

# New, non-invasive texture measurement method for archaeology

Máté Sepsi<sup>1</sup>, Márton Benke<sup>2</sup>, Valéria Mertinger<sup>3</sup>

<sup>1</sup> *University of Miskolc, Miskolc-Egyetemváros H3515 Hungary, femsepsi@uni-miskolc.hu*

<sup>2</sup> *University of Miskolc, Miskolc-Egyetemváros H3515 Hungary, fembenke@uni-miskolc.hu*

<sup>3</sup> *University of Miskolc, Miskolc-Egyetemváros H3515 Hungary, femvali@uni-miskolc.hu*

**Abstract** – During the preparation of metal objects, the technological processes like casting, plastic deformation and heat treatments evolve characteristic crystallographic fingerprint called texture, in the microstructure of metals. This texture remains unchanged for centuries. So, the characterization of texture is a conclusive explanation regarding the former process or processes. A new, non-invasive texture measurement method was developed for centreless X-ray diffractometers. By using this method, the most widespread texture visualization the pole figures can be realized. The paper introduces the advantage and the limitation of the new method especially for archaeological application.

**Keywords:** non-invasive, non-destructive crystallographic texture, X-ray diffraction

## I. INTRODUCTION

Crystalline metallic materials are typically polycrystalline. The position of the polycrystals may be random called isotropic and may be oriented or so-called anisotropic. Crystallographic anisotropy so called crystallographic texture (shortly texture) can be caused by many effects such as unidirectional crystallization with controlled cooling [1]. In this case, the deviation of the crystals from the random distribution is from its nature and extent of the heat dissipation, if we think of concrete shaped objects, then it can be determined by the composition and geometry (size, shape) of the mould and the object. That is, the crystallization texture is very varied and non-stable because in most of the cases this texture is modified in subsequent stages of processing. In contrast, plastic deformation, especially cold forming process, produces a characteristic crystalline arrangement and texture. Similarly, strong and characteristic changes are caused by the heating and annealing associated with the deformation operation. One of the great challenges of today's engineering practice is to influence and design the texture of metals with the proper technology. The nature of the extinguishing texture is clearly dependent on the metal crystalline lattice, the nature and degree of plastic deformation. Depending on the temperature of the heat treatment, so-called recrystallization processes can also cause characteristic changes in the texture of a given type

of alloy. The recrystallized texture is generally depending on the crystal lattice of materials, but several process parameters make typical modifications.

The method of producing metallic objects leaves a fingerprint in the metal, which, unless otherwise exposed, remains hidden for centuries. Based on the quantitative description of the texture, with sufficient knowledge of physical metallurgy, the shaping history of metallic object can be determined. So, the crucial problem is to determine the texture. Most common representation of texture is the pole figure which is a two-dimensional stereographic projection in which the positions and intensities of specific crystallographic orientations are plotted in relation to the specimen geometry. Stereographic projection is a two-dimensional projection of a three-dimensional crystal such that the angular relationships between different planes, different directions and between crystalline planes, and directions in the crystal can be easily read out from the projection. Thus, a stereographic projection is an “angle-true” projection in just the same way as a geographic atlas is a two-dimensional “area-true” projection of the three-dimensional globe [1]. Fig. 1. shows an example for [111] pole figures for aluminium and copper after cold rolling and after annealing. Both pole figures were determined by conventional X-ray diffractometer.

The conventional techniques to measure crystallographic texture are based on neutron, X-ray or electron diffraction, which involve the determination of several pole figures and ODF (Orientation Distribution Function) for investigated materials. The general differences between these methods are the size of radiated volume and the spatial resolution [2,3,4]. Except for neutron diffraction, which is limited by source and the activation process, other methods are destructive. Sample cutting is usually necessary for conventional texture measurements by X-ray diffraction (XRD) and a very dedicated sample preparation technique is required for TEM (transmission electron microscopy) and electron backscatter diffraction (EBSD) investigations. The full 3D representation for crystallographic texture is given by the ODF which can be achieved by evaluation of a set of non-equivalent pole figures. Non-destructive determination of the pole figures by XRD method in many cases, such as when the test object is unique or valuable or when the

sampling is forbidden by many other reasons can be beneficial [5,6,7].

