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Crystal Orientation Measured by XRD and Annotation of the Butterfly Diagram

Zhenqi Guo,* Tao Fu,† and Hengzhi Fu‡

**Instrument Analytical Center, Northwest University, Xi'an, 710069, P.R. China; †State Key Laboratory of Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an, 710049, P.R. China; and ‡State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an, 710072, P.R. China*

An improved X-ray diffraction rotating orientation measurement method is proposed that can measure the crystal lattice orientation quickly and accurately. The method can also directly assess the quality of preferentially oriented specimens and quasi-single crystals through use of the butterfly diagram to measure the crystal orientation distribution.

INTRODUCTION

Many kinds of crystallographic problems can be encountered in materials research. The relationship between the properties of bulk objects and their inner lattice orientations is important in all crystalline materials other than randomly oriented polycrystals or powders. The measurement of crystal orientation and its distribution is increasingly of interest in the development of anisotropic and single-crystal materials because of the close association with the bond characteristics in the materials, their excellent properties, the crystal growth process, etc.

X-ray diffraction (XRD) is an effective method for studying the inner crystalline structure of a material, but current instruments and techniques are designed with either single crystals or polycrystals in mind. If a conventional polycrystal or powder XRD method is used to study a single-crystal material, the results may be different from the standard patterns. This is illustrated in Fig. 1(a), which compares the diffraction pattern obtained from a block of high-quality Nd-Fe-B supermagnetic steel prepared by a special process with that from the same material in powder form. This disparity between the two patterns results because conventional XRD analysis uses the converged focus principle and $\vartheta/2\vartheta$ scanning. In this, the detector receives only the X-rays reflected from the crystal planes parallel to the surface. Thus, it can be imagined that, for a single-crystal material, the diffraction pattern may show either strong peaks from a certain plane or no peaks at all in the whole scanning range, making it difficult to assess the actual crystal quality.

THE ROTATING ORIENTATION XRD METHOD

The rotating orientation XRD method (RO-XRD) requires that the crystal structure parameters be known or that the diffraction angles of the planes have been measured by conventional XRD experiments on powder or polycrystalline material. The diffraction principle diagram is shown in Fig. 2. In it, the specimen is fixed on a rotating table attached to the instrument while the detector is set at the diffraction angle $2\vartheta_0$ of one plane. While the specimen is ϑ-scanning (between 0 and $2\vartheta_0$), it rotates at a fairly high speed around the normal axis of the

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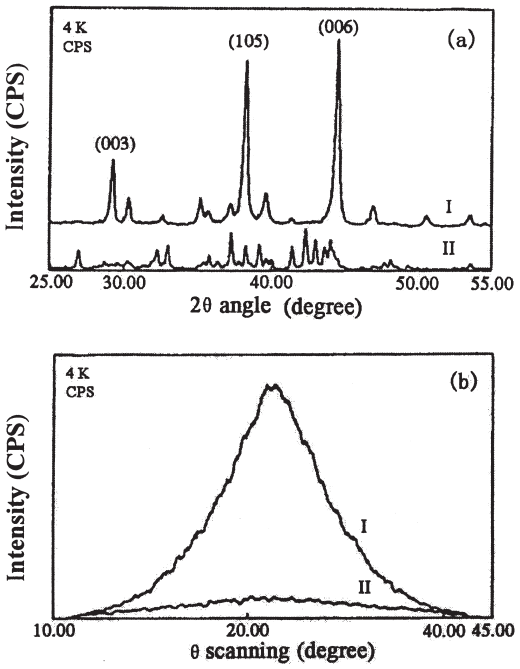

FIG. 1. (a) Conventional XRD pattern from a specimen of $Nd_2Fe_{14}B$; (b) RO-XRD pattern from the (006) plane of $Nd_2Fe_{14}B$ ($2\vartheta_0$ fixed at 44.50°). I—block form; II—powder form.

specimen surface. In the process, there will be some plane whose deviation angle ϕ of the crystal plane from the surface place is between 0 and $2\vartheta_0$, so that its normal axis crosses the horizontal plane twice. When this happens, the diffraction ray must be in the horizontal plane, the ϑ-scanning offsets the deviation angle ϕ, and the detector at $2\vartheta_0$ may receive reflected rays. The detailed crystal information at different deviation angles may also be displayed in the scanning diagrams.

