

Metallographic Investigations of Silver Alloys Used for Minting

Stephanie Greil^{1, a*}, Christian Edtmaier^{1, b}, Roland Haubner^{1, c}
and Lukas Lauter^{2, d}

¹Technische Universität Wien, Institute of Chemical Technologies and Analytics,
Getreidemarkt 9/164-CT, A-1060 Vienna, Austria

²Münze Österreich, Am Heumarkt 1, A-1030 Vienna, Austria

^{a*}stephanie.greil@tuwien.ac.at, ^bchristian.edtmaier@tuwien.ac.at, ^croland.haubner@tuwien.ac.at,
^dlukas.lauter@Austrian-Mint.at

Keywords: Silver alloys, electrochemical polishing, electrochemical etching.

Abstract. A typical metallographic preparation (i.e. mechanical grinding and chemical etching) and electrochemical etch-polishing was carried out to observe the microstructure of pure silver and two silver-copper alloys (Sterling silver Ag 925 and Ag 333) in circular blanks used for coin production. The obtained micrographs revealed cold working effects on the coin rim caused by the rimming process. These rim effects are the reason for local differences in the mechanical properties of circular blanks, posing a challenge to tool lifetime. To quantify these effects, a micro hardness-mapping was performed and analyzed.

Introduction

The use of noble metals and their respective alloys in metallurgical practice dates back more than 3000 years [1]. Even though they play an eminent role in the jewelry and minting industries, detailed mechanical properties of the silver and gold alloys used for coinage are by large unavailable in the literature [1-3]. The typical steps in coinage are casting, rolling, annealing, rimming and minting [1]. Optimizing each of these metal forming processes requires knowledge of such properties in detail.

The state of the art method for investigating silver alloys is a typical metallographic preparation by automated polishing machines using diamond suspensions, followed by etching with ammonia-peroxide solution [4-6]. In order to achieve high contrast and avoid scratches, as well as to avoid cross contamination during the preparation process, an electrochemical preparation approach [6, 7] refined and optimized. This work focuses on these two metallographic approaches for the metallography of fine silver (also called Ag 999) and silver-copper alloys (Ag 925 and Ag 333). In addition, hardness mapping of circular blanks after typical mechanical deformation during the coinage process was performed [1].

Methods and Experiments

Mechanical polishing: Circular rounds of fine silver Ag 999 (99.9 % Ag), Sterling silver Ag 925 (92.5 % Ag, copper bal.) and Ag 333 (33.3 % Ag, copper bal.) were examined. The samples were cut and embedded in resin before metallographic investigations. For manual grinding the following grit sizes of SiC papers were used: 1200-2000-4000. For polishing, diamond suspensions of particle sizes 9 µm, 3 µm and 1 µm were used with an automated polishing machine. Finally, the samples were etched with a (1+1+2) solution of ammonia, hydrogen peroxide and water [6].

Electrochemical polishing: Sections of circular blanks (14 x 1,5 x 2 mm) are too small to be to have an electrical contact affixed for an electrochemical polishing process in an electrochemical polishing process. An alternative embedding procedure was applied to electrically connect the materials, to insulate the surrounding area and to avoid undesired electrochemical side-reactions. In order to achieve these requirements, a two layer hot-mounting procedure was performed was performed. The first layer consisted of an insulating resin surrounding the silver surface being in contact with the electrolyte. The second layer, a thermoplastic acrylic resin with an iron filler, was

placed on top of the insulating layer, to allow electrical contact with the sample (Fig. 1). The mounted sample was then prepared for electrochemical polishing and etching by grinding with SiC papers of grit size 1200 and 2000. A Struers LectroPol-5 device was used for electro-polishing (Fig. 1).

Selected adjustments of voltage and time are given in Table 1. Preliminary tests were carried out on a small, directly electrically contacted silver block to determine those parameters. However, due to the different nominal compositions of the examined alloys and the different sizes of the samples, the parameters had to be adapted carefully and optimized for each sample. Furthermore, typical commercial electrolytes for silver samples based on alcoholic phosphoric acid are efficient solely for fine Ag, but appeared to be inefficient for silver alloys. Thus an aqueous solution of 5 % citric acid in 1 % ammonia was used for Ag-Cu alloys.

Microhardness mapping: Hardness measurements were carried out on embedded and polished samples. Various Vickers hardness HV0.05 indentations were arranged in a 150 μm space grid pattern. The resulting hardness data were then color-mapped, to allow visual interpretation of hardness as a function of position within the cross-section (Fig. 2).

