical Faculty in Bor, Serbia.[22,23] The investigations were performed in 0.1 M NaOH by cyclic voltammetry and open circuit potential measurements.

RESULTS AND DISCUSSION

Hardness, electrical conductivity and steady-state open circuit potentials of all the investigated samples are presented in Table II. The table illustrates the changes in the mechanical and electrical characteristics of the CuAg 4 at. % alloy during thermomechanical treatment resulting in so-called anneal hardening.

It can be seen that sample PM1 had lower hardness and electrical conductivity values in comparison with those of the IM1 sample. The porosity of the

sintered material decreased its properties in comparison with the more compact cast material.

TABLE II. Some properties of the CuAg 4 at. % alloys in different stages of thermo-mechanical treatment

Abbreviation	Hardness, HV	Electrical conductivity, MS m^{-1}	Steady-state open circuit potential, V *vs.* SCE
IM1	80	42.6	−0.200
IM2	170	40.4	−0.209
IM3	194	42.1	−0.152
IM4	97	50	−0.157
PM1	48	38	−0.198
PM2	156	46.3	−0.208
PM3	182	46.9	−0.205
PM4	93	50.4	−0.210

The hardness of both samples increased during cold rolling, due to deformation strengthening. Although the PM2 sample still had lower hardness in comparison with the suitable hardness of the IM2 sample, a more intensive hardness increase was achieved with the PM2 sample, because porosity elimination and deformation strengthening occurred simultaneously. The electrical conductivity of the PM sample was increased after cold rolling but the electrical conductivity of the IM sample decreased with deformation. This was the result of two opposing effects.[2] A porosity decrease during cold rolling increases the electrical conductivity (effect 1). However, lattice distortion (effect 2) during the cold rolling decreases the electrical conductivity. In the PM sample, the first effect was stronger than the second one and as a result, the electrical conductivity increased. On the other hand, with the IM sample, the second effect was stronger than the first one, which resulted in a decrease in the electrical conductivity.

The anneal hardening effect appeared in both cold deformed samples during annealing at 260 °C as the result of silver segregation to dislocations, analogous to the formation of Cottrel atmospheres in interstitial solid solutions, which resulted in increases in the hardness and electrical conductivity of samples IM3 and PM3.

After annealing the cold deformed samples at 600 °C, the hardness of both samples dropped significantly, because of the formation and growth of new undeformed grains, *i.e.*, recrystallization starts to occur. The hardness values for the IM4 and, especially, for the PM4 sample were higher compared to those of the initial state, implying that the recrystallization had not occurred in full. Annealing at 600 °C led to an increase in the electrical conductivity, because of recovery and the beginning of recrystallization (samples IM4 and PM4).

The electrochemical investigations included measurements of the open-circuit potential (OCP) and cyclic voltammetry. The open-circuit potentials for all

the samples are given in Table II. It is obvious that there is no big difference in the OCP values between the samples obtained by the two different metallurgical techniques. On the other hand, annealing led to some positive change in the OCP of casted samples, because silver as the nobler component appeared as an independent phase, while all PM samples had very similar OCP values (around –0.200 mV vs. SCE). The voltammograms were recorded from –1.6 up to 1.0 V vs. SCE, $i.e.$, from hydrogen evolution up to the beginning of gaseous oxygen evolution. To recognize which current wave corresponds to copper and which one to silver, the voltammograms obtained for the alloy (samples IM4 and PM1) were compared with those obtained on the pure metals, copper and silver (Fig. 1). The results of the first scan obtained at a scan rate of 20 mV s^{-1} are presented.
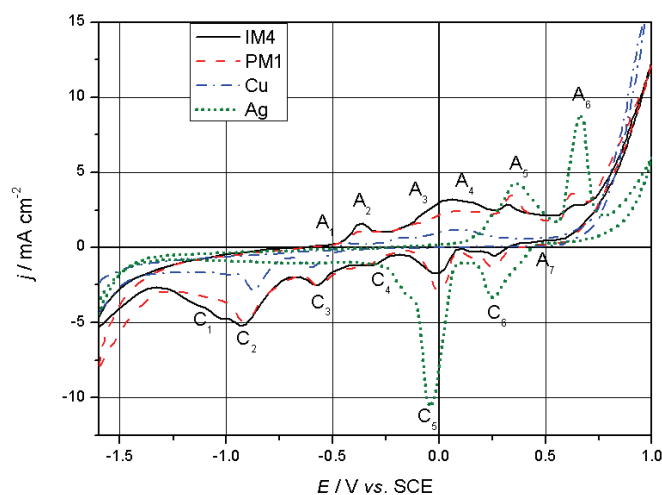
Fig. 1. Cyclic voltammograms of pure metals Cu and Ag, and samples IM4 and PM1 in 0.1 M NaOH at a scan rate of 20 mV s^{-1}.