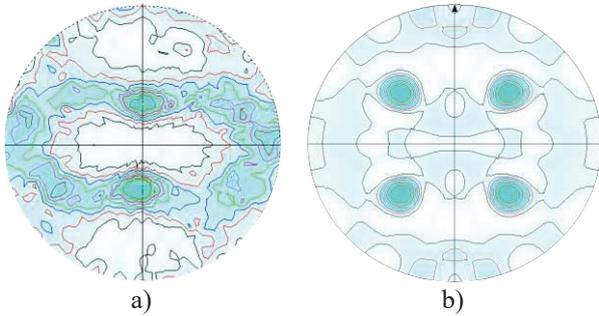


Fig. 1.  $\{111\}$  Pole figure of a) aluminium sample H17 after cold rolling b) of copper after recrystallization determined by conventional XRD.

The present paper introduces new texture measurement methods developed for mobile centreless X-ray diffractometers which are originally developed for residual stress measurements [8] and never had been used for texture determination. With the new patented methods, the pole figure measurements can be realized with centreless diffractometers in modified X (CHI), X (CHI), and  $\Omega$  (OMEGA) modes [9,10,11]. Using these methods, pole figures can be obtained with all the benefits of centreless diffractometers: no need for sample cutting, flexibility in case of large components with complex shapes, short measuring time and portability. The various methods have been convincingly validated on industrial objects, cold rolled aluminium sheets. Typical examples are shown in Fig. 2. The  $\{111\}$  pole figures were determined by centreless diffractometer on the same aluminium samples than the conventional one on Fig.1. Notice that our own method has a lower psi angle (max radius of pole figure), of  $60^\circ$  while the conventional method has a value of  $75^\circ$ . That is why the location of maximum along the radius is different.

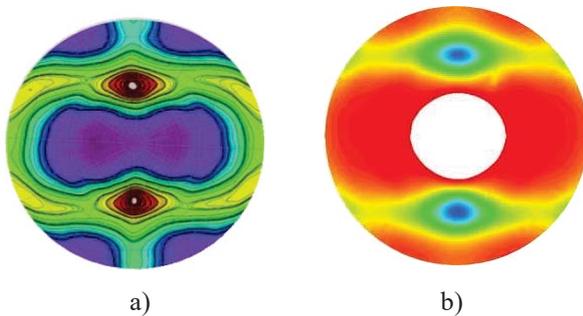


Fig. 2.  $\{111\}$  Pole figure of aluminium sample H17 after cold rolling (same than in Fig.1.) determined by centreless diffractometer in a) OMEGA mode, b) in modified (CHI) mode

The example in Fig. 3. shows the sensitivity and the resolution of our own method. The pole figures of plain series  $\{311\}$  are made of two sheets of aluminium rolled to a hardly different reduction determined by modified CHI mode. The nature of the two pole figures and the calculated texture number also show which is the more strongly deformed plate.

The purpose of this manuscript is to highlight the aspect of the methods that is important for the study of archaeological finds and provides essential information for prospective users to perform the investigation.

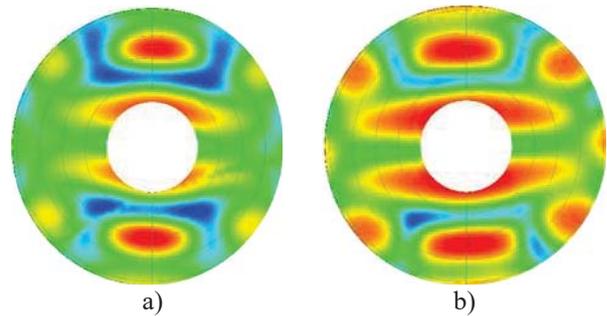


Fig. 3.  $\{311\}$  Pole figure of aluminium sample determined by centreless X ray diffractometer in modified (CHI) mode a) sample H20K, texture number 1,51 and b) sample H10K, texture number 2,00 after hardly different reduction of cold rolling

## II. EXPERIMENTAL

For validation, 3003 type cold rolled aluminium sheets were investigated. Conventional pole figure measurements were carried out with a Bruker D8 Advance type powder diffractometer equipped with an Eulerian cradle and  $\text{CoK}\alpha$  radiation source operating with 40 kV tube voltage and 40 mA tube current. Pole figures were measured up to  $75^\circ$  tilting with  $5^\circ$  increment and visualized by the equipment's own TexEVAL software. The new method was introduced using a Stresstech XStress 3000 G3R type centreless diffractometer with  $\text{CrK}\alpha$  source operating with 30 kV tube voltage and 9 mA tube current.

