

RAMAN SPECTROSCOPY STUDY OF ANODIC FILM ON Ag₄₃Cu₃₇Zn₂₀ ALLOY

Zorica Lazarević¹, Stevan Dimitrijević², Miodrag Mitrić³, Silvana Dimitrijević⁴,
Milica Petrović¹, Martina Gilić¹, Nebojša Romčević¹

¹Mining and Metal Institute of Physics, University of Belgrade, Belgrade, Serbia, lzorica@yahoo.com

²Innovation Center Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,
11000 Belgrade, Serbia, stevad@gmail.com

³Vinča Institute of Nuclear Science, University of Belgrade, Belgrade, Serbia, mmitric@vinca.rs

⁴Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia,
silvana.dimitrijevic@irmbor.co.rs

ABSTRACT

The aim of the present work is characterization of electrochemically treated Ag₄₃-Cu₃₇-Zn₂₀ alloy in near neutral chloride solutions by the X-ray diffraction and Raman spectroscopy. At potential of +0.25 V, a complex multilayer film is formed. XRD shows that it consists of CuCl and zinc hydroxichlorides with small amount of Cu₂O, probably formed in the film pores. It can be concluded that the Raman spectroscopy is observed almost all the modes that are registered with the XRD analysis.

Keywords: alloy, XRD, Raman spectroscopy

1 INTRODUCTION

Silver based brazing filler alloys have been widely used in various industries including high-tech like: electronics, automotive, aerospace and similar. They are suited filler materials for joining ferrous and non-ferrous metals, and alloys, except aluminum and magnesium. Inclusion of cadmium in brazing fillers gives the following advantages: reduces the brazing temperature, lowers cost and improve mechanical properties of alloys. Owing to the inherent toxicity of cadmium, legislation all over the world restricting the use of cadmium in brazing alloys, especially for application in the food industry and medicine. Cadmium-free silver brazing alloys that can replace Ag based brazing alloys containing cadmium, are the ternary AgCuZn or multi-component alloys based on them or Ag-Cu system with the addition of Ga, Sn, In and Ni [1]. The investigated alloy has the composition of BS1845:1984 Ag5 commercial alloy, i.e. Ag₄₃-Cu₃₇-Zn₂₀. Electrochemical behavior of ternary brazing alloys of the Ag-Cu-Zn system has not been extensive investigated. Some interest existed in the eighties, but the investigations had a limited scope. The main aspects of the studies were a type of corrosion at brazed joints, open circuit potential in chloride solutions (brazing alloys and binary silver alloys) and electrochemical galvanic action between the coexisting phases as responsible for corrosion of filler metal and interface [2].

The aim of present work has been characterized by the X-ray diffraction and Raman spectroscopy electrochemically formed Ag₄₃Cu₃₇Zn₂₀ alloy after treatment in near neutral chloride solutions (in 3.5 wt.% NaCl).

2 EXPERIMENTAL

High purity metals (99.99%) for electrode preparation were produced by the recycling process. More details of the process and analytics can be found elsewhere [3]. The alloy for

the electrode was prepared by two consecutive steps of ingot casting in a graphite mould. The second, repeated, process was performed in the aim to correct composition caused by high zinc losses for small charges. The obtained ingot was lathe machining into cylinder with 7.14 mm diameter. It was subjected to homogenization annealing at 873 K ($T \approx 0.9 T(m)$) for 24 h in nitrogen atmosphere and slowly cooled to the room temperature in the same protective atmosphere. Finally, the specimen was mounted in polytetrafluoroethylene (PTFE) mould. Chemical composition (wt.%) of the alloy used in the present study was 43.5% Ag, 37.7% Cu, 18.8% Zn, and trace elements (Sn, Pb, Fe, Ni) as analyzed by the inductively coupled plasma atomic emission spectroscopy. Chemical composition fulfills the requirements for BS1845:1984 Ag5 standard.

The all chemicals were of analytical grade produced by Merck (Germany). All solutions were prepared with ultra-pure water of resistivity not less than $18 \text{ M}\Omega \text{ cm}^{-1}$. Test solution, 3.5 wt. % NaCl, was prepared by dissolving 35 g of NaCl in 1000 ml glass flask to the total mass of solution of 1000 g. pH value was adjusted to pH=6.70.