The voltammograms in Fig. 1 proved that the mechanism of the anodic oxidation of the alloy in NaOH medium consisted of at least six steps. The first step in the oxidation process of the investigated alloy was the formation of a monolayer of adsorbed OH$^-$ species.[18,19] This reaction is attributed to the current peak marked as A_1. The next step during the anodic polarization was the formation of a lower copper oxide, Cu_2O, connected with the peak A_2. Peak A_2 appeared only on the voltammograms for samples of the alloy, both IM4 and PM1, and for pure copper. The same was valid for the peak A_3; hence, this peak is connected with formation of a higher oxide of copper, CuO. Current peaks A_4, A_5 and A_6, registered on the voltammogram for pure silver, are very well defined on the voltammogram for the sample of alloy obtained by the PM method, but they appear only as waves on voltammogram for the sample IM4. Peaks or waves A_4 and A_5 are

connected with formation of the lower oxide of silver, Ag_2O (type I and type II), and the peak A_6 is related with formation of higher silver oxide, AgO.[11–13,18–21] In the cathodic direction, the anodic reaction products are sequentially reduced in the corresponding reverse order, C_6, C_5, C_4, C_3, C_2, and C_1. The anodic current wave A_7, on the cathodic part of voltammograms, is associated with additional oxidation of elemental silver to Ag_2O.[20,21,24,25]

Within the aim of comparing the behavior of CuAg 4 at. % obtained by the IM method with the same alloy obtained by the PM method, first the sample IM1 was compared with the sample PM1 (Fig. 2), because these two samples are considered as the primary step for further thermomechanical treatment. The sample IM1 is a pre-saturated α solid solution, the synthesis procedure of which is described in detail elsewhere.[18] An optical microphotograph of the IM1 sample (Fig. 2b) shows that the structure was generally homogeneous with equiaxal grains of average size 50–100 μm. The sample PM1 was obtained by pressing an appropriate powder mixture at a pressure of 300 MPa and sintering at 790 °C for 1 h (Table I). The optical microphotograph of the sintered PM1 sample (Fig. 2c) shows a relatively homogeneous structure with equiaxal grains and spherical pores. According to the phase diagram, the PM1 structure mainly consists of a Cu-rich α solid solution with a small amount of an Ag-rich β solid solution. The structure of the sintered sample was more fine-grained compared to the coarse-grained cast structure. The obtained voltammograms, presented in Fig. 2a, confirmed that in sample PM1, silver-rich grains still existed because the independent current peaks corresponding to silver are very well defined. It is obvious that the time of sintering was not long enough to complete the process of alloying.

On voltammogram for the cast alloy (sample IM1), the anodic currents are lightly higher than those obtained for the sintered sample and the current peaks A_3 and A_4 are hardly distinguishable because they overlap. Other current peaks on this voltammogram corresponding to the oxidation of silver are noticeable only as small shoulders because all these peaks are superposed on the current wave of copper oxidation. This indicates that the highest amount of silver present in the alloy was in form of a solid solution in copper. However, low but noticeable waves at potentials corresponding to the formation of silver oxide on the voltammogram obtained for the sample IM1 indicate that a small amount of silver was also present as an independent component.

