

## *SAXS Intensity Measurements by Photographic Methods*

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### SYNOPSIS

Photographic method for measurement of small-angle X-ray scattering (SAXS) is improved. Intense point-focussing incident beam is obtained by using doubly bent crystal monochromator made of aluminium single crystal. Microphotometry and the subsequent calculation to obtain profiles, Guinier and Porod radii, integrated intensities, and so on are facilitated by using microcomputer. Integrated SAXS intensities measured from an Al-Zn alloy which has been treated under the same heat treatment conditions are coincident with one another with probable errors less than  $\pm 6\%$ . Ratio of the integrated intensities obtained from two Al-Zn alloys of different composition is reasonable compared with the quasi-equilibrium phase diagram.

### 1. INTRODUCTION

Nowadays, the intensity of small-angle X-ray scattering (SAXS) is measured mainly by means of pulse counting methods. On the other hand the measurement by the photographic methods, although they are inexpensive and highly position-resolvable ones, has been almost discarded, for they need many efforts in processing and in converting the density to the intensity. Recently, Vonk and Pijpers<sup>(1)</sup> suggested that film methods were more advantageous than methods involving

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step-scanning counter, and comparable with measurements using a position-sensitive counter. The authors also designed and constructed an apparatus to measure SAXS intensities photographically. The apparatus is composed of two parts, an SAXS camera and a microphotometer, as usual. However, point collimation is employed by the use of a doubly bent pure aluminium single crystal monochromator to avoid distortion of the scattering pattern by the beam dimension. And the microphotometer is controlled by the recent electronics. The tedious and somewhat inaccurate procedure in the usual manner for conversion of the film density to the scattering intensity is replaced by a programmed manner in cooperation with the microphotometry.

The apparatus is used to investigate the decomposition of aluminium-rich alloys. The integrated intensities from aged Al-4 and 10mass% Zn alloys were measured to examine the precision of this method.

## 2. APPARATUS

### 2.1 SAXS camera

To separate  $\text{CuK}\alpha_1$  radiation from  $\text{CuK}\alpha_2$  and to obtain point-collimated intense beam, small focal spot ( $1.0 \times 0.5 \text{ mm}^2$ ) of the X-ray source and doubly bent pure-aluminium single crystal monochromator (diameter of Roland circle: 1100 mm, the shorter radius of the toroidal surface: about 100 mm) were adopted (Fig.1). The monochromator was asymmetric Johansson type. The surface made an angle of  $5^\circ$  with (111) plane. The beam reflected by the monochromator focusses on the film ( $F_s$ ). The size of the focus is  $0.2 \times 0.8 \text{ mm}^2$ . Distances from the X-ray source (T) to the monochromator (M) and from the monochromator to the focus (F) are 255 mm and 465 mm, respectively.

The third slit ( $S_3$ ), the cooled specimen (S) and the film ( $F_s$ ) are put in the vacuum chamber (C) to prevent the scattering by the air and the frost on the specimen.

The specimen is attached between holder blocks of copper in the liquid nitrogen bath. The holder with a specimen is attached magnetically to the bottom of the cryostat of liquid nitrogen and transferred rapidly into the chamber with the aid of dried nitrogen gas stream, and then the chamber is evacuated. Total dose of the incident radiation during the exposure is monitored by measuring the radiation scattered to an angle of about  $90^\circ$  by the air just behind the second slit ( $S_2$ ). For the present specimen the air is suitable as scatterer.