Inverse light optical microscope (LOM), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX) were used to investigate the microstructure.

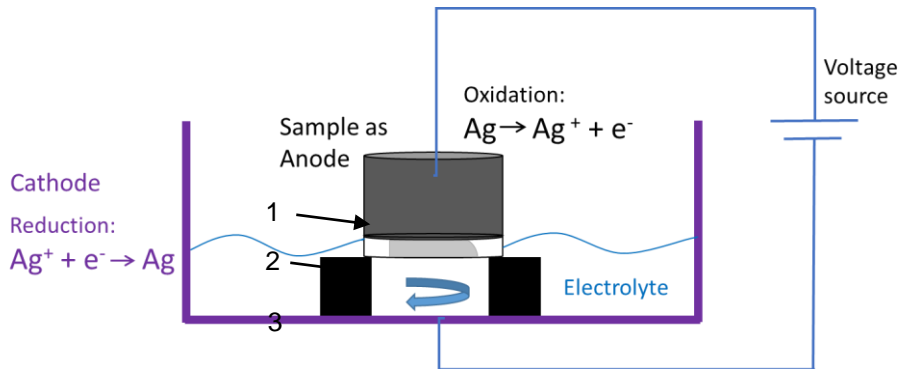


Fig. 1 Experimental set-up of electrochemical etching and polishing. Contacting the sample was carried out by embedding in (1) conductive and (2) insulating resin, (3) distance holders

Table 1 Parameters for the electrochemical polishing and etching procedure

material	polishing		etching	
	voltage [V]	time [s]	voltage [V]	time [s]
Ag 999	34	5	4	5
Ag 925	4	10	2	1
Ag 333	12	2	-	-

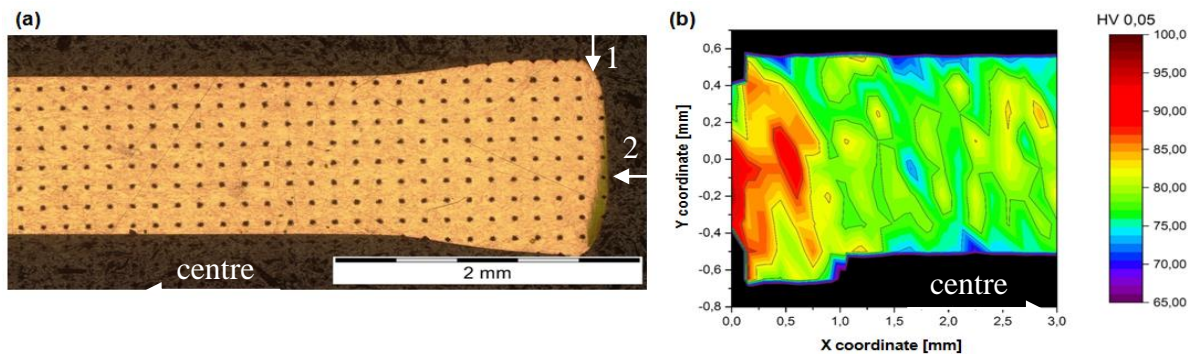


Fig. 2 Microhardness HV0.05 mapping: (a) indentations on a polished cross-section (b) typical plot of local hardness scatter on a sample's cross-section

Results and Discussions

Limitations and comparison of metallographic methods: The typical metallographic preparation by mechanical polishing using diamond suspensions resulted in a highly scratched surface and in cross contamination. SEM/EDX analysis on Ag specimens showed that the spots in Fig. 3a are gold from simultaneously prepared Au samples. Furthermore, carbon was detected and can be assigned to diamonds from polishing suspensions that were used. It is clear that due to the soft sample surface such diamond particles will be incorporated (Fig. 3) and cannot be removed by continued polishing.

Comparing mechanical polishing with subsequent chemical etching and electrochemically polished/etched material reveals some limitations of both methods. Fig. 4 compares micrographs of Ag 333 after mechanical polishing process (Fig. 4a) and after electrochemical polishing and etching (Fig. 4b) respectively. The overall sample surface is covered with scratches after mechanical polishing, while the surface of the electrochemically treated samples is free of scratches and has high contrast.