A robot armed XStress Robot centreless diffractometer was also used to extend the theta limitation.  $\text{CuK}\alpha$  and  $\text{CrK}\alpha$  radiations were used with 30 kV and 9 mA in both cases. The absorption corrected pole figures were visualised by Origin software. Absorption correction was performed on Al powder. The defocusing correction was eliminated in case of robot system because the whole diffracted peak area was taken into calculation process [4].

## III. OVERVIEW OF THE NEW METHOD

In general, three different modes can be distinguished based on goniometer tilting relative to sample:  $\Omega$  (OMEGA), X (CHI) and modified X. The names refer to the axis around which the goniometer circle (holding the source and detectors) is tilted. Tilting and rotation are a

general procedure during residual stress and also texture measurements. With a centreless diffractometer, there are two ways to mount the detector holding arms, thereby implementing both the OMEGA and modified CHI configurations (Fig. 4.). During operating the centreless diffractometer in contrast to conventional ones, the measured object is stationary while the diffractometer is tilted around the object. This is the reason that makes it particularly suitable for examining archaic objects. However, the main difference in stress and conventional texture measurement is not the tilting of the sample but the beam path. Therefore, the transition between the two methods (stress measurement and texture measurement) is not obvious. In an earlier article, we have shown the mathematical relationships that can be made between the two systems. We now give a summary of the different modes in which the experiment can be examined from the user's point of view.

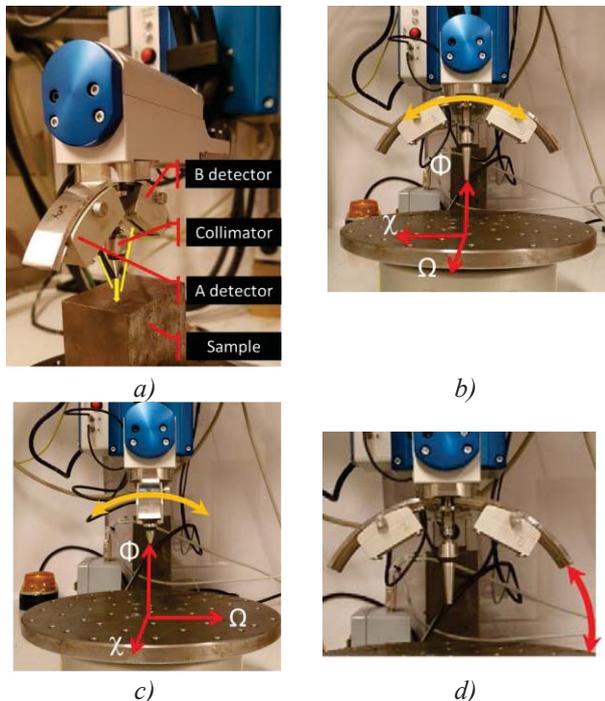


Fig. 4. Centreless diffractometer a) main parts, b) modified CHI mode, c) OMEGA mode, yellow arrows are indicating the direction of the tilting during measurements d) red arrow is highlighting tilting limit in OMEGA mode,  $X, \Omega, \Phi$  tilting angles

In OMEGA mode, the beam pass is very simple, but here the detector arms will hang over a certain angle of tilting on the test object. So, the theoretical maximum tilting angle  $X_{max}$  is limited and determined by the Bragg angle ( $\Theta$ ) of diffracted peak regarding the pole figure  $\{hkl\}$ .

$$\chi_{max} = \Theta \quad (1)$$

The real limitation depends on the surface geometry of sample if it is flat concave or convex. Which is again a

very important aspect from the user's point of view. The limitation can be about  $\pm 10^\circ$  relating to the theoretical maximum. The Fig.5. shows an example for a flat and for a curved object surface investigation.

For cubic system:

$$\theta = \arcsin\left(\frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2a}\right) \quad (2)$$

Where  $\lambda$ - is the wavelength of X-ray beam,  $a$ - is the lattice parameter of the material,  $h, k, l$  the Miller indexes of the plane series which pole figure is interested. OMEGA mode is very useful in that case where the centre part of the pole figure is informative. Fig. 6. shows an example for pole figure determined in OMEGA mode. This solution is also very useful to complete the pole figure determined by modified CHI mode.

