Neutronographic Texture Analysis of Zirconium Based Alloys

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Abstract. Neutron diffraction is a very powerful tool in texture analysis of zirconium based alloys used in nuclear technique. Textures of five samples (two rolled sheets and three tubes) were investigated by using basal pole figures, inversion pole figures, and ODF distribution function. The texture measurement was performed at diffractometer KSN2 on the Laboratory of Neutron Diffraction, Department of Solid State Engineering, Faculty of Nuclear Sciences and Physical Engineering, CTU in Prague. Procedures for studying textures with thermal neutrons and procedures for obtaining texture parameters (direct and inverse pole figures, three dimensional orientation distribution function) are also described. Observed data were processed by software packages HEXAL and GSAS. Our results can be summarized as follows: i) All samples of zirconium alloys show the distribution of middle area into two maxima in basal pole figures. This is caused by alloying elements. A characteristic split of the basal pole maxima tilted from the normal direction toward the transverse direction can be observed for all samples. ii) Sheet samples prefer orientation of planes (100) and (110) perpendicular to rolling direction and orientation of planes (002) perpendicular to normal direction. iii) Basal planes of tubes are oriented parallel to tube axis, meanwhile (100) planes are oriented perpendicular to tube axis. Level of resulting texture and maxima position is different for tubes and for sheets. The obtained results are characteristic for zirconium based alloys.

1. Introduction

Zirconium is a metal with below-normal c/a ratio (c/a1,633). The main characteristics of this element are described at [1]. Zirconium has very low absorption cross-section of thermal neutrons, high hardness, ductility, and corrosion resistance. Therefore, zirconium alloys are used in the nuclear industry (Zircaloy) as fuel rod cladding, especially in water reactors [2].

Most of the texture measurements are related to the basal pole distribution, which plays an important role. Less is known the distribution of prism or pyramidal plane poles. These are strong indicators for degree of annealing, and, moreover are important for quantitative determinations of textures, for example, by analysis of the orientation distribution function (ODF) [3]. The slip planes of hexagonal close packed metals should rotate into the plane of rolled sheet. Accordingly the texture in which the basal plane (which is the slip plane) lies in or near the rolling plane is predominant [4].

In our work the texture of two rolled sheets (Zrp, ZZ13) and three tubes (Zry2, ZiT, and ZrW) were investigated by direct pole figures, inversion pole figures, and orientation distribution function (ODF).
2. Experiment

The texture measurements were performed on the diffractometer KSN-2 at Laboratory of Neutron Diffraction, Department of Solid State Engineering, Faculty of Nuclear Sciences and Physical Engineering. Our laboratory developed, and tested experimental, and calculation techniques for quantitative texture analysis based on the ODF combined with the diffraction of thermal neutrons.

2.1. The KSN-2 diffractometer

The texture experiments were carried out on the KSN-2 diffractometer using the TG-1 texture goniometer with automatic data collection. The monochromatic wavelength was 0.1362 nm, and single-crystal Cu(200) was used like monochromator. The experimental data were measured in transmission or reflection arrangement. Depending on the requirements, the specimens consisted of one or several sheets of the examined material. Pole figures were measured for (100), (002), (101), (110), and (102) reflections of zirconium samples. The measured data were corrected for absorption, irradiated volume, and they were normalised. The experimental data processed in this manner were used to calculate the coefficients of expansion to express the measured direct pole figures using spherical functions.

The KSN-2 diffractometer was used simultaneously for diffraction patterns measurement of zirconium or zircaloy samples. By means of these experimental data the inversion pole figures were calculated, and then all these diagrams were used in the quantitative texture analysis by means of Rietveld procedures. The KSN-2 diffraction device offers good intensity and the best resolution value of $\delta d/d = 0.007$ in the region $d \sim 1.0 \div 0.1$ nm ($d$ is interplanar spacing).

The high penetration of neutrons through the majority of materials is the main advantage for examination of the textures of coarse-grained materials like oriented zirconium sheets. Quantitative texture analysis (three-dimensional distribution function - ODF) in connection with neutron diffraction is extensively used in this research field. For example, texture influences both the behaviour of polycrystalline materials during thermal or mechanical treatment, and the anisotropy of various properties in technical materials. Consequently, there are several areas in physic and metallurgy where texture studies should be performed. Among these problems we can put nuclear technology (investigations of fuel elements and fuel tubes based on the zirconium alloys). Our work is focused on research of the textural properties of zirconia-based materials after thermal and mechanical processing using thermal neutron diffraction.