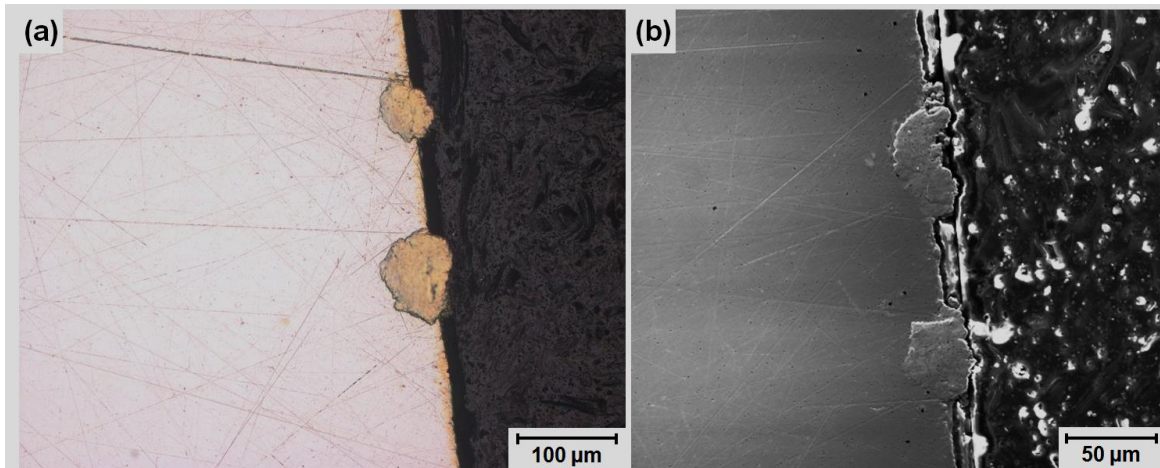


Fig. 3 Cross contamination during simultaneous mechanical polishing of gold Au999 and silver Ag 999 with diamond suspensions: (a) gold spots on pure silver (LOM), (b) image of the same site

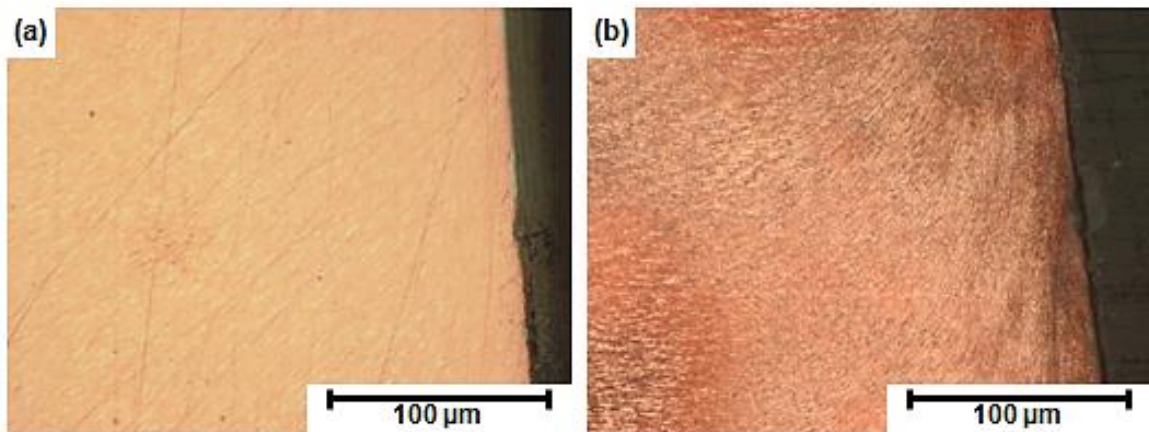


Fig. 4 Comparison of the preparation method on Ag 333: (a) mechanically polished, showing scratches and (b) electrochemically etch-polished material with no visible scratches

Electrochemically polished and etched samples: All circular blanks were produced from large metal strips and their rim areas indicate the direction of punching. Applying optimized voltage and time as using a convenient electrolyte allowed micrographs of high contrast to be obtained for all the examined materials (Fig. 5).

Fine silver shows a microstructure of varying grain sizes from approx. 40-200 μm (Fig. 5 a-c). Close to the edge of the blanks the grains are elongated (Fig. 5 b), in contrast with the center, where the microstructure is rather polygonal.

