Enhancement of XRF intensity by using Au-coated glass monocapillary

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Results on using X-ray optics with a monocapillary attached to a microfocus Mo X-ray tube for a high-intensity XRF analysis are reported. Au-coated glass monocapillaries with 400 and 700 μm inner diameters were used to obtain focused and intensive incident Mo X-rays for the measurements of XRF intensities from pure metal samples. Intensity enhancements obtained by using the Au-coated monocapillaries were found to be up to 1.5 times higher than those obtained by using similar inner diameter uncoated glass capillaries. The XRF intensity profiles were measured by the wire scanning method to investigate the reasons. The traces of the incident X-rays were calculated by taking into account of X-ray total reflection of the incident X-rays from the inner wall of the capillaries. The calculated XRF intensity profiles agree with those of the measured XRF intensity profiles. The observed enhancements in XRF intensity were the results of the incident X-rays emitted from the Mo X-ray tube being totally reflected on the inner wall of the Au-coated monocapillaries. © *2011 International Centre for Diffraction Data.* [DOI: 10.1154/1.3591166]

Key words: micro-XRF, Au-coated glass monocapillary, X-ray total reflection

I. INTRODUCTION

Capillary X-ray optics is very important in developing a micro-X-ray fluorescence (micro-XRF) instrument in a laboratory (Rindby *et al.*, 2000). A micro-XRF instrument consists of a microfocus X-ray tube and a capillary optics. Several applications of micro-XRF have been reported (Nozaki and Nakazawa, 1986; Yamamoto and Hosokawa, 1988; Bjeoumikhov *et al.*, 2005). In order to obtain an incident micro-X-ray beam for an XRF analysis, the simplest approach is to use a collimator (Jones, 1993). However, the collimator with a small pinhole cannot focus incident X-rays emitted from an X-ray tube, and the X-ray beam remains to be diverged after passing through the pinhole. On the other hand, a monocapillary can provide a small incident X-ray beam about 10 μm in size (Ohzawa *et al.*, 2004), and the X-ray intensity obtained by the monocapillary is higher than that obtained by a conventional collimator. In the case of a monocapillary, a portion of the incident X-rays emitted from an X-ray tube with incident angles of less than the critical angle for total reflection can be totally reflected from the inner wall of the capillary (Hosokawa, 2004). The critical angle (θ_c) can be calculated using the following equation:

$$\theta_c \cong \frac{1.65}{E}\sqrt{\frac{Z}{A}\rho}, \tag{1}$$

where E is the incident X-ray energy, Z is the atomic number, A is the atomic mass, and ρ is density of the material (Klockenkämper, 1996). Parallel, focused, or diverging X-rays can be generated depending on the dimensions and material used of a capillary. Glass is commonly used as a capillary material from the point of view of ease of processing and smoothness on the inner wall. However, the X-ray intensities of the incident beam transmitted through a glass monocapillary is not very high because the incident angles of the incident X-rays impinged onto the inner wall of a capillary are small, and the divergence angle of the X-ray beam emitted from the capillary is about a few milliradians. Thus, we investigated a potential enhancement of the X-ray intensity by using a new type of glass monocapillary. The critical angle for total reflection of an incident X-ray beam depends on the density of the inner wall of a capillary. In case the density of the inner wall material of a capillary is high, θ_c is also high, indicating that a large amount of the incident X-rays emitted from an X-ray tube can be totally reflected by the inner wall of the capillary. For a capillary with an inner wall coated by a high-density material such as a metallic layer, an enhancement in the incident X-ray intensities from the capillary, which leads to high X-ray fluorescence from a sample, can be obtained.

In this study, we report on the results in the enhancement of XRF intensity obtained by using incident X-rays from Au-coated glass monocapillaries with inner diameters of ∅ =400 and 700 μm.