2.2. Samples

**Rolled sheets**

Sample Zrp was composed of 11 sheets of circular shape with a diameter of 50 mm. The thickness of one sheet was 0.25 mm. The sheets were cold – rolled with 92% reduction. Table 1 shows the composition of Zrp.

| Table 1. Chemical composition of sample Zrp. |
|------------------|------------------|------------------|------------------|
|                  | Cu [at%]         | Fe [at%]         | Mo [at%]         | W [at%]          |
| Zrp              | 0.72             | 0.82             | 0.43             | 0.12             |

Sample ZZ13 was forged and hot rolled to the thickness 3.3 mm. Then the sample was annealed at 664°C. Table 2 shows the composition of ZZ13.

| Table 2. Chemical composition of sample ZZ13. |
|------------------|------------------|------------------|------------------|------------------|
|                  | Hf [at%]         | Ca [at%]         | Mg [at%]         | O [at%]          | H [at%]          |
| ZZ13             | 0.41             | 0.044            | 0.096            | 0.055            | 0.0011           |
Tubes

All tubes (Zry2, ZiT a ZrW) were extruded, and then cold-rolled with inter-annealing (700°C) to the final sizes. Table 3 shows the composition of tubes, and Table 4 shows parameters of tubes. There $\nu$ is tube length, $\phi_i$ is outside tube diameter, and $\phi_e$ is internal tube diameter.

### Table 3. Chemical composition of tubes.

|       | Sn [at\%] | Fe [at\%] | Cr [at\%] | O [at\%] | H [at\%] | N [at\%] | C [at\%] |
|-------|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Zry2  | 1.13       | 0.35      | 0.16      | 0.011     | 0.0010    | 0.0050    | 0.0012    |
| ZiT   | 1.07       | 0.41      | 0.19      | 0.011     | 0.0020    | 0.0060    | 0.0012    |
| ZrW   | 1.09       | 0.43      | 0.21      | 0.011     | 0.0015    | 0.0045    | 0.0012    |

### Table 4. Parameters of tubes.

|       | $\nu$ [mm] | $\phi_i$ [mm] | $\phi_e$ [mm] |
|-------|------------|----------------|---------------|
| Zry2  | 36.9       | 11.2           | 12.1          |
| ZiT   | 30         | 8              | 9.1           |
| ZrW   | 30         | 8              | 9.2           |

3. Methods of texture analysis

The results of our texture measurement are represented by direct pole figures, inverse pole figures, and the orientation distribution function. Direct pole figures were measured for samples Zry2, and ZiT. Inverse pole figures were calculated for samples Zrp, ZZ13, Zry2, ZiT, and ZrW.

The direct pole figure is a stereographic projection of spatial distribution of poles of the particular plane to the project plane which is parallel to the significant sample plane. Two different methods were used for direct pole figures determinations.

First method is conventional, and the distribution pole density for selected reflection ($2\theta_{hkl}$ is fixed) is measured for the different direction in the sample coordination system defined by R, N, and T axis.

Secondly, the Rietveld refinement method was used for the pole figure determination. In this case the Rietveld refinement method was introduced by the harmonic analysis texture procedure to the Rietveld software code GSAS [5]. So it is taking into consideration the influence of preferred orientation on the level of intensity measured in the neutron diffraction patterns. In harmonic analysis procedure the crystal coordination is given by reflection index (hkl). Sample coordinates ($\alpha$, $\beta$) are determined by the sample orientation on the diffractometer. For example, in case of rolling sheets (mmm sample symmetry), $\alpha$ is angle between RD (rolling direction), and TD (transverse direction), and $\beta$ is angle between ND (normal direction), and SV (scattering vector). Before definition of the sample coordinations ($\alpha$, $\beta$) we need to define instrument coordination system (I, J, K). In this case I is normal to the diffraction plane, and J is parallel with the direction of the incident neutron beam. Then we define a standard set of rotating goniometr system: Eulerian angles ($\phi_1$, $\phi$, $\phi_2$). Experimental diffraction patterns were treated by the GSAS software procedure [5], and the value of selected pole figures was obtained. As a result of this refinement procedure is the matrix harmonic coefficients $C_i^{n,m}$. The harmonic coefficients are used to the calculations of the direct pole figure some selected (hkl) reflections.

The quantitative description of texture is given by ODF (Orientation Distribution Function) defined as
where \( f(g) \) is ODF, \( dV \) the volume of grains of orientation \( g \) within the element of orientation space \( dg \), and \( V \) the volume from which data are collected.