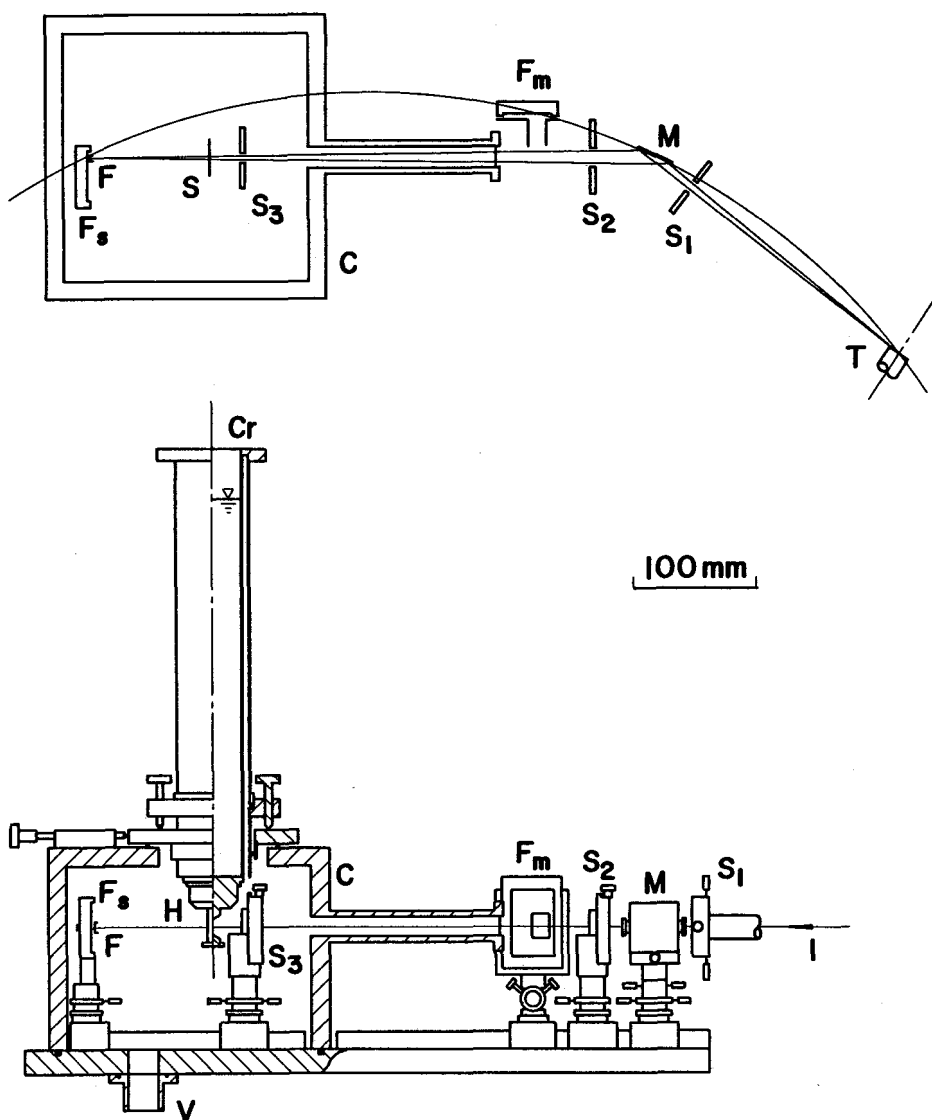


Fig.1 SAXS camera. T:X-ray source. M:double bent monochromator.  
 $S_1 \sim S_3$ :slits.  $F_m$ ,  $F_s$ :films. S:specimen. F:focus of incidence.  
 H:specimen holder. C:chamber. V:to vacuum pump. I:incidence.  
 Cr:Cryostat

The intensity standards are recorded by exposing each film,  $F_s$  and  $F_m$ , to a constant flux of  $\text{CuK}\alpha$  radiation reflected by the quartz monochromator.

The film used is Fuji Industrial X-ray Film #150. The processing of the film is: developing for 6 min in the designated solution of Rendol, stopping for 15 sec in 3% acetic acid and fixing for 10 min

in Renfix solution

## 2.2 Microphotometry system

Schematic diagram of the microphotometry system is shown in Fig.2. The microphotometer (Narumi-Shokai Ltd., C-type microphotometer) is totally controlled with an microcomputer (Sharp Corporation, MZ-1200) run with BASIC language. TTL levelled pulses generated by the microphotometer at every 10  $\mu\text{m}$  movement of the film stage are used to determine the position to measure the density. At the position output from the microphotometer, 1 volt per density of 3.00, is digitized with a 12 bits A/D converter and registered on the microcomputer memory. At the same time, the output is recorded on a chart. The conversion of the density, the smoothing of the intensity data and other calculations are performed by using the microcomputer.