II. EXPERIMENTAL

A. Capillary

The four straight glass monocapillaries with and without Au coating used in this study (see Figure 1) were supplied by Horiba Ltd., Kyoto, Japan. The length and outer and inner

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Figure 1. (Color online) Photographs of straight glass monocapillaries: (a) and (b) for inner diameter of 700 μm without and with Au coating, respectively; (c) and (d) for inner diameter of 400 μm without and with Au coating, respectively.

diameters for the capillaries shown in Figures 1(a) and 1(b) were 100 mm, 2 mm, and 700 μm, respectively. The length and outer and inner diameters for the capillaries shown Figures 1(c) and 1(d) were 110 mm, 6 mm, and 400 μm, respectively. Each of the capillaries shown in Figures 1(b) and 1(d) has an Au electroplated inner coating of 100 nm thick. Each of the capillaries was attached to a special holder that is attached to the window of an X-ray tube to obtain a high-intensity and focused incident X-ray beam for XRF measurements as described below.

B. XRF instrumentation

Figure 2(a) shows an overview of the XRF setup with an X-ray tube, a monocapillary, a sample stage, and a SDD X-ray detector. The X-ray tube with a Mo target (MCBM 50-0.6B, RTW, Germany) was operated at 50 kV and 0.5 mA. A glass capillary was attached to the Mo X-ray tube to obtain a focused and intensive incident X-ray beam for an XRF measurement. The incident X-ray beam irradiated the surface of a sample perpendicularly, and a silicon drift X-ray detector (SDD) (X-Flash detector type 1201 Bruker, Germany) (sensitive area: 10 mm^2; energy resolution: <148 eV at 5.9 keV) was used for a rapid measurement of XRF intensities from the sample. The XRF signals were collected at a take-off angle of 45°.

Details on the setup with the Mo X-ray tube, the capillary stage, the sample stage, and the detector are shown in Figure 2(b). The capillary stage attached to the Mo X-ray tube can precisely be adjusted to an optimum position by using an x-y stage (GYMO3S-S1, Kohzu Precision Co., Ltd., Kawasaki, Japan). The capillary can also be rotated to a selected rotation angle to get a maximum incident X-ray beam. The sample was placed on an X-Y-Z sample stage (YA10F-R1/R2 and ZA07A-R3S, Kohzu Precision Co., Ltd., Kawasaki, Japan), which was controlled by three stepping motors with a precision of ± 0.5 μm. The three motor drivers and a motor controller (NT2400, Laboratory Equipment Co., Japan) were used to control the translation stages. Fluorescent X-ray signals detected by the SDD were analyzed by a multichannel analyzer (NT2400/MCA, Laboratory Equipment Co., Japan).

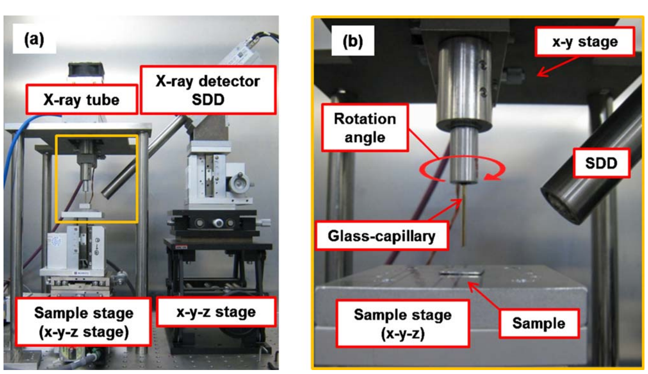

Figure 2. (Color online) Experimental setup of the overall (a) and the enlarged view (b) of the XRF instrument.

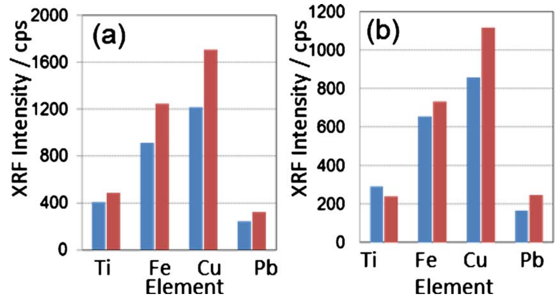

Figure 3. (Color online) Measured XRF intensities: (a) the 700 μm inner diameter glass capillaries and (b) the 400 μm inner diameter glass capillaries. Left (blue online) and right (red online) bars were the XRF intensities obtained without and with the Au-coated capillaries.