The thermomechanical treatment that leads to anneal hardening consisted of cold rolling and further annealing below the recrystallization temperature. For this reason, in the next step of thermomechanical treatment, the IM1 and PM1 samples were subjected to final reduction of 20, 40 and 60 % by cold rolling. The samples obtained after the reduction of 60 % were chosen as samples IM2 and PM2 for electrochemical investigations because they resulted in highest final hardening. Voltammetric curves of samples IM2 and PM2 are presented in Fig. 3a,

from which it could be seen that the voltammograms of the CuAg 4 at. % alloys obtained by the PM and IM method, both cold rolled to a final reduction of 60 %, almost do not exhibit any peak that would correspond to the formation of silver oxide, which indicated that the highest amount of silver present in the alloy was in the form of a solid solution in copper. At this stage of thermomechanical treatment, both samples behaved as a homogenous phase and the peak currents were the lowest. Optical microphotographs of the IM2 and PM2 samples presented in Fig. 3a and b, respectively, show that the equiaxal grains had been deformed and elongated in the rolling direction. Moreover, in PM2 sample, porosity had decreased significantly due to sealing of the pores. In previous studies, it was shown that the slip lines in the cast samples formed during the plastic defor-
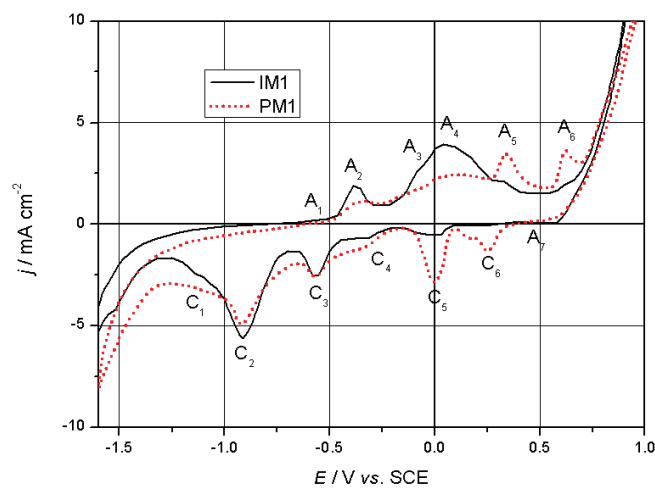
(a)
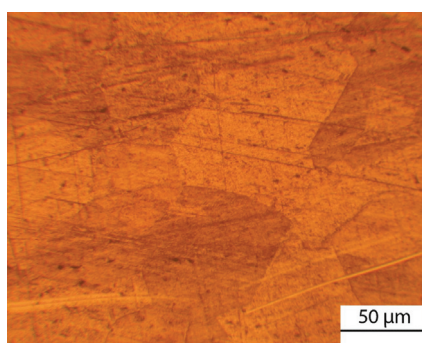
(b)
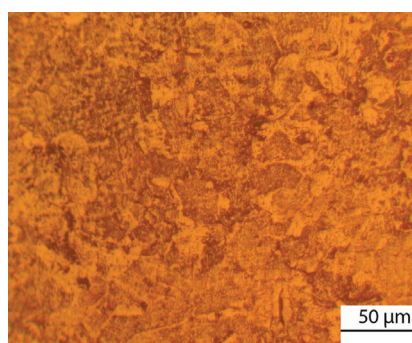
(c)

Fig. 2. Comparison of the CuAg 4 at. % alloys obtained by the IM method when in form of an undeformed α solid solution and by the PM method after pressing and sintering; a) cyclic voltammograms under the conditions: $v = 20$ mV s^{-1}, 0.1 M NaOH, $t = 25\pm0.5$ °C; optical microphotographs of the b) IM1 and c) PM1 sample.

mation were more extensive than in the sintered samples,[2,3,18,19] as is evident in Fig. 3b and c. This could be an explanation for differences in behavior between these samples during further treatment.