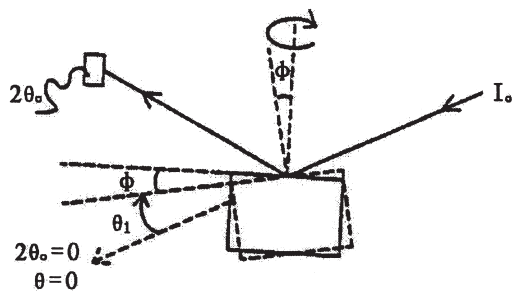

FIG. 2. Diffraction principle diagram of the RO-XRD method.

Figure 3 is an example of the type of scan produced using the RO-XRD method. The scan, which has a symmetrical pattern that can be described as a butterfly diagram, can provide much useful information on crystal orientation.

USES OF THE RO-XRD METHOD

DETERMINING PREFERENTIALLY-ORIENTED, POLYCRYSTALLINE, OR QUASI-CRYSTAL STRUCTURE

The RO-XRD Method can be used as a criterion for determining if a material is preferentially oriented, polycrystalline, or a quasi-crystal. Only single crystals, quasi single-crystals, and large grains in polycrystals can exhibit step lines when the specimen is rotated around the axis normal to the surface. Randomly oriented polycrystalline materials and powders do not possess this attribute, but give Cauchy distribution function curves centered at ϑ_0 that gradually decrease. In the XRD patterns of semiconductor films prepared by various methods (Si, ZnO,GaAs, β-SiC, etc.), only peaks of one type of plane can be obtained using conventional $\vartheta/2\vartheta$ scanning. Using the RO-XRD method, some specimens will give butterfly diagrams while others will give patterns little different from those of their powders. Figure 1(b) is a comparison of RO-XRD patterns obtained from the (006) plane of both block

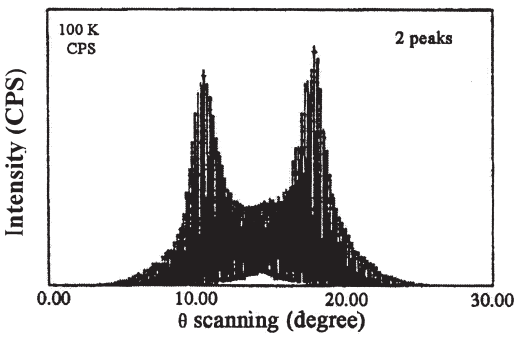

FIG. 3. The RO-XRD pattern from the (012) plane of a Sb-5%Bi specimen. Test conditions: CuKα, 35kV, 10mA, fixed $2\vartheta_0$ = 28.50°. Result: ϑ_1 = 10.66°, ϑ_2 = 18.08°, ϕ = 3.70°, FWHM = 2.4°.

and powder form of Nd-Fe-B magnet material. Though the block is polycrystalline, the grains are preferentially oriented along the c axis. With reference to Fig. 3, the diffraction intensity under the step lines near ϑ_0 is not zero. This means that the Sb-5%Bi specimen contains some polycrystallinity, and thus, can only be considered a quasi-single crystal.

CRYSTAL ORIENTATION CHARACTERISTICS AND DEVIATION ANGLE ϕ

Details of various crystal orientation distributions can be displayed in one diagram (the butterfly diagram) through scanning. Figure 4 shows the RO-XRD pattern from the (111) plane of a directionally solidified Cu specimen. By contrast, a symmetrically distributed Gaussian common tangent curve is obtained when a specimen has only one type of orientation [Fig. 5, taken from the (200) plane of Ni-based DD3 alloy]. Its full width of half maximum intensity (FWHM) corresponds to the degree of orientation scatter. If the maximum positions of the common tangent curves are ϑ_1 and ϑ_2, then:

$$0.5(\vartheta_2 + \vartheta_1) = \vartheta_0,$$

where ϑ_0 is the Bragg angle of the d value of the plane;

$$0.5(\vartheta_2 - \vartheta_1) = \phi,$$

where ϕ is the spatial deviation angle, which can thus be seen directly on the butterfly diagram.