III. RESULTS AND DISCUSSION

A. Enhancement of incident X-ray beam

To study intensity gains of the incident Mo X-ray beam obtained by the Au-coated glass capillaries, XRF intensities from pure metals of Ti, Fe, Cu, and Pb were measured. The measuring times were 100 s for Fe and Cu and 300 s for Ti and Pb. The measured XRF intensity profiles obtained by using the capillaries with $\varnothing=700$ and 400 μm are graphically shown in Figures 3(a) and 3(b), respectively, and the values of the measured XRF intensities are listed in Table I. For the 700 μm capillaries with and without Au coating, the intensity-enhancement ratios were found to be 1.20 for Ti $K\alpha$ (4.5 keV), 1.36 for Fe $K\alpha$ (6.4 keV), 1.40 for Cu $K\alpha$ (8.0 keV), and 1.32 for Pb $L\alpha$ (10.5 keV). For the 400 μm capillaries, the ratios were measured to be 0.82 for Ti $K\alpha$, 1.12 for Fe $K\alpha$, 1.30 for Cu $K\alpha$, and 1.48 for Pb $L\alpha$. The above results show that significant intensity gains were obtained by using the Au-coated capillaries, except for Ti $K\alpha$ when the 400 μm capillaries were used.

B. Profile of incident X-ray beam

The XRF profiles measured from a Cu wire ($\varnothing$ $=30$ μm) and a Ti wire ($\varnothing=50$ μm) were used to study the transmission characteristics of the uncoated and Au-coated glass monocapillaries. The wire scanning method was used with the experimental conditions of a total scanning distance of 1 mm, step size of 20 μm, and time per step of 100 s for the Cu wire or 300 s for the Ti wire. The distance from the edge of the capillary to the Cu or Ti wire was 3 mm. Figures 4 and 5 show the measured Cu $K\alpha$ XRF profiles for the 700 and 400 μm capillaries as a function of the scanned distance, respectively. It should be noted that the peak intensi-

TABLE I. Measured XRF intensities and intensity-enhancement ratios obtained with and without Au-coated glass capillaries.

Element	700 μm glass capillaries			400 μm glass capillaries		
	Noncoated (cps)	Au coated (cps)	Enhancement ratio	Noncoated (cps)	Au coated (cps)	Enhancement ratio
Ti	408	490	1.20	291	240	0.82
Fe	914	1247	1.36	655	731	1.12
Cu	1217	1706	1.40	859	1117	1.30
Pb	245	324	1.32	167	247	1.48

ties of the measured Cu $K\alpha$ XRF profiles for the Au-coated capillaries are two times higher than those for the uncoated capillaries. Each of the measured XRF profiles shown in Figures 4(a), 4(b), and 5(b) has a single peak, while the XRF profile shown in Figure 5(a) had two peaks. The Ti $K\alpha$ XRF profiles were found to be almost the same as those of the Cu $K\alpha$ XRF profiles, indicating that the shapes of the XRF intensity profiles are independent of the characteristic X-ray wavelengths from the samples.

Dependences of the XRF intensity profile for the 400 μm capillaries with and without Au coating on the rotation angle, as defined in Figure 2(b), were also investigated using the wire scanning method. Figures 6(a)–6(c) show the Cu $K\alpha$ XRF profiles for the uncoated glass capillary measured at three different rotation angles of 0°, 90°, and 180°, respectively, and each of the three XRF profiles has two peaks. Figures 6(d)–6(f) show the Cu $K\alpha$ XRF profiles for the Au-coated glass capillary measured at rotation angles of 0°, 90° and 180°, respectively, and each of the three profiles has a single sharp peak. Similar results were also observed at other rotation angles.

C. Optics for incident X-ray beam

The distributions of the incident Mo X-ray beams after passing through the glass capillaries with and without Au coating were studied from the enhancements in the measured XRF intensities and the shapes of the XRF profiles.

