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Archaeological application of centreless X-ray diffractometers for non-destructive pole figure measurements

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Abstract – **Based on the crystallographic texture, the parameters of metal forming, heat treatment of metallic objects can be very well reconstructed as far as conventional technology (eg rolling, deep drawing, etc.) was applied. The characterization of the texture, except for the neutron diffraction, has been possible only by the destructive method. We have developed and validated the non-destructive texture measurement method for centreless diffractometers. The diffractometers, by their function, allow non-destructive testing, thus providing a whole new dimension for the examination of archaic objects. The texture of archaic objects can thus be determined, but the production of these objects is not comparable to the metal forming operations used today. Therefore, we made silver model objects with the help of goldsmiths, then subjected to non-destructive texture testing of the objects and determined pole figures. The obtained information will greatly assist in understanding the pole figures on archaic objects and in exploring the technology employed.**

Keywords: non-invasive, non-destructive crystallographic texture, X-ray diffraction, silver metal spinning

I. INTRODUCTION

Measuring, controlling, and designing crystallographic texture is a very well-known technique in the industry as texture formation can be well controlled by the applied technological processes. Based on reverse engineering theory, we assume that the characterisation of the texture can be used to reconstruct the applied technological operation for archaic objects. This logical theory was not widely used in archaeometry because texture characterization, except for neutron diffraction, was only possible in a destructive way until last year. Neutron diffraction is an excellent test method but is not suitable for high spatial resolution and the limited access to the neutron source is also a disadvantage. An example of X-ray diffraction is found for small objects where parallel beam alignment with the Göbel mirror can be a solution [1]. Kockelmann [2] examined 16th-century silver / copper coins from the Vienna Museum with neutron diffraction to determine whether they were original or fake. The rolling texture of the tested coins was the original coin in the silver and copper phase, while the fake coins differed not only in their composition but also in their texture as they were produced primarily by casting.

In 2007, Artioli [3] studied 20 copper axes from different sites with neutron diffraction from the Neolithic to the early Bronze Age. On the basis of his work, the axes can be divided into the following groups in terms of production: cold forming and subsequent annealing, pure annealed, cast, very slow cooling during casting, With ODF characterization, he found such details in their production (preserved for more than five thousand years by the alloy itself) that the cold forming took place in one or two directions or the cold forming applied before softening or after casting. In addition to neutron diffraction results, studies on XRD have already been published by Chiari et al. [4]. In their work, present a mobile XRF - (X-ray Fluorescence Spectrometry) XRD equipment that attempts to determine the age and similarities in the production of museum objects with similar considerations. Their article highlights the mobility of their X-ray diffraction equipment and its benefits, as well as the growing requirements for non-destructive testing of these mobile devices on the spot. Our experience is similar to advancing in the field of archaeometry, laboratory testing of objects is often very difficult, and museums support on-site measurements primarily because moving and monitoring high-value objects requires armed security personnel. Because of this need, transportable equipment may have advantages over neutron diffraction, where the neutron source is stationary and operates with long exposure times and activates objects.

In the last two years we have developed and patented a new non-destructive pole figure measurement method for centreless X-ray portable diffractometers in modified X mode [5]. The math of the method, comparison the centreless measurements with the conventional one and validation process on a rolled aluminium sheets are performed in detail in our earlier paper [6]. The method has been further developed over the past year and it has been shown that it is also possible to construct a semi full pole figure from data originally acquired during residual stress measurement (reverse modified CHI mode) [7]. The validation was also done on industrial material.

On an archaic object, the Seuso treasure [8] was first subjected to an onsite residual stress measurement in the Hungarian National Museum for the production technique. Then came the idea that by measuring a pole figure we could get much more relevant information. The stress measurement data was subjected to describe the anisotropy (specific section of pole figure) of the Perfume Box [9]. After developing the method, we measured each piece of the Seuso treasure and determined the complete pole figures. The specified pole figures are not similar to the pole figures of a metal produced by one of the known industrial metal forming technologies, therefore, model silver objects were produced by very well-known goldsmiths Tamás Zoltán, Miklós Varga and István Kéry. They have the experience of a whole human being, especially working on silver. They have applied two different methods the metal spinning and wrinkling to produce silver cups and the pole figures were determined on the model objects. In the present work, the production of model objects and their non-destructive pole figures are presented. The measured and calculated pole figures on the model objects which head been subjected to the well documented production help to interpret pole figure of archaic silver objects where the production technology is not yet clearly described.