The common representation of ODF is given by equation:

\[
\frac{dV(g)}{V} = f(g) \, dg,
\]

where \( f(g) \) is ODF, \( dV \) the volume of grains of orientation \( g \) within the element of orientation space \( dg \), and \( V \) the volume from which data are collected.

The obtained direct pole figures were then processed by HEXAL [6], and the sections of the Euler orientation space were calculated. The interpretation of ODF was realized by the ideal orientations [1].

In both cases, resulting pole figure are used like input data for ODF values determination by means software code HEXAL [6] or popLA [7]. HEXAL software package (the hexagonal symmetry of the crystals and orthorhombic symmetry of the specimen) was used, and the ODF values were obtained together with all texture characteristics (pole figures, inverse pole figures, ODF - \( f(g) \) values, fiber texture with \(<110>\) and \(<001>\) axis parallel to rolling direction, parameters of the ideal orientations \((hkl)<uvw>\), texture index \(J\), volume fraction coefficient \(f\)).

Measured diffraction patterns were used at the same time for the inversion pole figure determinations. The inverse pole figure shows how the selected direction in the sample reference frame is distributed in the reference frame of the crystal. The pole density values were calculated by Mueller formula [6]. Figure 1 shows the distribution of poles in the inverse pole figure of zirconium.

![Figure 1. Distribution of poles in inverse pole figure.](image)
4. Results

Direct pole figures obtained by using software package GSAS are show at Figure 2 (pole (002)), Figure 3 (pole (100)), and Figure 4 (pole (101)). Direct pole figures obtained by using software package HEXAL are show at Figure 5 (pole (002)), Figure 6 (pole (100)), and Figure 7 (pole (101)).

**Figure 2.** Direct pole figures (002) determined by means of Rietveld procedure (package GSAS) of sample Zry2 (left), and sample ZiT (right).

**Figure 3.** Direct pole figures (100) determined by means of Rietveld procedure (package GSAS) of sample Zry2 (left), and sample ZiT (right).
Figure 4 Direct pole figures (101) determined by means of Rietveld procedure (package GSAS) of sample Zry2 (left), and sample ZiT (right).

Figure 5. Direct pole figures (002) (obtained by using software package HEXAL) of sample Zry2 (left), and sample ZiT (right).
Figure 6. Direct pole figures (100) (obtained by using software package HEXAL) of sample Zry2 (left), and sample ZiT (right).

Figure 7. Direct pole figures (101) (obtained by using software package HEXAL) of sample Zry2 (left), and sample ZiT (right).

The ODF representations are shown at Figure 8 (sample Zry2), and Figure 9 (sample ZiT). Table 5 shows the ideal orientation of samples Zry2, and ZiT. ODF - f(g) values are also given at this Table.
Figure 8. The orientation distribution (ODF) for $\phi_2 = 0^\circ$ calculated from measured pole figures (package HEXAL) of sample Zry2.

Figure 9. The orientation distribution (ODF) $\phi_2 = 0^\circ$ calculated from measured pole figures (package HEXAL) of sample ZiT.
Table 5. Ideal orientations, and ODF - f (g) values of samples Zry2, and ZiT.

| Point | sample Zry2 | ODF’s values f(g) | sample ZiT | ODF’s values f(g) |
|-------|-------------|-------------------|------------|-------------------|
| A     | (110)[-555] | 2.20              | (110)[-550] | 2.20              |
| B     | (110)[-115] | 2.20              | (110)[-115] | 3.28              |
| C     | (111)[-321] | 2.20              | (111)[-550] | 3.28              |
| D     | (112)[-311] | 3.20              | (111)[-523] | 2.29              |
| E     | (112)[-5-34] | 2.20             | (111)[-325] | 2.26              |
| F     | (113)[-4-22] | 2.20              | (113)[-301] | 3.28              |
| G     | (114)[-511] | 1.20              | (118)[-5-31] | 2.26              |
| H     | (115)[-3-21] | 1.20              | (113)[-550] | 2.26              |
| I     | (118)[-501] | 1.20              | (112)[-512] | 2.26              |
| J     | (110)[-442] | 1.20              |            |                   |
| K     | (110)[-114] | 1.20              |            |                   |

The calculated inverse pole figures of zirconium samples Zrp, ZZ13, Zry2, ZrW, and ZiT are shown at Table 6. There (0, 45) means direction between ND, and TD.