1. 700 μm capillary

The calculated traces of the incident Mo $K\alpha$ X-rays inside the 700 μm inner diameters of the glass capillaries without and with Au coating are shown in Figures 7(a) and 7(b), respectively. The dark gray (blue online) lines indicate the traces of the incident Mo $K\alpha$ X-rays that pass directly through the capillary, and the light gray (yellow online) lines indicate the traces of the totally reflected Mo $K\alpha$ X-rays. The Cu wire was scanned at the lines from X_1 to X_2, as shown in Figures 7(a) and 7(b), to obtain the Cu $K\alpha$ XRF intensity profiles. It should be noted that the incident Mo $K\alpha$ X-rays irradiating the inner wall of a capillary are absorbed or pass through the wall of the capillary when the incident angle to the inner wall was greater than the critical angle. Since the critical angle for glass was <0.1°, practically no incident Mo Ka X-rays from the X-ray tube impinged onto the inner wall of the uncoated glass capillary were totally reflected from the inner wall. The traces of the incident X-rays, which do not impinged onto the inner wall of the uncoated glass capillary, are plotted as dark gray (blue online) lines shown in Figure 7(a). As shown in Figure 7(b), there are two components of the Mo $K\alpha$ X-rays that impinge onto the inner wall of the Au-coated capillary. One component is the incident Mo $K\alpha$ X-rays, which are not reflected by the inner wall of the glass capillary dark gray (blue online) traces, and the other component is the totally reflected Mo $K\alpha$ X-rays by the Au-coated inner wall of the capillary light gray (yellow online) traces. An effective accepting angle of ω_b=1.1° for the Au-coated capillary shown in Figure 7(b) is larger than the effective accepting angle of ω_a=0.7° for the uncoated glass capillary shown in Figure 7(a). The XRF intensity can thus be enhanced by the Au coating due to the superposition of the two components of Mo $K\alpha$ X-rays and the high effective accepting angle of ω_b=1.1°. Figures 7(c) and 7(d) are the measured Cu $K\alpha$ XRF intensity profiles obtained by using the glass capillaries without and with Au coating, respectively. The broad XRF intensity profile shown in Figure 7(c) was produced by the incident X-rays emitted directly from the Mo X-ray tube [see the dark gray (blue online) traces in Figure 7(a)]. The XRF intensity profile shown in Figure 7(d) was the superposition of both the unreflected direct Mo

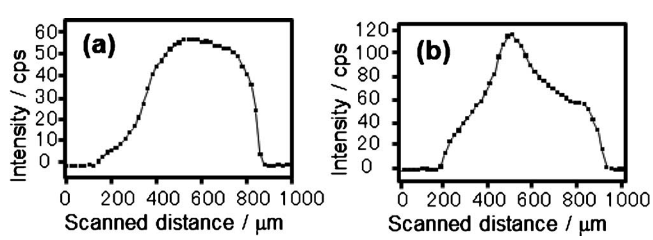

Figure 4. Measured XRF intensity profiles of Cu $K\alpha$ fluorescent X-rays (8.04 keV) obtained using the 700 μm capillaries: (a) without Au coating and (b) with Au coating.

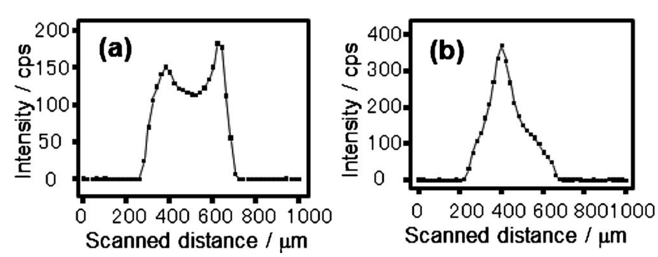

Figure 5. Measured XRF intensity profiles of Cu $K\alpha$ fluorescent X-rays (8.04 keV) obtained using the 400 μm capillaries: (a) without Au coating and (b) with Au coating.