The X-ray Powder Diffraction (XRPD) patterns of investigated sample were obtained on the Philips PW-1050 diffractometer, operated at 40 kV and 30 mA, using Ni-filtered Cu $K_{\alpha 1,2}$ radiation. The Bragg–Brentano focusing geometry was used with a fixed 1° divergence and 0.1° receiving slits. The patterns were taken in $10\text{--}100^\circ 2\theta$ ranges with a step of 0.05° and exposure time of 6 s per step. For the X-ray structural phase analysis, software EVA 9.0 Release 2003, Bruker AXS GmbH, Karlsruhe, Germany, was used.

The micro-Raman spectra were taken in the backscattering configuration and analyzed using a JobinYvon T64000 spectrometer, equipped with a nitrogen cooled charge-coupled-device detector. As an excitation source we used the 532 nm line of a Ti:sapphire laser. The measurements were performed at 20mW laser power.

RESULTS AND DISCUSSION

Figure 1 shows the results of X-ray diffraction (XRD) of the specimen after the potentiostatic test. The peaks of both phases, $(\text{Ag}_{1-x-y}\text{Cu}_y\text{Zn}_x)$ solid solution and Cu_3Zn (α -brass) are present, as well as before the potentiostatic test. X-ray structural phase analysis was applied for identification the new phases formed after potentiostatic test using the EVA 9.0 computing program. It can be noticed that beside the peaks that belong to $(\text{Ag}_{1-x-y}\text{Cu}_y\text{Zn}_x)$ solid solution phase, the peaks that correspond to pure Ag phase also have appeared. They have been formed by reduction of Zn and Cu content in solid solution during the potentiostatic polarization at +250 mV. The peaks of $(\text{Ag}_{1-x-y}\text{Cu}_y\text{Zn}_x)$ solid solution phase are positioned at somewhat larger 2θ values than the peaks of pure Ag phase. This difference increases with an increase of 2θ angles, meaning that the lattice parameter of Ag-rich phase is smaller than the lattice parameter of pure Ag phase, which can be explained by larger ionic radius of Ag than ionic radii of Zn and Cu. Noticeable increase of relative ratio of $(\text{Ag}_{1-x-y}\text{Zn}_x\text{Cu}_y)$ solid solution and pure Ag phases with the increase of 2θ angle implies that electrode surface is covered by pure Ag in thin layer beneath which is $(\text{Ag}_{1-x-y}\text{Cu}_y\text{Zn}_x)$ solid solution phase.

Figure 2 shows the Raman spectra of the $\text{Ag}_{43}\text{Cu}_{37}\text{Zn}_{20}$ alloy recorded after anodic potentiostatic polarization treatment at +0.25 V for 5 min in 3.5% wt. NaCl solution at room temperature. The main Raman peaks are indicated in the spectrum. The presence of silver (Ag), cuprous chloride (CuCl), zinc hydroxychloride ($\beta\text{-Zn(OH)Cl}$), cuprous oxide (Cu_2O) and simonkolleite ($\text{Zn}_5(\text{OH})_8(\text{Cl})_2 \cdot \text{H}_2\text{O}$) is registered.

Very strong silver peaks (cyan circles) indicate the formation of Ag areas, segregate from the Cu-Zn alloy. Observed Ag peaks at 920, 1189, 1234, 1368, 1442 and 1577 cm^{-1} are in general agreement with the previously published results [4].

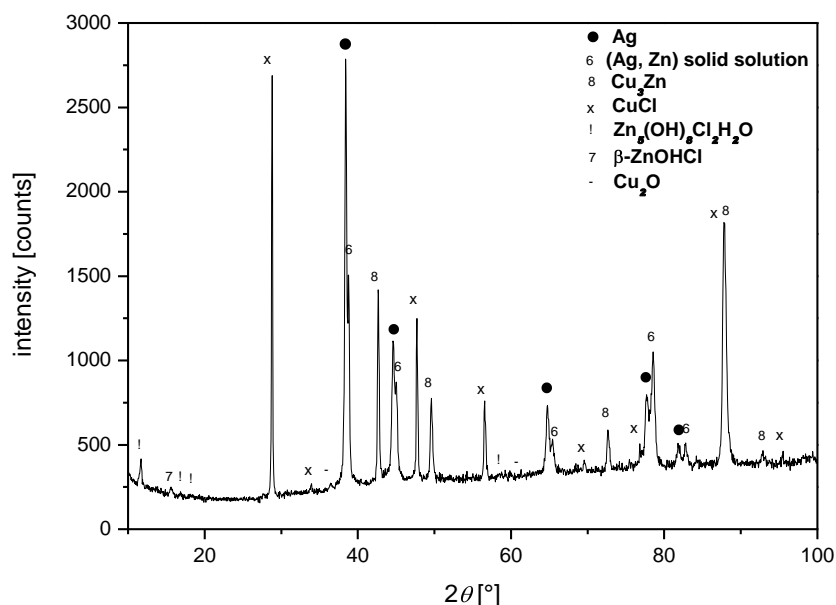


Figure 1 XRD pattern of the $\text{Ag}_{43}\text{Cu}_{37}\text{Zn}_{20}$ electrode after anodic potentiostatic polarization treatment at +0.25 V vs SCE for for 5 min in unbuffered 3.5% wt. NaCl solution at 25 °C