Table 6. Calculated inverse pole figures of samples Zrp, ZZ13, Zry2, ZrW, and ZiT.

|          | P_{002, ND} | P_{002, (0,45)} | P_{100, RD} | P_{100, TD} | P_{110, RD} |
|----------|-------------|----------------|-------------|-------------|-------------|
| Zrp      | 3.01        | N              | 2.74        | 1.73        | 1.68        |
| ZZ13     | 2.78        | N              | 2.60        | 0.98        | 3.12        |
| Zry2     | 1.70        | 1.73           | 1.17        | 0.89        | 2.78        |
| ZrW      | 1.16        | 1.81           | 3.77        | 0.75        | 0.72        |
| ZiT      | 1.17        | 2.40           | 2.95        | 0.44        | 0.79        |

5. Discussion

Both methods used for direct pole figures calculations give comparable results (Figures 2 – 7).

The addition of alloying elements breaks the central area into two maxima (see basal pole figures - Figure 2, and Figure 5) [4].

A characteristic split of the basal pole maxima tilted from the radial toward the tangential direction for samples can be observed in basal pole figures for Zry2 (Figure 2), and ZiT (Figure 3). Tubes were mainly compressed in the radial direction, whereas the compressive forces in the tangential direction were comparatively small. Hence the resulting texture is consistent with the texture for sheets [3].

The middle orientation of cold-rolled zirconium is (002)[10-10] (Figure 2, and Figure 3). There is a tendency for [100] direction to align with the transverse direction.

The same results can be seen from inverse pole figures of tubes (Table 5). The (100) planes are oriented parallel to transverse direction. The (100) pole density maximum is tilted from the rolling direction towards the transverse direction.
The basal planes of tubes are oriented parallel to tube axis. The angle position of (002) pole maxima of sample Zry2 is tilted by 45° from the normal direction (Table 5). A similar situation occurs for sample ZiT, but the value of pole density is lower (Table 5).

The (110) planes are oriented perpendicular to rolling direction. Sample Zry2 shows the largest value of $p_{110,\text{RD}}$ ($p_{110,\text{RD}} = 2.78$, Table 5).

Sheet samples prefer orientation of planes (002) perpendicular to normal direction. The angle position of (002) pole maxima of sample ZrW is tilted by 45° from the normal direction (Table 5).

The (100) planes are oriented perpendicular to rolling direction. The (100) pole density maximum is tilted from the rolling direction towards the transverse direction.

An analogous situation can be observed for planes (110). These are also oriented perpendicular to rolling direction. Sample ZZ13 shows the largest value of $p_{110,\text{RD}}$ ($p_{110,\text{RD}} = 3.12$, Table 5).

From the ideal orientations, frequent occurrence of the (110)[-555], (110)[-115], and (118)[-5-31] is obvious (Table 4).

6. Conclusions
Our laboratory developed and tested experimental and computing techniques for quantitative texture analysis based on the ODF combined with the diffraction of thermal neutrons. Neutron diffraction is a very powerful and suitable tool for microstructure, and texture characterization of these zirconium based alloys, and generally grain-oriented materials.

Zirconium alloys have a very suitable physical, mechanics, corrosion or neutron absorption properties to be used in nuclear technique, and industry. From these reasons is very important to investigate the all scale properties of zirconium, and zirconium alloys.

Our results in quantitative texture analysis are in agreement with the results the other authors in this branch of research [2], [8], [9]. Level of resulting texture and maxima position is different for sheets, and for tubes. Substantial influence also has a final tube thickness. The results obtained are characteristic for zirconium based alloys.

References
[1] Kruzelova M 2010 Study of Zirconium Based Alloys by Neutron Diffraction - Master’s thesis (Prague: Czech Technical University).
[2] Murty K L 1989 Eighth International Symposium 1023 570 – 595.
[3] Tenckhoff E 2005 Journal of ASTM International 2.
[4] Barrett C S 1952 Structure of Metals (McGraw-Hill 2nd ed.).
[5] Von Dreele R 1997 J. Appl. Cryst 30 517 – 525.
[6] Dlouha M, Kalvoda L, Vratislav S, Cech B 1991 Kov. Mater. - Metall. Mater. 29 289-299
[7] Kallend J S, Kocks U F, Rollett A D, Wenk H 1991 Textures and Microstructures 18 1203-1208.
[8] Nikulina A V 2004 Metal Science and Heat Treatment 46 458 – 462.
[9] Hsun H 1974 Texture of metals - Technical report (United States Steel Corporation).

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