Cyclic voltammograms of the CuAg 4 at. % alloy obtained by IM and PM method in a stage when they exhibit anneal hardening effect (samples IM3 and PM3) are presented in Fig. 4a, from which, it could be seen that after annealing below the recrystallization temperature, the sintered alloy retained its corrosion stability, whereas the peak currents for the cast alloy increased. The current peaks corresponding to the oxidation of silver were hardly distinguishable for the sample obtained by the PM method, while on the voltammogram obtained for the sample synthesized by melting and casting (IM3), these peaks reappeared. After
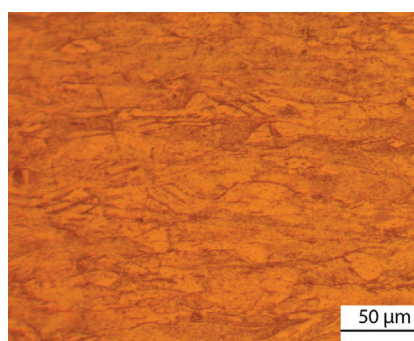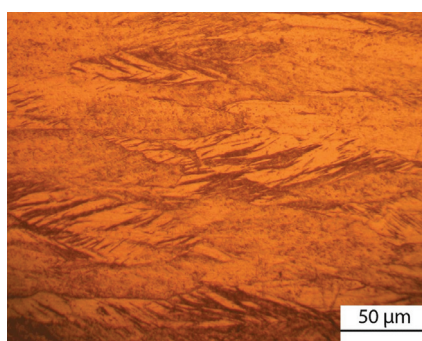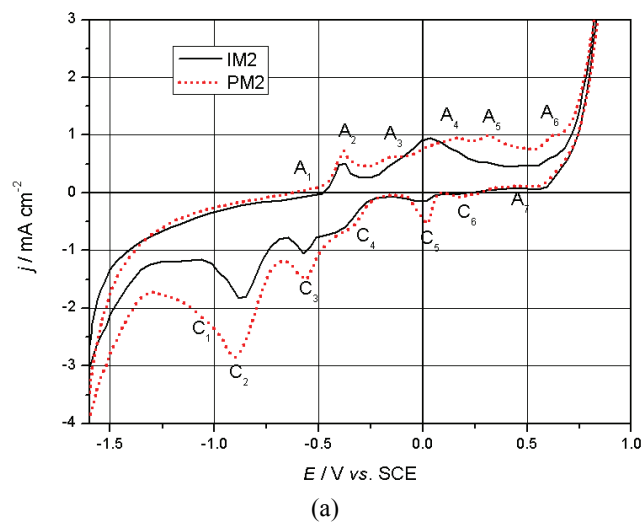

(a)

(b)

(c)

Fig. 3. Comparison of the CuAg 4 at. % alloys obtained by the IM and PM methods, both cold rolled to final reduction of 60 %; a) cyclic voltammograms under the conditions: $v = 20$ mV s^{-1}, 0.1 M NaOH, $t = 25\pm0.5$ °C; optical microphotographs of the b) IM2 and c) PM2 sample.

annealing at 260 °C, the oxidation of silver in the cast CuAg 4 at. % alloy sample was more pronounced because of segregation of solute atoms (silver) on the dislocations and the higher non-homogeneity of the structure. show The microstructures of the cold rolled IM and PM alloys after annealing at 260 °C, which led to a hardening of their structures due to anneal hardening effect, are shown in Fig. 4b and c, respectively. Several explanations have been proposed for the origin of this phenomenon, among which two propositions are thought to be rational. The first proposition is the formation and collapse of short-range order and the second one is the segregation of solute atoms to stacking faults. The grains are still elongated along the rolling direction and the slip lines and slip bands are still very clear, especially for the IM3 sample.
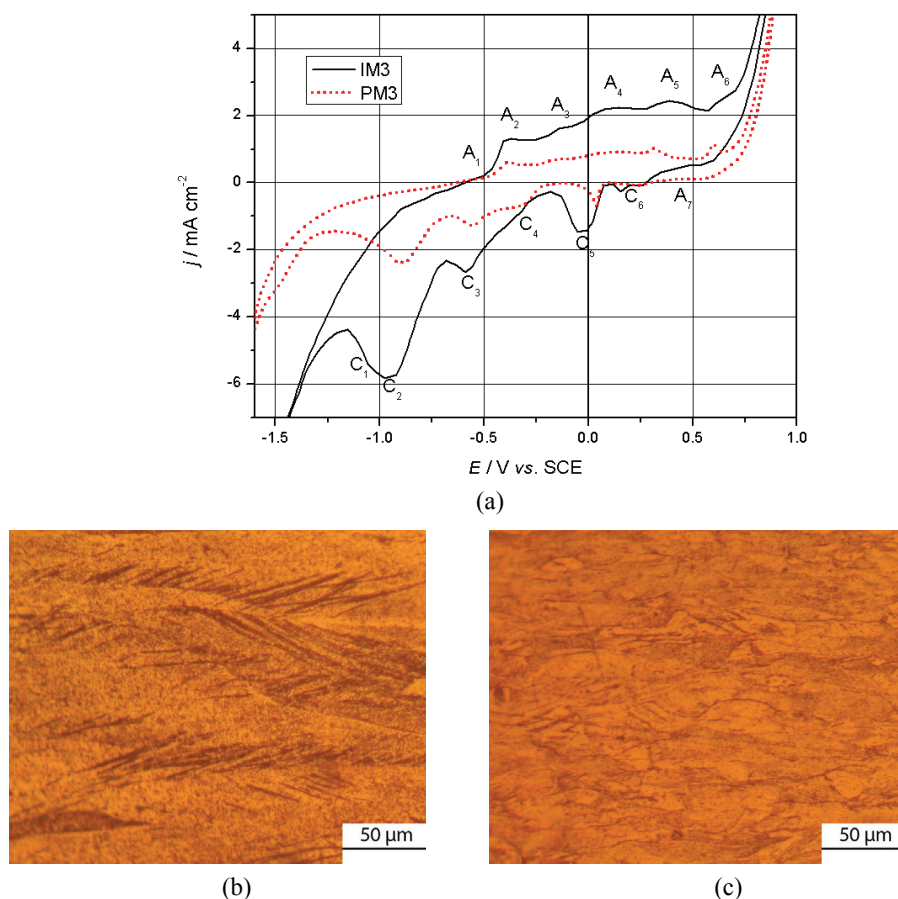