II. MODELLING OBJECTS

Since silver has excellent formability, most of the metal forming techniques can be applied on it. However, our metal forming experiences based on modern industrial techniques not necessary help us in research to understand the production technology of archaic objects. Fortunately, the silver and coppersmiths keep a lot from the suspected early techniques. According to the silversmith master suggestion, in the first step two model cups were produced by wrinkling and metal spinning techniques. In both cases, pure 2 mm thick initial silver sheets were available for the model objects in 120x120 mm dimension. First, the silversmith annealed the sheets by gas jet and rolled them on a hand-driven rolling mill, and cut disk by scissors (Fig. 1.).

The process of the wrinkling was the following: The base of the cup was marked off on wooden form by steel hammer, just like the wrinkles on the future cylinder. After placing of contours and wrinkles, the subsequent process was the shrinking and hammering of the wrinkles from the bottom to top in overlapping circles (Fig.2.). The hardened silver was annealed again by gas jet and cleaned by hot borax solution after the hammering, and the placing and shrinking of wrinkles and annealing was repeated twice more to decrease the angle closed by the cylinder and base of the cup. The last hammering was performed on metal anvil (Fig.3.). On the last pictures the finished wrinkled silver cup and the initial sheet can be seen.

Fig.1. Annealing rolling and cuting the initial silver sheet.

Fig.2. Initial steps of preparing wrinkling cup. Placing contours, wrinkles and hammering of wrinkles

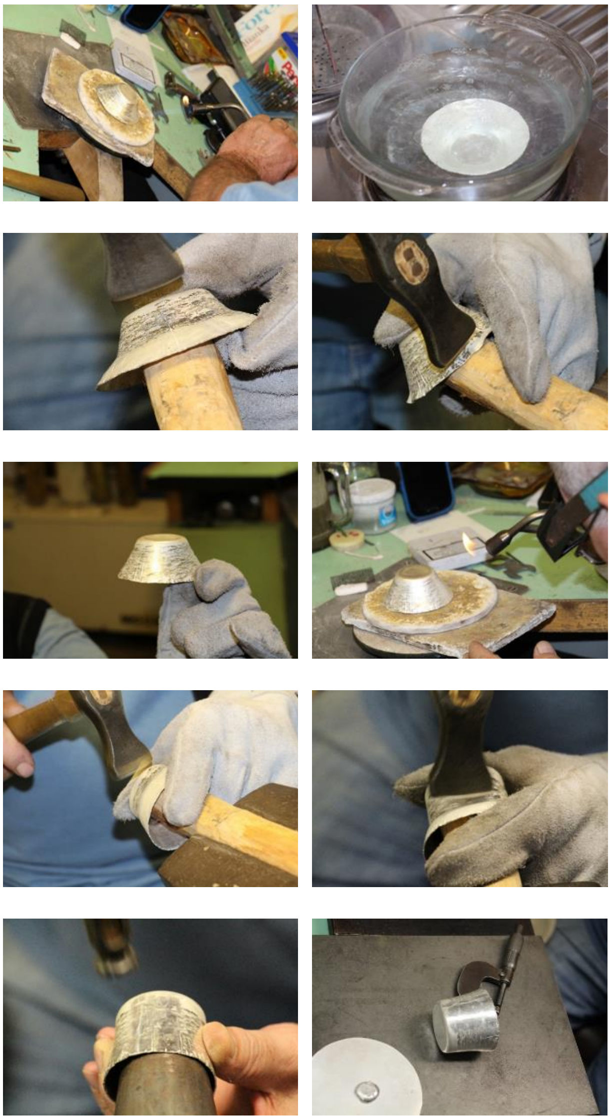


Fig.3. Subsequent steps of preparing wrinkling cup. Annealing two times, cleaning and hammering from the bottom to the top

