Micro-X-Ray Diffractometer Focused by Polycapillary Optics and Its Applications for Materials

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Abstract. The analysis of small samples and micro areas of large samples are significant in material, environment and geology fields. This work reports the study of a micro-X-ray diffractometer developed by our laboratory and its applications for not only micro-X-ray diffraction (μ-XRD) analysis but also micro energy dispersive X-ray fluorescence (μ-EDXRF) analysis. The accomplishment of the two analysis methods in one instrument makes it possible to characterize micro materials in situ by a very efficient way. In order to demonstrate the feasibility of this diffractometer, the samples difficult to be measured by the conventional diffractometer were studied. Firstly, a cooper wire with a diameter of 140 μm was analysed as a micro sample. Then two different points of a TiN film were analysed to discuss their phase transitions in micro areas. Moreover, the phase distribution of a two-dimensional area on an iPhone mainboard was scanned. The phase mapping was acquired by data processing. These researches highlight the abilities of this diffractometer in the applications on micro material characterizations. As a result, this diffractometer can adapt to the analyses of elemental composition, mineralogical composition and their distributions in the micro materials. It can also provide useful reference information for the micro phase transitions. Therefore, it can be concluded that this micro-X-ray diffractometer has potential prospect in the micro material analysis and any other related fields.

1. Introduction

The characterization of micro materials has always been an essential topic in material science. Currently, different techniques for micro analysis have been developed, such as X-ray inspection techniques, including micro-X-ray diffraction (μ-XRD) and micro energy dispersive X-ray fluorescence (μ-EDXRF). The two techniques can provide data of chemical elemental composition analysis and crystalline structure analysis, respectively [1,2,3,4,5,6]. Generally, the crystalline analysis in a certain area is carried out by the standard X-ray powder diffraction instrument. It uses a linear X-ray source to irradiate the sample to obtain the lattice information based on Bragg’s law in a rectangular area on the sample. The size of this area is usually more than 1 mm×10 mm. For the micro analysis, micro-X-ray beam with the size less than 1 mm is introduced. Collimators consisted of pinhole or slit are usually used to cut the X-rays to the necessary size [7,8]. However, since there is a distance between the collimator outlet and the measured point, the irradiation size on the sample will be much larger than the collimator outlet size. Thus, a smaller collimator is needed to constrain the X-ray beams. The
use of collimators however decreases the intensity of the X-ray beams on the sample, which results in longer measurement time.

To solve this problem, a type of micro-X-ray diffractometer is designed and developed by our laboratory. In this device, polycapillary optics has been employed. The polycapillary optics is a kind of glass device which consists of thousands of capillaries. The X-ray beams can transport inside the capillaries based on total reflection theory. Finally, the X-ray beams are collected and focused by the polycapillary into micro-X-ray beams. The intensity of the X-ray beams in the X-ray focal spot will increase by two to three orders of magnitude \[9,10,11,12\]. This characteristic of polycapillary optics, combining with the intelligent automatic control system, makes the analysis of each micro area possible. In addition, this instrument is controlled by the software developed by our laboratory. With the help of the software and hardware, this instrument can carry out µ-XRD analysis as well as µ-EDXRF analysis. In this paper, we will introduce this diffractometer, and discuss its applications for micro material characterizations.

2. Materials and methods

2.1 Samples

In order to verify the ability of this diffractometer to measure small samples, a section of copper wire worked in precise instruments was studied. The diameter of this wire is 140 μm. It is too slim for conventional instrument to locate its detected point. The copper wire and detected point is marked in Figure 1.

![Figure 1. Copper wire of 140μm diameter and the detected point](image1)

The micro areas of the normal size sample were also measured. These areas are irregular and easily entirely covered by the irradiation of conventional instrument, so the microanalysis tends to be necessary here\[13\]. The sample is showed in Figure 2. The part A and part B is TiN films. The part C is the explored substrate of 304 steel. Part A and B look very similar under the optical microscope. There are two detected points (a and b) in Figure 2.