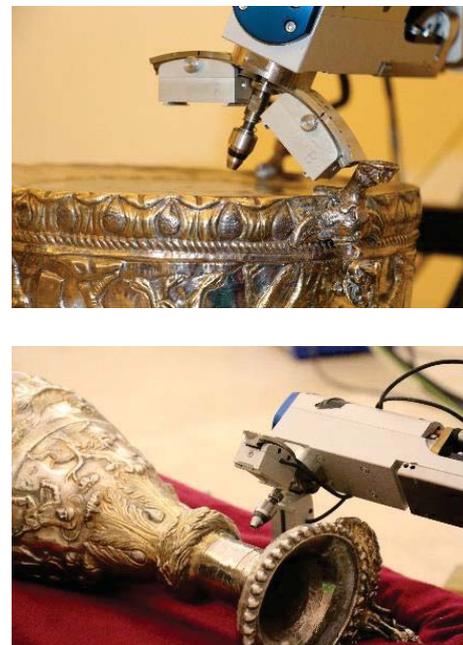


Fig.5. Tilting limit in case of flat or concave object surface in OMEGA mode



Fig.6. Silver  $\{311\}$  pole figure determined in OMEGA mode.

In modified CHI mode, finding the common intersections of the two (stress and texture) systems requires more complex calculations and an unmeasured area remains at small  $\chi$  angles due to the configuration of detectors. High tilting angle is limited only by the geometry of the investigated objects as it is clear from the Fig. 7. The pole figure was determined by modified CHI mode in the same point than it was at Fig. 6. Fig. 8 shows how the two methods complement each other and that the full pole figure can be obtained.



Fig.7. Modified CHI configuration helps us to achieve a larger tilting angle when the object under examination is convex

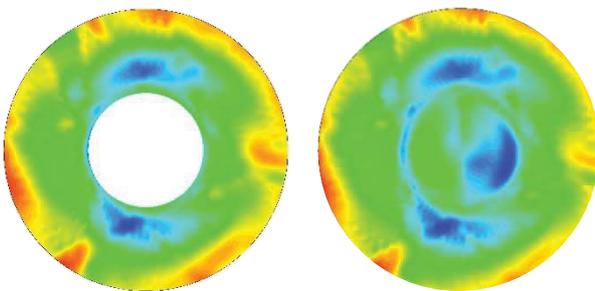


Fig.8. Silver {311} Pole figure determined by a) modified CHI and b) modified CHI and OMEGA modes

To explore further limitations of this method, let's look at a series of steps to create a pole figure:

1. Calculate the Bragg angle ( $\Theta$ ) for the pole figure to be measured.
2. Using a stress free and isotropic reference sample, calibrate the position-sensitive detector scale to the selected  $\Theta$  range and determine the working distance of the selected collimator for the centreless diffractometer.
3. Select the location to be measured (check the freedom of movement during the test).
4. Calculate the measurement coordinates (tilting angles) for both OMEGA and modified CHI modes.

5. At the start of the measurement routine, the collimator touches the surface to be examined, stands at working distance, and begins exposure at various tilting angles and using a 360° full rotation at each angle.
6. Perform the test in both OMEGA and modified CHI mode.
7. For each exposure point, a defocusing correction is also must be performed, and the intensity values can be plotted using transformation relationships.

The test routine reveals that the object should be rotated around the collimator axis. Therefore, a tripod for the G3R portable diffractometer was adapted regarding the geometry and size of the test objects. Fig.9. shows such an arrangement and an onsite museum measurement.



Fig.9. On site measurement with the special holders and rotating table

For the testing side, the CHI mode provides the most obvious solution. In this case, the beam path is identical to the conventional technique, but this solution requires a robot armed centreless diffractometer which can perform any kind of motion or arrangement even the modified CHI or OMEGA modes. Fig.10. shows modified CHI mode and the Fig.11. the CHI mode arrangement respectively on a model silver object. The robot arm can perform rotation and tilting with high flexibility as well as the radiation is also changeable. Cu Cr, Mn X Ray tube are available in the market so the testing material should not be a problem also the penetration depth is variable.