(a)

(b)

(c)

Fig. 4. Comparison of the CuAg 4 at. % alloys obtained by the IM and PM methods, both exhibiting the anneal hardening effect; a) cyclic voltammograms under the conditions: $v = 20$ mV s^{-1}, 0.1 M NaOH, $t = 25\pm0.5$ °C; optical microphotographs of the b) IM3 and c) PM3 sample.

The voltammograms of both the IM and PM samples annealed above the recrystallization temperature (IM4 and PM4) are presented in Fig. 5a. The voltammograms of both samples contain distinctly separate current waves of silver oxide formation, which means that silver, that was in the form of a solid solution, remained in that form after cold rolling, whereas in the annealing process, it was extracted as a second pure metal phase. After recrystallization annealing at 600 °C for 30 min, the peak currents increased to the value they had before cold deformation and the current densities were lower for the sample PM4, obtained by the powder metallurgy method, than for the sample IM4. The microstructure of the samples IM4 and PM4 are shown in Fig. 5b and c, respectively. No newly deformed, recrystallized grains were observed in the structures. In PM4 sample,
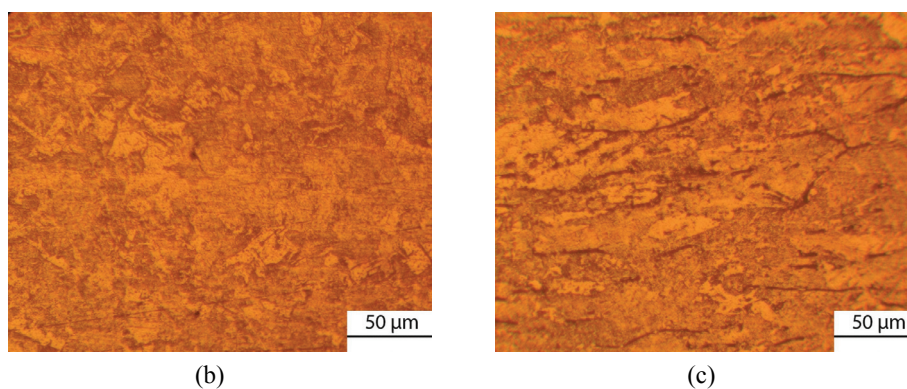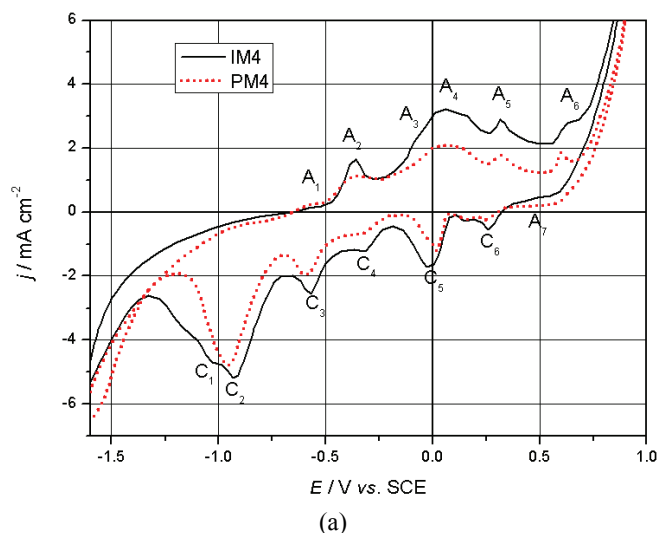