![Figure 2. Micro area of the TiN film and the detected points](image2)

The distribution of crystalline phase in a certain area was also analyzed. In order to highlight the advantages of this diffractometer in two-dimensional XRD scanning, one of the solder contact point on the mainboard of an iPhone was selected as the sample. It is shown in Figure 3. The detected area is a two-dimensional area of 1.0 mm × 0.6 mm in the marked frame.
2.2 Methods

Combining the X-ray diffraction technology and polycapillary optics technology, our laboratory developed a type of micro-X-ray diffractometer focused by polycapillary optics. The structure of the micro-X-ray diffractometer is shown in Figure 4. This diffractometer is mainly composed of the microfocus X-ray tube (Cu target, focal spot size is 50 μm × 50 μm), SDD X-ray detector (produced by Amptek company of America, energy resolution at 5.90 keV is 145ev, effective area of beryllium window is 25 mm²), polycapillary X-ray optics (input focal length is 66 mm, length is 98 mm, output focal length is 27.6 mm, the focal spot diameter at the energy of Cu-Kα is 115 μm), Ni filter (thickness is 17 μm, installed between microfocus X-ray tube and polycapillary X-ray optics), slit (width is 0.2 mm for μ-XRD), 0-θ goniometer (accuracy is 0.001°), XYZ sample stage (accuracy is 0.001 mm), and the intelligent automatic control system mainly composed of programmable logic controller (PLC). The microfocus X-ray tube and the polycapillary X-ray optics are installed on one side of the goniometer. The optics converges the X-ray beams from the microfocus X-ray tube into the micro-X-ray beams. The X-ray detector and the slit are installed on the other side of the goniometer. The center line of the detector beryllium window passes through the center of the slit. The center line of the micro-X-ray beams and the detector beryllium window meet at the center of the goniometer. The detected point of the sample coincides with the focal spot of the X-ray at the center of the goniometer as well.

The controlling software of this diffractometer is developed based on LabVIEW code[14]. The software can be used to configure the voltage and current of the microfocus X-ray tube, rotation parameters of goniometer, motion parameters of XYZ sample stage and various setting information of X-ray detector, respectively.

There are two modes of operations of the micro-X-ray diffractometer, μ-XRD analysis mode and μ-EDXRF analysis mode. The two modes are switched by the settings inside the software. The configuration of the measuring head in the μ-EDXRF mode is slightly different from that in the μ-XRD mode. In the μ-EDXRF mode, the incident X-ray Irradiates at a fixed 45° angle relative to the...
sample surface on the point to be measured. The beryllium window of the X-ray detector is fixed at 135 ° to receive the fluorescent X-ray excited from the sample surface. The experimental conditions are listed in the Table 1.

|                         | μ-XRD | μ-EDXRF |
|-------------------------|-------|---------|
| **Anode Material**      | Cu    | Cu      |
| **Focal size /mm**      | 0.115×0.115 | 0.115×0.115 |
| **HV /kV**              | 30kV  | 30kV    |
| **Current /mA**         | 0.5mA | 0.5mA   |
| **2θ range /°**         | 30-120/ | /       |
| **Step Size /°**        | 0.1   | /       |
| **XRD Monochromator**   | Ni filter | /       |
| **Incident angle of X-ray /°** | / | 45      |
| **Receive angle of detector /°** | / | 135     |

3. Results and discussions
3.1 Analysis of micro sample

The measurement live time of each step is 5 s (step time) for the copper wire. The results are shown in Figure 5. According to the data from International Centre for Diffraction Data (ICDD), the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 0 0) planes of Cu (JCPDS 04-0836) are figured out.

![Figure 5. The μ-XRD pattern of the copper wire](image_url)

Some studies showed that compared to X-ray collimators composed of pinholes or slits, polycapillary X-ray optics could shape wider diffraction peaks. Although the full width at half maximum (FWHM) of the diffraction peaks increased, the higher intensity of the X-ray beams in the area of the focal spot would save measurement time. The diffraction peak also formed faster after the application of polycapillary X-ray optics. The increase in the diffraction intensity is helpful for creating smooth Gaussian peaks to reduce the uncertainty of the position of the diffraction peak [15].
3.2 Analysis of micro areas

At present, the overall analysis method is mostly used in the phase analysis of thin films. While microanalysis can be used to supplement more details. It is also one of the effective methods to study the phase transition in the micro areas. In Figure 6, there is the µ-EDXRF spectra of the detected points on the TiN film with a measurement live time of 60s. The main element of the film is Ti. Since the fluorescent X-ray excited from N element has a low energy, it is absorbed by the air seriously. The Fe and Cr are from the substrate of 304 steel.