Due to the electric tip effect, the electrochemical treatment has a strong influence on the edges of the samples. The outermost sample layer is dissolved, the edges of the sample are rounded (Fig. 5a, d, g) and the etch attack of microstructure close to the edge is stronger (Fig. 5b, h). These effects are stronger when the electrochemical treatment is longer. The investigation of near-surface areas is more difficult in electrochemically treated samples, on account of these edge effects. Mechanical polishing results in sharp edges, thus near-surface zones can be easily investigated.

Due to the very low solubility of copper in silver and also silver in copper, copper forms extremely fine precipitates can form in the silver or copper matrix during cooling (Fig. 5i). The microstructure in Sterling silver Ag 925 shows a high contrast under polarized light produced with a differential interference contrast filter (Fig. 5e), as well as in polarized light (not shown). The microstructure is formed by silver-rich matrix and fine copper-rich precipitates (Fig. 5 d-f). The microstructure of Ag 333 is even finer so that the copper precipitates cannot be detected using LOM (Fig. 5 g-i). The microstructure is formed by small amounts of primary copper-rich phase and eutectic composition of silver-rich and copper-rich phases. The punching texture of these samples is clearly visible.

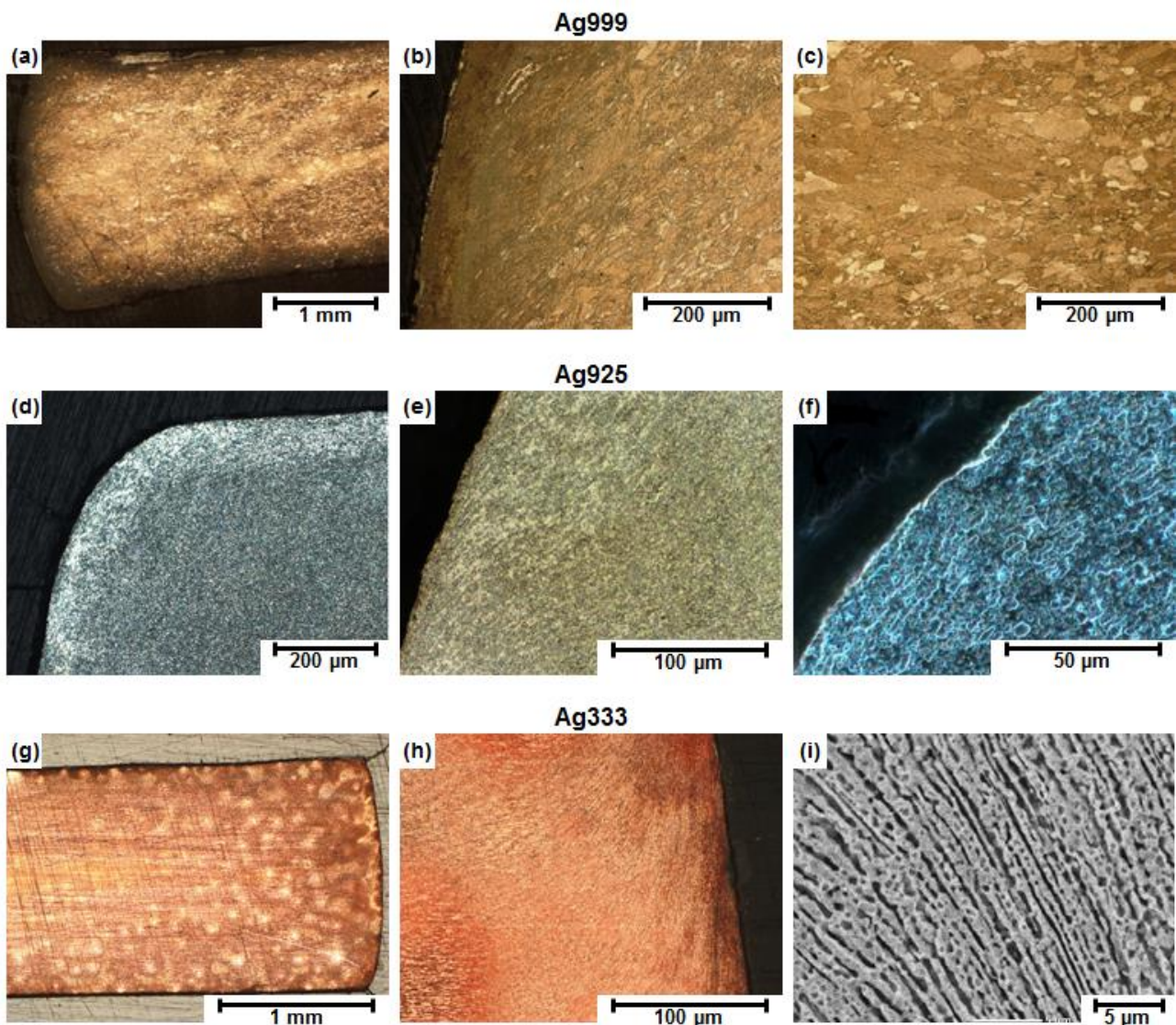


Fig. 5 Electrochemically etched silver and silver alloys: (a-c) fine silver Ag 999 (d-f), sterling silver Ag 925, (g-i) Ag 333, (a-h) LOM, (i) SEM

Hardness mapping. Micro hardness mapping revealed the influence of the rolling and rimming process used during the minting on the material. The difference from the hardest to the softest measured micro hardness is about 30 % across all samples.

In fine silver Ag 999, the region close to the surface has 100 HV0.05, thus it is the hardest area of the circular blank (Fig. 6a). Furthermore, a gradient in hardness from the edge to the center ($Y = \text{const.}$, $X = \text{adjustable}$) of the circular blank is visible. Interestingly, such a gradient in hardness can also be observed in the Y-direction, as the hardness is again higher rimmed edges, as compared to the edges ($X = \text{const.}$, $Y = \text{adjustable}$). However, the larger the distance from the rimmed edge, the lower the hardness. Sterling silver has similar properties, with hardness decreasing from about 90 HV0.05 at the rim and on the surface to 75 HV0.05 in the bulk material (Fig. 6 b). Ag 333 is hardest at the outermost rim region with a 165 HV0.05 and hardness decreasing with distance from these rims (Fig. 6 c). Due to the fine Cu-precipitates Ag 333 is the hardest of all investigated materials. Parallel to the sample surface, aligned areas of increased hardness (115 HV0.05) are visible. These lines may result from segregation due to the rolling process of the metal strips before the circular blanks are punched out of the material.