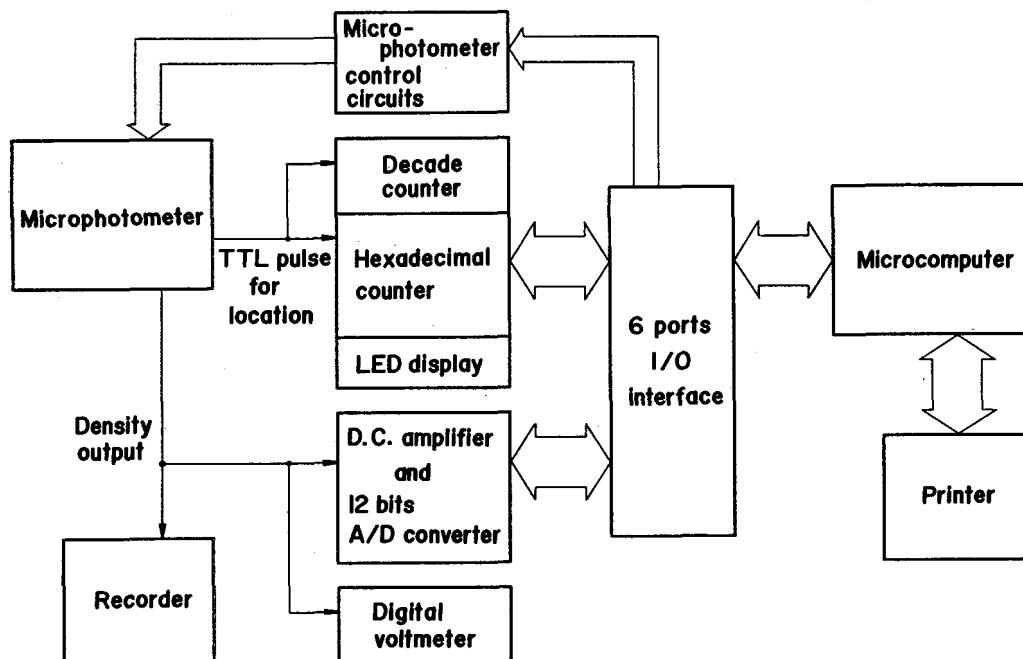


Fig.2 Block diagram of photometry system

## 3. OPERATION

Scattering pattern from Al-4mass%Zn alloy aged for 360 ks at 263 K is given in Fig.3(a), exposed for about 90 hours. Vertical white region in the photograph is the shadow of the beam trap of copper strip, and the black spot in the centre of the region the

trace of direct beam. Rectangles in a row at the bottom are the intensity standards. Fig.3(b) and (c) show a microphotometer chart and a smoothed intensity curve obtained by reading the density at every  $0.002 \text{ nm}^{-1}$  of  $s$  ( $=2\sin\theta/\lambda$ ,  $2\theta$ : scattering angle,  $\lambda$ : wavelength of the X-ray), respectively. With the SAXS equipment, the microphotometry system, and the data treatment as mentioned, the intensity curve of high signal-to-noise ratio is obtained with little effort. Namely, by means of the film method it seems to be possible

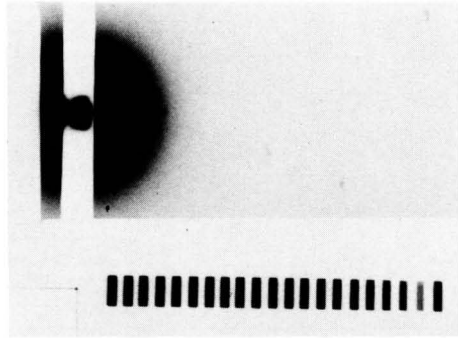


Fig.3(a) Scattering pattern of Al-4mass%Zn alloy aged for 360 ks at 263K after quenching from 613K into iced water.