The TiN thin films are amorphous with nanocrystalline structures. Studies have shown that nanocrystalline embedded in the amorphous phases is the basis of high hardness of TiN films [16]. The µ-XRD patterns of the TiN film (Figure 7) showed the presence TiN (JCPDS 38-1420) with orientations of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) by 1 s step time. The phases differ obviously from the two patterns. In Figure 7 (a), the strangest peak is TiN (2 2 0) plane. While in Figure 7 (b), it is TiN (1 1 1) plane showing the highest intensity. The TiN (2 2 0) plane seems disappeared. That indicates the microstructure of the film changes significantly after more Ti depositing.

\[\text{Figure 6. The µ-EDXRF spectra of TiN film, (a) point a; (b) point b}\]

\[\text{Figure 7. The µ-XRD patterns of TiN film, (a) point a; (b) point b}\]
Combining Figure 6, with the increasing deposited Ti, the pressure accumulated inside the film promotes the phase transition [17,18]. The partial phase transition, to a certain extent, will lead to the lattice transformations of TiN becoming unbalanced. When the transformations develop in a bad direction, they easily evolve into the macroscopic failure of the whole film. Since the macroscopic failure of the films often starts with the micro creep, the micro area analysis of film can provide useful reference information for the promotion or reinforcement of the film.

3.3 Analysis of two-dimensional XRD scanning

The μ-EDXRF spectrum of the solder material is in Figure 8 with a measurement live time of 600s. The Sn is the main element. In Figure 9, except for a hump peak, there is an obvious diffraction peak near 90° with step time of 2 s. The data in Figure 9 is compared with the compounds containing Sn according to the ICDD data. The diffraction peak at about 90° well matches the position of SnO₂ (3 1 2) plane (SnO₂, JCPDS 41-1445).

![Figure 8. The μ-EDXRF spectra of the solder material](image)

![Figure 9. The μ-XRD patterns of the solder material](image)
The 1.0 mm × 0.6 mm area on the solder contact point (Figure 3) is divided into 10 × 6 points for μ-XRD two-dimensional scanning. Scanning step is 0.1 mm. The range of 2θ of each point is 88° ~ 94°. The step angle of the goniometer is 0.5°. The step time is 1 s. 60 diffraction patterns are obtained by the scanning. The integral area of SnO2 (3 1 2) diffraction peak is arranged in two-dimensions by using MATLAB software so as to analyze the distribution of the phase in the area of detected. The phase mapping is shown in Figure 10.

From Figure 10, it can be seen that the distribution of SnO2 (3 1 2) changes clearly from the left side to the right side of the scanning area, which may be related to the temperature difference caused by the different heat dissipation conditions. The right side is closer to the boundary of the mainboard comparing with the left side. This may result in the phase difference between the two sides of the scanning area due to the different temperatures.

4. Conclusion

The polycapillary technology and X-ray diffraction technology are combined for the development of the micro-X-ray diffractometer in our laboratory. This diffractometer shows unique advantages in the phase study of micro materials, which are difficult to be studied by the conventional diffractometer before. This diffractometer has the characteristics of non-destructive. It can adapt to the analysis of small samples and the micro areas of large samples. It can also carry out the two-dimensional scanning analysis to acquire the distribution of certain phase in the areas of interest. By using this micro-X-ray diffractometer, the micro-X-ray diffraction analysis and micro energy dispersive X-ray fluorescence analysis are both realized for the samples in situ. This diffractometer provides a new idea for micro material characterization. Furthermore, it can be predicted that this micro-X-ray diffractometer will have an important application prospect in the fields of special materials, geosciences, environment and so on.

5. Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 11575026).

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