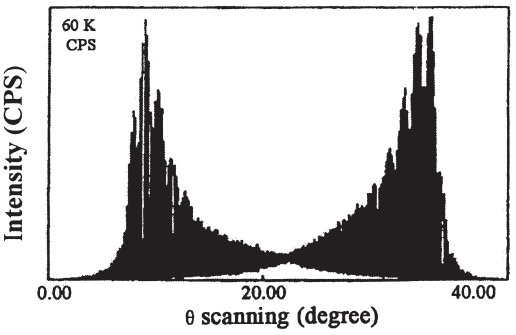

FIG. 4. The RO-XRD pattern from the (111) plane of a directionally solidified Cu specimen. Test conditions: CuKα, 35kV, 10mA, fixed $2\vartheta_0 = 43.30°$.

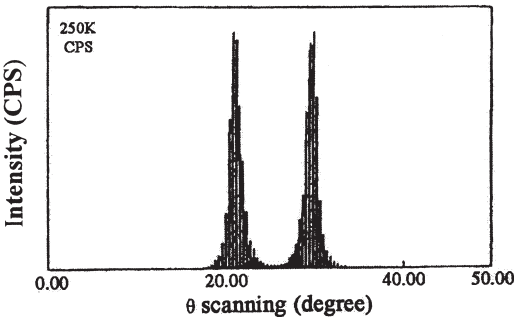

FIG. 5. The RO-XRD pattern from the (200) plane of a Ni-based DD3 alloy specimen. Test conditions: CuKα, 35kV, 5mA, fixed $2\vartheta_0 = 50.80°$. Result: $\vartheta_1 = 21.00°$, $\vartheta_2 = 29.90°$, $\phi = 4.45°$, FWHM = 1.2°

DETERMINING THREE-DIMENSIONAL ORIENTATION OF A SINGLE CRYSTAL

X-ray measurements can only reveal the surface condition of a specimen. To determine whether a three-dimensional object is a single crystal or not, and what the crystal orientation is, measurements must be taken in three dimensions.

1. Having determined the spatial deviation angle ϕ from the butterfly diagram, the rotating table is moved to ϑ_1 (or ϑ_2), the specimen being allowed to rotate slowly around its surface normal axis. The horizontal line on the surface of the specimen is the projecting line of the normal axis of the crystal plane when the diffraction intensity is the strongest. If the crystal needs to be cut, the cut is made vertically at the angle ϕ from the projecting line in the horizontal plane.
2. The spatial deviation angle ϕ and the projecting lines of the other two surfaces of the object can be measured using the above method. The object can be said to be a single crystal if the intersecting angles of the inner planes comply with the relationship of the angles between the planes of the crystal system of the specimen. If it is otherwise, the crystal orientation of the bulk crystal has changed.

Metals and alloys are not transparent or powdered, so the crystal planes cannot be

determined by polar microscopy. However, by using the RO-XRD method, we can determine them and various (hkl) crystallons can be cut out. One of the authors has cut a Ni-based DD3 high-temperature alloy into a 6×7×8mm single crystal and reconfirmed the microstructure of the cuboid so produced [1]. Also, a single-crystal gem of α-Al_2O_3 has been measured by this method, and the error in the angle ϕ was found by transmission electron microscopy to be only 0.2° [2]. This is due predominantly to the very high precision of the XRD method.

Research into anisotropy has provided many useful materials. Much emphasis is now placed on the exploitation of natural single crystals and on the research and synthesis of man-made single crystals. The related physical and chemical analysis methods must keep up with the developments in this materials science. Deployment of the RO-XRD method using conventional XRD instruments can lead to resolution of many of the structural questions surrounding these newly developed materials.

CONCLUSIONS

(1) The RO-XRD measurement method is fast and highly accurate, and easy to employ in the determination of crystal orientations and their distribution. (2) The butterfly diagram obtained using this method can provide directly much information on the orientation of materials, such as whether a specimen is a single crystal or polycrystal, the crystal plane near the specimen surface, the crystal orientation deviation angle ϕ and the projecting line, and the degree of scatter in the preferred orientation.

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