#### IV. SUMMARY

New non-destructive texture measurement methods for centreless diffractometers were introduced in the last year [10,13]. This paper gives a short overview about the advantage and limitations for testing of archaeological objects. The examples were given by the measurement series of Seuso treasure at the Hungarian National Museum Budapest.

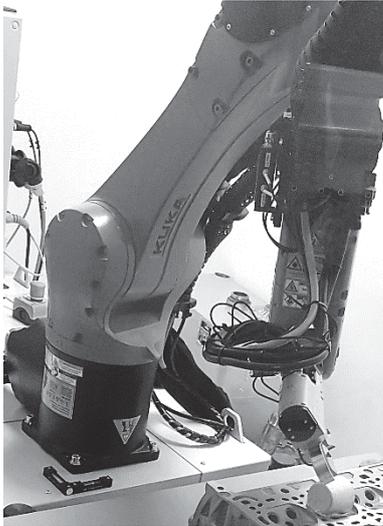


Fig. 10. Robot armed centreless diffractometer working in modified CHI mode.



Fig. 11. Robot armed centreless diffractometer working in modified CHI mode.

#### V. ACKNOWLEDGEMENTS

The present paper was supported through the National Research, Development and Innovation Office – NKFIH K119566 project. The described article was carried out as part of the EFOP-3.6.1-16-00011 “Younger and Renewing University – Innovative Knowledge City – institutional development of the University of Miskolc aiming at intelligent specialisation” project implemented in the framework of the Szechenyi 2020 program. The realization of this project is supported by the European

Union, co-financed by the European Social Fund.

#### VI. CITATIONS AND REFERENCES

- [1] S. Suwas, R. Ray Kumar “Crystallographic Texture of Materials”, Springer-Verlag, London, 2014.
- [2] O. Engler, V. Randle “Introduction to Texture Analysis – Macrotecture, Microtexture and Orientation Mapping”, CRC Press. 2010
- [3] A. Rollet, F. Humphreys, M. Hatherly, “Recrystallization and Related Annealing Phenomena”, 3rd ed. Elsevier, 2017
- [4] U. Kocks, C. N. Tomé, H. R. Wenk “Texture and Anisotropy”, Cambridge University Press 2005.
- [5] A. Duran, L. Herrera, M. Jimenez de Haro, A. Justo, J. Perez-Rodriguez “Nondestructive analysis of cultural heritage artefacts from Andalusia, Spain, by X-ray diffraction with Göbel mirrors” *Talanta* 76, Issue 1, pp 183-188, 2008
- [6] A. Adriaens “Nondestructive analysis and testing of museum objects: An overview of 5 years of research” *Spectrochimica Acta Part B* 60 pp 1503 – 1516, 2005
- [7] C. Giacomo, S. Philippe, H. Arlen, “Non-conventional applications of a noninvasive portable X-ray diffraction/fluorescence instrument” *Appl. Phys. A* 122:990 2-17, (2016)
- [8] M. Fitzpatrick, A. Fry, P. Holdway, F. Kandil, J. Shackleton, L. Suominen. “A National Measurement Good Practice Guide, Determination of Residual Stresses by X-ray Diffraction” - Issue 2 No. 52 (Teddington: Crown) 2005
- [9] M. Benke, V. Mertinger, M. Sepsi and V. Karpati Measuring Methods for Centerless X-ray Diffractometers to Obtain Pole Figures and their Cuts in  $\Omega$  and Modified  $\Psi$  Modes, Hungarian patent P1600500
- [10] M. Sepsi, V. Mertinger, M. Benke “Sample cutting-free pole figure measuring method for centreless diffractometers in modified X mode” *Mat. Char.* 151 351–357, 2019
- [11] V. Mertinger, M. Sepsi, M. Benke “Non-destructive texture measurement methods for centreless X-ray diffractometers in reverse modified X(CHI) mode” *J. Phys.: Conf. Ser.* 1270 012012, 2019 Proc. of 7th International Conference on Recrystallization and Grain Growth. Gent, 2019 .
- [12] M. Sepsi, V. Mertinger, M. Benke “Utilization of spatial resolved qualitative texture assessment method on an object of the Seuso Treasure” *IOP Conf. Ser.: Mater. Sci. Eng* 375 012036, 2018