(a)

(b)

(c)

Fig. 5. Comparison of the CuAg 4 at. % alloys obtained by the IM and PM methods after recrystallization annealing; a) cyclic voltammograms under the conditions: $v = 20$ mV s^{-1}, 0.1 M NaOH, $t = 25\pm0.5$ °C; optical microphotographs of the b) IM4 and c) PM4 sample.

some places with elongated grains were still visible, implying that the recrystallization was not complete, which is in agreement with the results of the hardness measurements.

CONCLUSIONS

The electrochemical behavior of samples of CuAg 4 at. % alloy obtained by the powder metallurgy method during oxidation in an alkaline medium was compared with behavior of the same alloy obtained by melting and casting (so-called ingot metallurgy). It was shown in cyclic voltammetric investigations that the oxidation of both copper and silver in the CuAg 4 at. % alloy samples obtained by the ingot metallurgy method was more pronounced than in the samples obtained by the powder metallurgy technique in all stages of thermomechanical treatment leading to anneal hardening. This was the consequence of the more fine-grained structure of the sintered samples in comparison to the cast structure. The oxidation was the slowest in the case when only the α phase (solid solution of silver in copper) was present in the structure. This structure was obtained after cold rolling to a final reduction of 60 %.

Annealing below the recrystallization temperature led to anneal hardening of both the IM and PM samples. In this stage, sintered alloy retained its corrosion stability, whereas the current densities for the cast alloy increased and peaks characteristic for silver reappeared. The oxidation of the silver in the cast CuAg 4 at. % alloy samples after annealing at 260 °C was more pronounced because of segregation of the solute atoms (silver) onto the dislocations and inhomogeneities of the structure.

И З В О Д

ПОРЕЂЕЊЕ ЕЛЕКТРОХЕМИЈСКОГ ПОНАШАЊА ЛИВЕНЕ И СИНТЕРОВАНЕ ЛЕГУРЕ CuAg 4 ат. % У ТОКУ ТЕРМОМЕХАНИЧКЕ ОБРАДЕ

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У раду је приказано поређење електрохемијског понашања у алкалној средини легура CuAg 4 ат. % добијених по две различите металуршке методе – методом металургије праха и такозваном ингот методом. Ова легура је посебно интересентна због тога што испољава ефекат ојачавања жарењем после одговарајуће термомеханичке обраде. Због тога је поређење изведено у свим фазама које та термомеханичка обрада подразумева. Методом цикличне волтаметрије утврђено је да је легура електрохемијски најстабилнија у фази након хладног ваљања са степеном деформације од 60 % без обзира на методу којом је легура синтетизована. Тада се легура понаша као хомогена фаза, на волтамограмима се не појављују пикови карактеристични за сребро и густине струје су

најниже. Накнадно жарење испод температуре рекристализације, које доводи до оја-
чавања, донекле нарушава хомогеност ливене легуре, док синтерована легура задржава
хомогеност и стабилност достигнуту након ваљања. Рекристализационо жарење, међу-
тим, доводи до повећања густине струје на волтамограмима и до поновне појаве свих
струјних пикова карактеристичних за оксидацију и редукцију оба присутна метала у
легури.

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