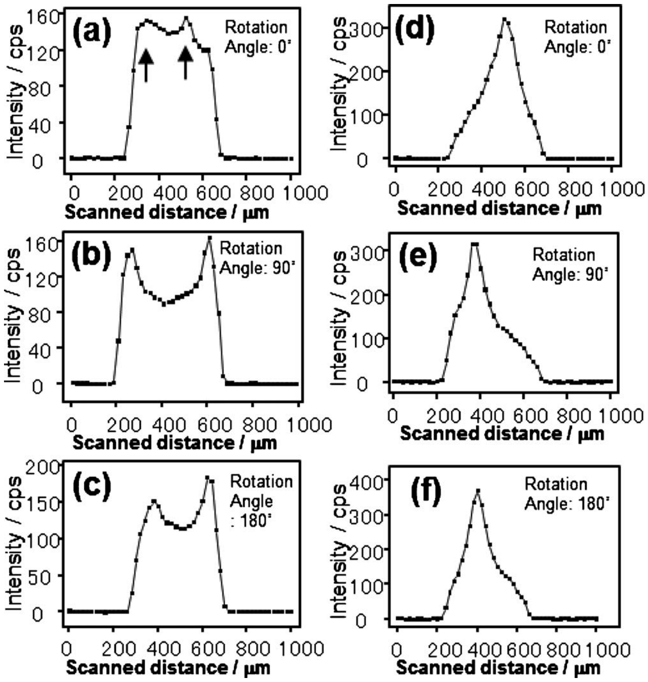

Figure 6. Measured XRF Cu $K\alpha$ intensity profiles obtained using the 400 μm capillaries: [(a)–(c)] without Au coating and [(d)–(f)] with Au coating. The rotation angles of the capillaries about their long axes were [(a) and (d)] 0°, [(b) and (e)] 90°, and [(c) and (f)] 180°. The arrows marked in (a) show the observed double peaks.

X-rays [dark gray (blue online) and broad profile] and the totally reflected X-rays [sharp and light gray (yellow online) peak].

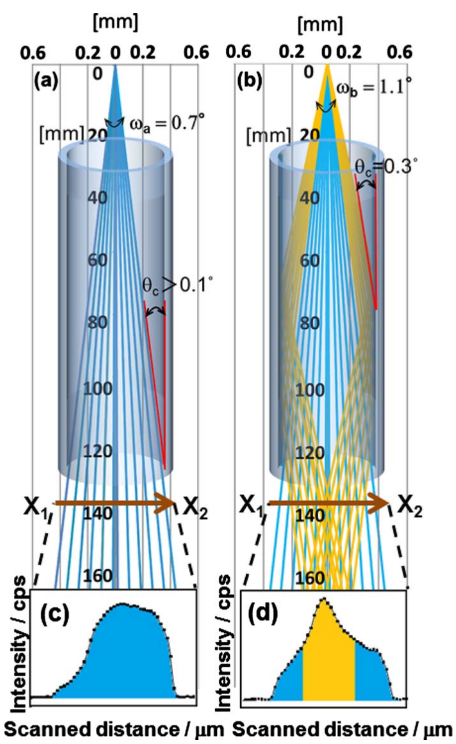

Figure 7. (Color online) Scheme of the optics of the incident Mo-$K\alpha$ X-rays in the 700 μm capillaries: (a) without Au coating and (b) with Au coating. The Cu wire was scanned at the lines from X_1 to X_2. The measured Cu $K\alpha$ XRF intensity profiles (c) and (d) correspond to the calculated X-ray traces shown in (a) and (b), respectively.