The other silver model cup was produced by metal spinning. The initial material was the same as in the previous case, circle-like disk from rolled and annealed sheet. Generally, the metal spinning is performed on a turner-like machine, the disk devote to form is pressed against a formed block on the driver by a tool called "spoon" while the disk is spinning. In our case the spoon was a round ended steel bar, pressed the disk from the middle to the edge on the formed block. During the process of metal spinning, an intermediate annealing was applied due to the extended hardening process of silver. The method for annealing was the same than it was subjected during the wrinkling procedure. Before removing the ready cup, the bottom which is conical and not flat was smoothed using a flat steel tool (Fig. 4.).

The figure clearly shows that the rim of the cup is heavily wrinkled. This was due to the fact that the machining pad was originally not optimized for metal spinning. This wrinkled rim was cut off with a lathe knife to prevent interference during further examinations.

The initial sheet with the rolling direction (RD and the model objects prepared by metal spinning and wrinkling can be seen on the Fig. 5. Blue numbered dots are mentioning the measured locations of the subsequent pole figure measuring.

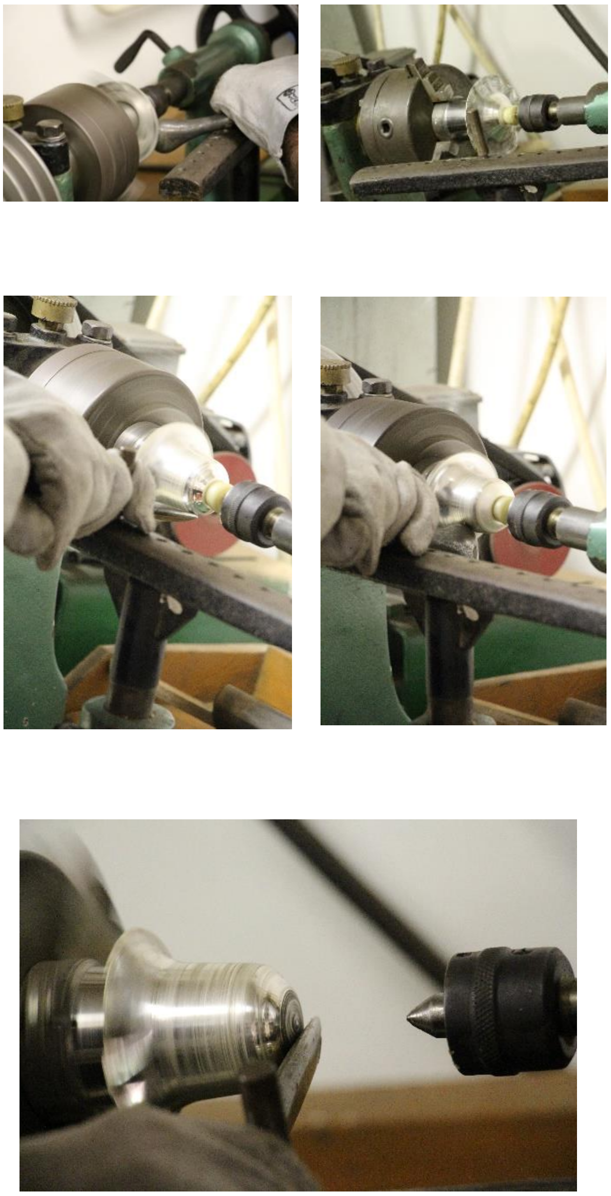


Fig.4. Subsequent steps of preparing metal spinning cup.