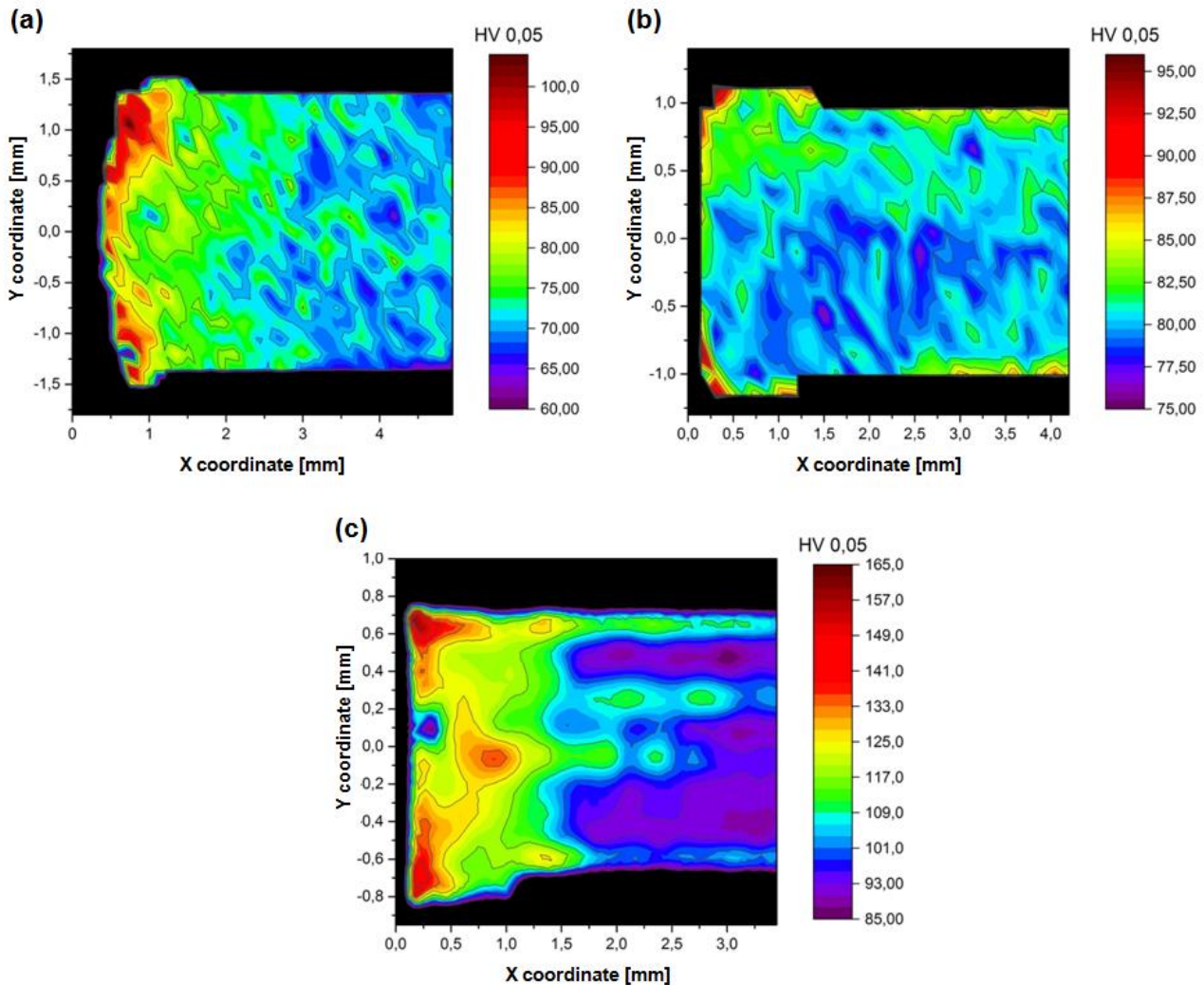


Fig. 6 Microhardness mapping of circular blanks. (a) Fine silver Ag999, (b) Sterling silver Ag925, (c) Ag333

Summary and Conclusion

Due to their softness, the metallographic preparation of silver-copper alloys is challenging, as typical methods such as grinding, polishing with diamonds and chemical etching do not give satisfying results, as scratches cannot be thoroughly removed. Electrochemical polishing with simultaneous etching proved to be an excellent alternative. To optimize the results, an electrolyte for silver-copper alloys was developed. For Ag 999, a commercial alcoholic solution of perchloric acid was used as electrolyte, while for Ag 925 and Ag 333 aqueous solutions of 5 % citric acid and 1 vol.% ammonia proved to be an excellent alternative electrolyte. Thus, a reliable, fast and non-toxic method to obtain micrographs of high contrast was developed.

While fine silver showed a homogeneous microstructure, but of varying grain size in its bulk, the alloys have fine copper precipitates beside primary Ag-rich phase (alloy Ag925). The microstructure of Ag 333 is even finer so that silver-rich precipitates cannot be detected using LOM. The microstructure is formed by primary Cu-rich phase and eutectic composed of silver-rich + copper-rich phases. Cold working effects from the rolling and rimming processes of these coinage samples were visible as texture in the micrographs.