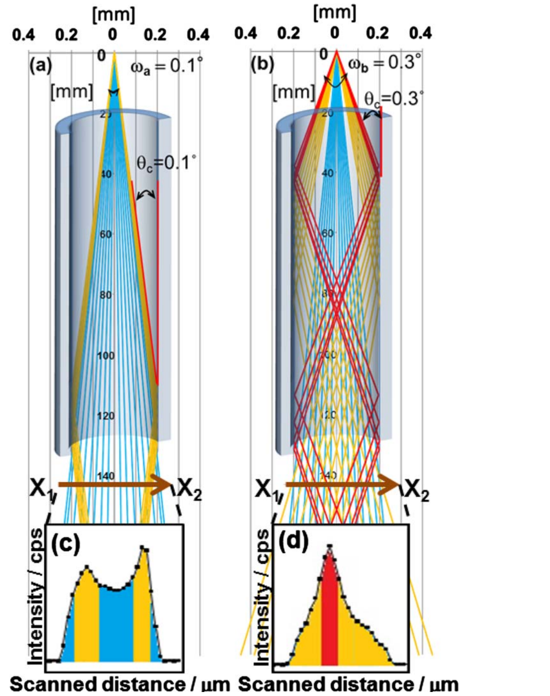

Figure 8. (Color online) Scheme of the optics of the incident Mo $K\alpha$ X-rays in the 400 μm capillaries: (a) without Au coating and (b) with Au coating. The Cu wire was scanned at the lines from X_1 to X_2. The measured Cu $K\alpha$ XRF intensity profiles (c) and (d) correspond to the calculated X-ray traces shown in (a) and (b), respectively.

2. 400 μm *capillary*

The calculated traces of the incident Mo $K\alpha$ X-rays inside the 400 μm inner diameters of the glass capillaries without and with Au coating are shown in Figures 8(a) and 8(b), respectively. As shown in Fig. 8(a), the incident Mo Ka X-rays are totally reflected only at the end of the inner wall of the 400 μm glass capillary. The strong gray (red online) lines shown in Fig. 8(b) show the traces of twice totally reflected Mo $K\alpha$ X-rays. Figures 8(c) and 8(d) are measured Cu $K\alpha$ XRF intensity profiles obtained without and with the Au coating glass capillary, respectively. The Cu $K\alpha$ XRF intensity profile shown in Fig. 8(c) was produced by the incident X-rays directly emitted from the Mo X-ray tube [dark gray (blue online) and broad profile] plus the totally reflected X-rays [two sharp and light gray (yellow online) peaks]. As shown by the light gray (yellow online) traces in Fig. 8(a), the two peaks in the XRF intensity profile shown in Fig. 8(c) were caused by the totally reflected X-rays at the edge of the uncoated glass capillary. On the other hand, only a single and sharp peak was observed for the case with the Au-coated capillary [see Figure 8(d)]. An examination of the X-ray traces shown in Figure 8(b) suggests that the single peak [strong gray (red online) region] was produced by total reflections twice from the Au-coated wall. The measured Cu $K\alpha$ XRF profile shown in Figure 8(d) was caused by three components of the incident Mo $K\alpha$ X-rays: the incident X-rays directly emitted from the Mo X-ray tube [dark gray (blue online) traces in Figure 8(b)], the one-time totally reflected X-rays [light gray (yellow online) traces], and the twice reflected X-rays [strong gray (red online) traces]. As a result of the superposition of the three types Mo X-ray beams irradiating the sample, the XRF intensities from the

Au-coated capillary were therefore enhanced. By the way, the reason for not having twice reflected incident Mo X-rays for the case of the uncoated glass capillary is because the effective accepting angle for the uncoated capillary ($\omega_a = 0.1°$) is three times smaller than that for the Au-coated glass capillary ($\omega_b = 0.3°$).

IV. CONCLUSION

We have successfully investigated the intensity enhancements of incident Mo $K\alpha$ X-rays by using glass capillaries with and without Au coating. Significant gains in the measured Cu $K\alpha$ XRF intensities were obtained by using the Au-coated glass capillaries. The intensity-enhancement ratios were 1.20 to 1.40 for the Au-coated glass capillary of 700 μm inner diameter and 0.82 to 1.48 for the Au-coated glass capillary with a 400 μm inner diameter. The shapes of Cu $K\alpha$ XRF intensity profiles were successfully explained by studying the calculated traces of the incident Mo $K\alpha$ X-rays. The two reasons for the observed intensity gains are the large effective accepting angle and the incident X-rays totally reflected on the inner wall of the Au-coated capillary. The enhancement effects of using 100 μm Au-coated glass monocapillaries as well as using Au-coated polycapillaries and tapered capillaries will also be investigated in the near future.

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