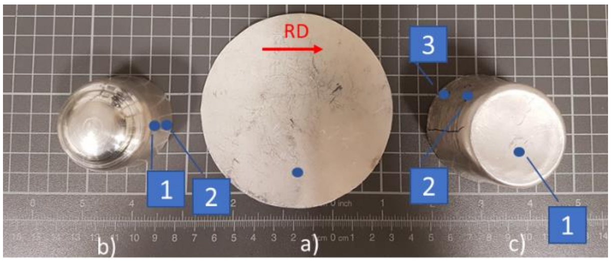
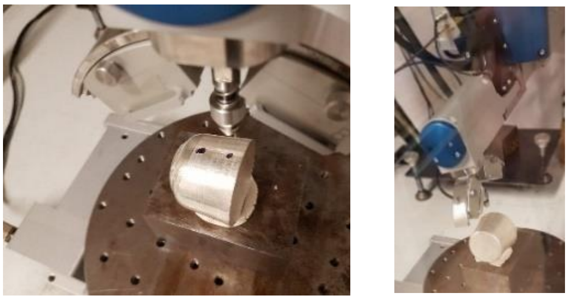


Fig.5. a) The initial sheet and the model objects: b) metal spinning cup, c) wrinkling cup. Blue numbered dots are mentioning the pole figure measured points while red arrow the rolling direction (RD).

III. POLE FIGURE MEASURMENTS

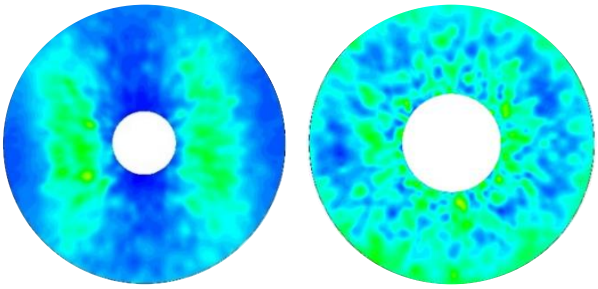
The new, reversed modified CHI method was introduced [6,7] using a Stresstech XStress 3000 G3R type centreless diffractometer with CrKα source operating with 30 kV tube voltage and 9 mA tube current. The used χ values were -59°+59°, with 5° increments, β was chosen as -90…+90°, with 5° increments, defocus correction was performed on Al powder. The measurements were performed both the {222} and the {311} plain series of silver. The defocus corrected pole figures were visualised by Origin software. Measurements were performed on the initial sheet (Fig.5.), at two locations on the cylinder of the metal spinning cup (lower cylinder, upper cylinder) and at three locations on the wrinkling cup (bottom, lower cylinder and upper cylinder). The Fig. 6. shows the measurements while Fig. 7-12. the {222} and the {311} pole figures of the objects. The texture number is increasing from the blue to green to the red colour.

The {222} pole figure of initial sheet behaves character. The same character and its homogeneous distribution of {311} can also be seen on the bottom of the wrinkling cup, but there is only a slight angular rotation between the two poles because the test site and the starting point of the pole figure are randomly selected. This is, of course, an expected result, as the operation, in contrast to the metal spinning, has left the base of the vessel almost unaffected. Do not forget that during the operation we applied the annealing of the vessel twice, which was needed to further deformation of the object, but it did not result in recrystallization. The recrystallization is the diffusion-controlled process which completely eliminates the effect of previous deformation in the crystal structure if the process can be fully completed. The lower part of the cylinder further enhances the shaping character, while the upper part shows a homogeneous character, which may be the result of strong multiple hammering or a combination with softening. The rate of recrystallization is proportional to the degree of shaping, so that recrystallization can begin at the top of the cup due to the intermediate softening.



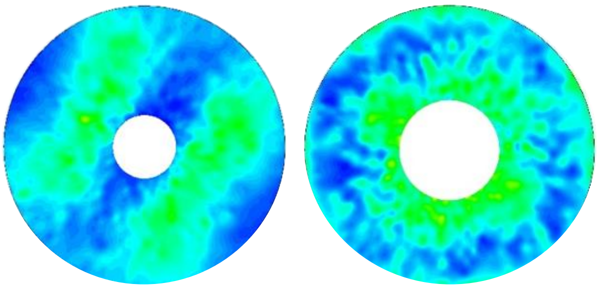
a) b)

Fig.6. Pole figures measurement of a) metal spinning and b) wrinkling cup by centreless X ray diffractometer.