Microhardness mapping was used to quantify the hardness increase caused by cold working during processing the silver parts. The rim areas of the circular blanks have an increased hardness of about 30 % compared to the bulk material. A hardness gradient from the edge and the rim towards the center of the circular blanks was detected. The micrographs and the corresponding micro hardness distribution in circular blanks may be used in the mint industry to improve the quality of their coinage.

Acknowledgements

The authors would like to thank “Münze Österreich AG” for the supply of samples and funding this project.

References

- [1] P. Hammer, Metals and Mint. 1993, Stuttgart: Deutscher Verlag für Grundstoffindustrie, 9-16 (in German).
- [2] G. Beck, et al., Precious Metals - Manual of Practice. 1995: Hüthig - Verlag Heidelberg (in German).
- [3] American Society for Metals, International. Handbook Committee, Metals Handbook: Volume 2: Properties and Selection: Nonferrous Alloys and Special- Purpose Materials. 1990: ASM International.
- [4] Buehler SumMet, The Science Behind Materials preparation. 2013; Available from: http://www.buehler-met.de/fileadmin/user_upload/pdf/buyersguide/Buehler_SumMet_DE_01.pdf.
- [5] G. Vander Voort. Metallographic Procedures for Precious Metals. 2012 [cited 2014 02. September]; Available from: <http://www.georgevandervoort.com/metallography-articles/1251-metallographic-procedures-for-precious-metals.html>.
- [6] G. Petzow, Metallographic, Ceramographic, Plastographic Etching. Materialkundlich-technische Reihe 2006, Berlin: Borntraeger (in German).
- [7] T. Jones, Electropolishing of precious metals, Metal Finishing 102 (2004) 45-57.