Cuprous chloride has the cubic zincblende structure with two atoms in the primitive cell so that there is only one triply degenerate fundamental optic mode, which is both the Raman and infrared active. The first-order phonons of CuCl visible in the Raman spectra (open triangles) are TO -phonon at 150 cm^{-1} and LO -phonon at 238 cm^{-1} [5, 6]. β -Zn(OH)Cl (green squares) are illustrated in Figure 2. Three main peaks are observed at 207 and 268 cm^{-1} , assigned to a Zn-Cl bond, and 386 cm^{-1} , attributed to a Zn-O vibration characteristic of this structure. Zinc hydroxychloride is also characterized by two main OH fundamental stretching bands at 920 and 1031 cm^{-1} [7, 8].

Cu_2O crystallizes in a cubic lattice with two molecules per unit cell and space group Pn3m. Since it exhibits inversion symmetry, its electronic and vibrational states are of definite parity. In the Raman spectra of treated alloy are seen several Cu_2O modes (black triangles). A weak mode at about 150 cm^{-1} can be a combination of TO -mode of CuCl and mode of Cu_2O . At 515, 621 and 690 cm^{-1} are modes of Cu_2O [9-11]. The Raman peaks at 207 and 386 cm^{-1} indexed by pink triangle, which agree very well with what are found in the [7], were assigned to $\text{Zn}_5(\text{OH})_8(\text{Cl})_2\cdot\text{H}_2\text{O}$ (simonkolleite). A peak at 207 cm^{-1} was attributed to the Zn-Cl bond and that at 386 cm^{-1} to Zn-O which had a vibration characteristic of a simonkolleite structure.

The presence of Ag, CuCl, β -Zn(OH)Cl, Cu_2O and $\text{Zn}_5(\text{OH})_8(\text{Cl})_2\cdot\text{H}_2\text{O}$ is in agreement with the XRD results.

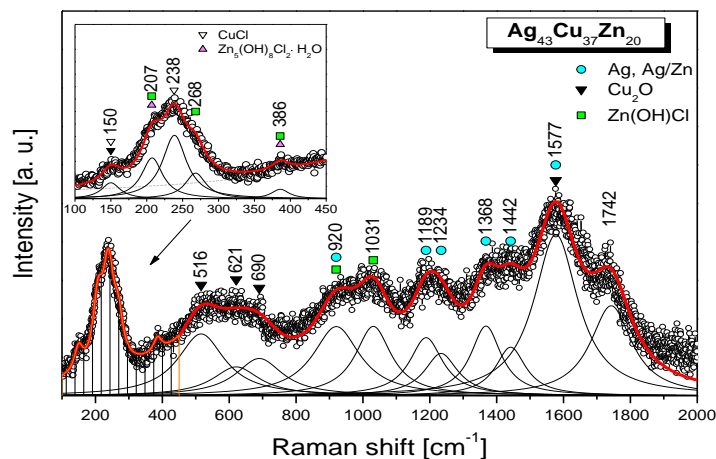


Figure 2 Raman spectra of the $\text{Ag}_{43}\text{Cu}_{37}\text{Zn}_{20}$ alloy at room temperature

CONCLUSION

The anodic film is a mixture of Cu_2O , CuCl , $\text{Zn}_5(\text{OH})_8\cdot\text{H}_2\text{O}$ and $\beta\text{-Zn}(\text{OH})\text{Cl}$. Phases of the alloy, Ag and Cu rich, show different behavior under anodic polarization. For analysis of the Raman spectra we assumed that all phonon lines were of the Lorentzian type, which is one of the common type of lines for this kind of analysis. It has already mentioned, phases of Ag, CuCl , $\beta\text{-Zn}(\text{OH})\text{Cl}$, Cu_2O and $\text{Zn}_5(\text{OH})_8(\text{Cl})_2\cdot\text{H}_2\text{O}$ were all registered by the XRD.

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