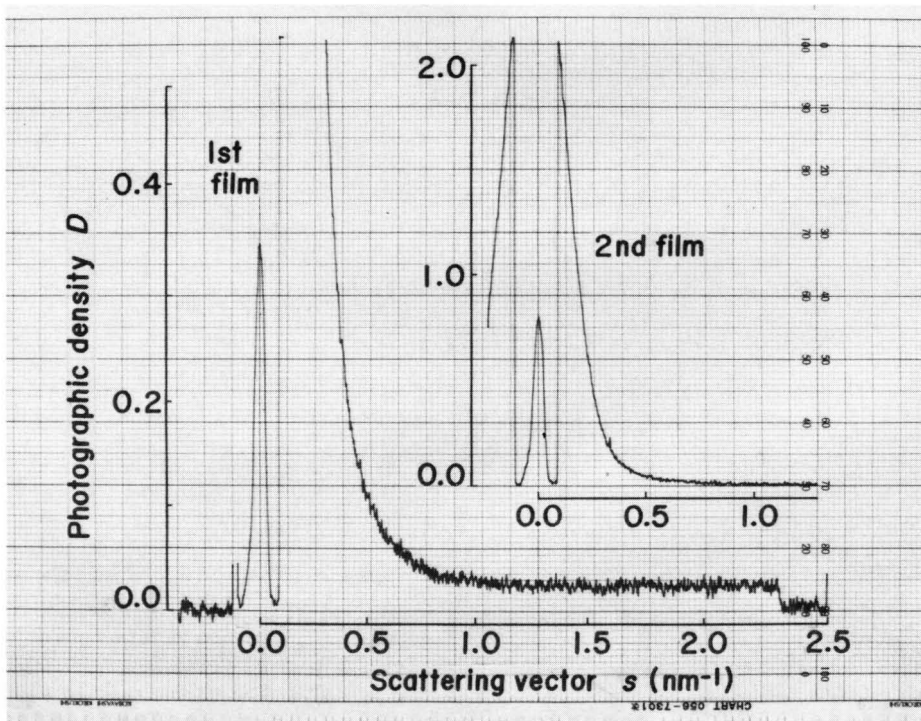


Fig.3(b) Microphotometer chart from (a)

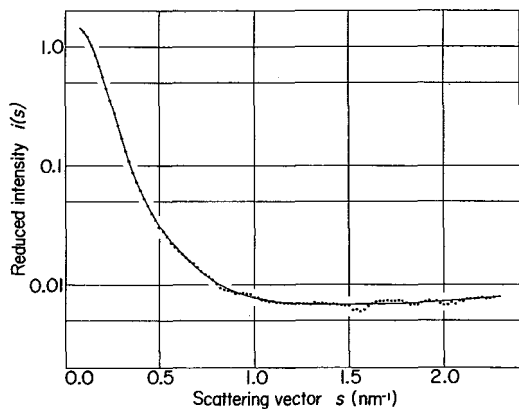


Fig.3(c) Intensity curve. The reduced intensity  $i(s)$  is the value of the measured intensity divided by square of the difference between the atomic scattering factors of zinc atom and aluminium atom.

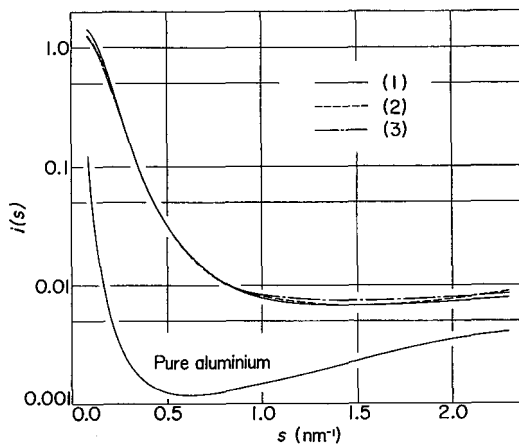


Fig.4 Comparison of measured intensity curves obtained from the same specimen. Curves (1), (2) and (3) correspond to the first, the second and the third measurement, respectively.

to obtain high accuracy of intensity measurements comparable with the counter methods.

#### 4. MEASUREMENTS OF INTEGRATED INTENSITY

The intensity curves of Fig.3(c) and other two separate measurements on the same specimen are shown in Fig.4. They are coincident with each other within a difference of  $\pm 5\%$ . The intensity profile consists of small-angle scattering from zinc-rich spherical G.P. zones grown during the ageing, Laue monotonic scatterings from the depleted matrix and from the G.P. zones, and thermal and incoherent scattering. Measured intensity on pure aluminium ( $i_{Al}(s)$ , Fig.4), which may be considered as the sum of the intensities of the thermal and incoherent scattering, is subtracted from the intensity of the alloy,  $i(s)$ . Laue monotonic intensity,  $i_L$ , which is independent of scattering angle, is estimated by the asymptotic Porod approximation (Fig.5) and subtracted,