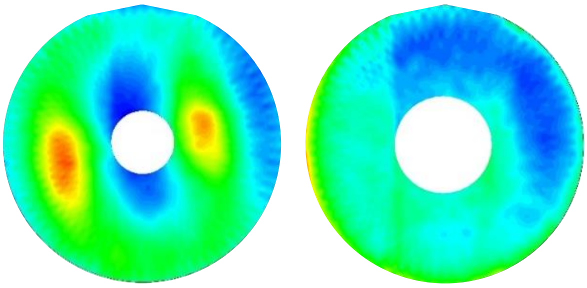
{222} {311}

Fig.7. Pole figures of initial silver sheet.



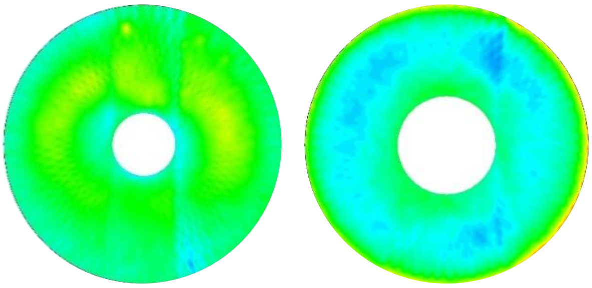
{222} {311}

Fig.8. Pole figures of the bottom of wrinkling cup.



{222} {311}

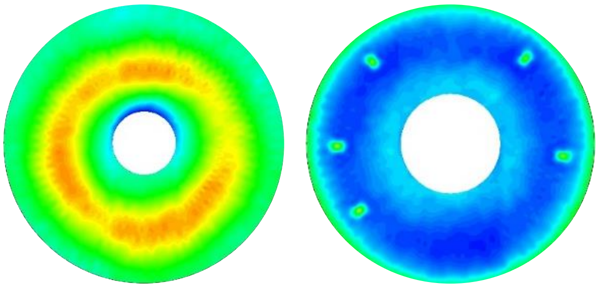
Fig.9. Pole figures of lower cylinder of wrinkling cup.



{222} {311}

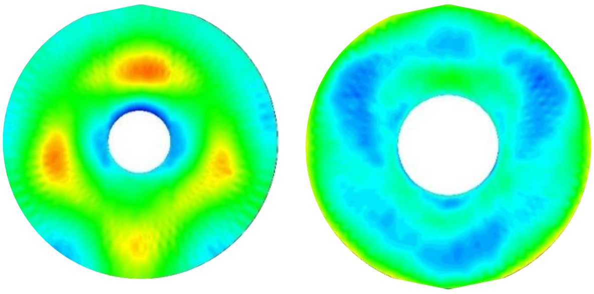
Fig.10. Pole figures of upper cylinder of wrinkling cup.

The pole figure of a metal spinning cup shows an image of a completely different character. The pole figure of {222} is reminiscent of a fibre texture at both the bottom and the top of the cylinder. The difference between the two textures may indicate the same shaping behaviour but different degrees. The metal spinning vessel received an intermediate annealing during the metal forming.



{222} {311}

Fig.11. Pole figures of lower cylinder of metal spinning cup.



{222} {311}

Fig.12. Pole figures of upper cylinder of metal spinning cup.

IV. SUMMARY

Silver model caps were produced by metal spinning and wrinkling techniques by silversmith masters. The pole figures were measured on the caps by the non-invasive X-ray diffraction methods in reversed modified CHI mode. We can conclude that the non-destructive pole figure method is a good way to distinguish between metal objects formed in different ways. The specific forming modes result in specific pole figures. By producing and examining a sufficient number of reconstructive objects, the mode of production of archaic objects can also be reconstructed.

V. ACKNOWLEDGEMENTS

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