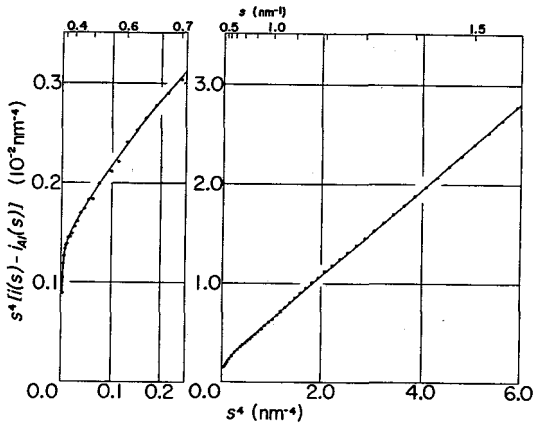


Fig. 5 Porod plot of curve (1) in Fig. 4.

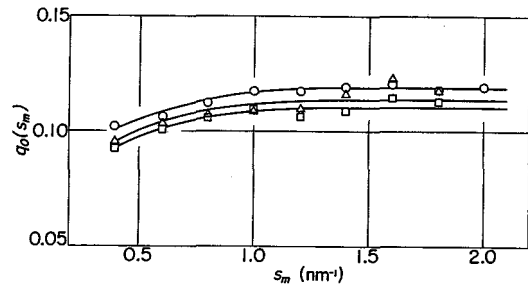


Fig. 6 Change of the obtained value of integrated intensity with  $s_m$ . Circle, triangle, and square correspond to the curves (1), (2) and (3) in Fig. 4, respectively.

thus the resultant gives the SAXS intensity from the G.P. zones only.

The previous workers measured upto an  $s$  of about  $0.5 \text{ nm}^{-1}$ , and the present measurements were extended near the boundary of the first Brillouin Zone. It is seen in Fig. 5 that the Porod approximation holds only at the  $s$  values larger than  $0.8 \text{ nm}^{-1}$ . Therefore, it may be possible that the values of the integrated intensities calculated in the previous studies are affected by the upper limit of  $s$  upto which the intensities are measured. About the present measurements (Fig. 4), variation of the value of the integrated intensity with  $s_m$  was examined by making use of the intensity data in the  $s$  range below  $s_m$ . In this calculation the intensities beyond  $s_m$  were approximated by the asymptotic rule as previous workers assumed. The integrated intensity is given as

$$q_0(s_m) = 4\pi \int_0^{s_m} s^2 [i(s) - i_{A1}(s) - i_L(s_m)] ds + 4\pi k(s_m) / s_m$$

where  $k(s_m)$  is the intercept of the tangent line at  $s_m$  with the

ordinate in Fig.5, and  $i_L(s_m)$  the gradient of the tangent.  $q_0(s_m)$  increases with  $s_m$  and attains to a saturated value at  $s_m$  of 1.0 to 1.2  $\text{nm}^{-1}$  (Fig.6), which is adopted as the integrated intensity ( $q_0$ ) of the alloy in the present work. It is thought that these results indicate that the measurements need to be performed upto the range of  $s$  or more.

The integrated intensities obtained from Al-10mass%Zn alloy, quenched from 573 or 673 K and aged for 90 ks at 293 K, was also measured.

These values are tabulated in Table 1. The probable errors are estimated to be  $\pm 6\%$  for 4mass%Zn alloy and  $\pm 4\%$  for 10mass%Zn one.

Table 1 SAXS integrated intensities of the Al-Zn alloys

alloy	quenching temperature (K)	$q(0)$ (arbitrary unit)	mean value of $q(0)$ (arbitrary unit)
4%Zn	613	0.119	0.114
		0.113	
		0.110	
4%Zn	613	0.113	0.114
		0.113	
		0.114	
10%Zn	573	0.486	0.486
		0.473	
		0.478	
10%Zn	673	0.497	0.486
		0.497	
		0.497	

Furthermore the ratio of the mean value of the integrated intensities of 10mass%Zn alloy to that of 4mass%Zn one is  $4.26 \pm 0.43$ , which is reasonable as compared with 4.1, the mean value of the ratio of the integrated intensities of each alloy at the ageing temperature calculated from the solvus of the G.P. zones obtained by several authors.<sup>(2)~(7)</sup> These results indicate that the system described in this article can improve the accuracy of measurements of the integrated intensities of SAXS.



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