

In situ observation of phase transformation in an Fe–Zn system at high temperatures using an image plate

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A unique system has been developed for *in situ* observation of phase transformation at high temperatures. Changes in powder-diffraction patterns from a heated specimen can be measured continuously by scanning an image plate located behind a slit. A heating system has been designed for a sheet specimen ($\sim 5 \times 6$ mm) using Joule heating, and it can heat the specimen up to 1100 K at a rate of up to 160 K s^{-1} , where effects of thermal expansion are minimized by a mechanism releasing stress. This system was applied to Zn-coated ($\sim 8 \mu\text{m}$ in thickness) steel. At temperatures higher than the melting point of Zn, different types of Fe–Zn intermetallics formed sequentially through rapid interdiffusion. Changes in phase and crystallographic structure were monitored with a time resolution of less than a few seconds. It has been found that an addition of a small amount of an element, such as P, into Fe changes the incubation time before the alloying reaction starts. This system has been shown to have the potential for application to *in situ* observation of other reactions at high temperatures.

Keywords: *in situ* observations; X-ray diffraction; image plates; galvanizing; phase transformations.

1. Introduction

In situ observation is one of the most important techniques for understanding near-surface reactions. When a reaction occurs in a short period of less than a few seconds and the structure differs through depth, synchrotron radiation has advantages for *in situ* observation of the reaction; a high flux shortens the measuring

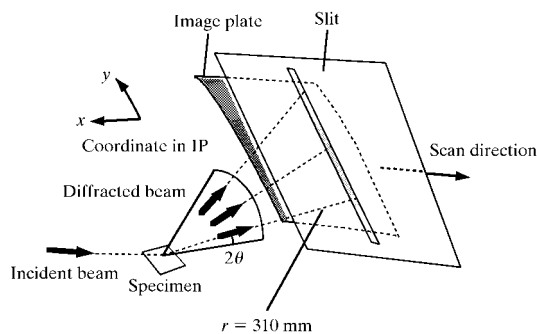


Figure 1 System geometry. The coordinates x and y in the IP correspond to time and diffraction angle 2θ , respectively.

time, and measurements with different energies provide information on different depths.

To detect a change in a structure, we have to measure diffraction intensities in a wide range of the reciprocal space simultaneously; a linear or area detector is used for this purpose (see, for example, Fujii *et al.*, 1979; Clarke *et al.*, 1991; Shimomura *et al.*, 1992). Image plates (IPs) have merits of high sensitivity and wide dynamic range (Miyahara *et al.*, 1986). Moreover, a large IP is easily obtained, which can measure a wide range of diffraction angle. However, a mechanism is necessary to record ‘snapshots’ of time-evolving diffraction patterns at different positions on the IP for application to *in situ* observation.

A unique system has been developed for *in situ* observation of phase transformation at high temperatures using an IP as a detector. This system and its application to the Fe–Zn system are described.

2. *In situ* observation system

2.1. Geometry

In this system, changes in the powder-diffraction pattern from a heated specimen can be measured continuously by scanning an IP located behind a slit (Figs. 1 and 2). The IP is placed on a curved holder, and ‘snapshots’ of Debye–Scherrer rings at a certain time are continuously recorded. The width of the slit and scanning speed of the IP determine the time resolution. A certain position in the IP is exposed to diffracted X-rays through a slit for a certain short time; a narrower width gives a better time resolution. However, when a narrow slit is used, only a limited part of the Debye–Scherrer ring is measured. At high temperatures, rapid crystal growth is often observed, resulting in a non-uniform Debye–Scherrer ring. The lower limit of the slit width should be determined so as not to miss the ring; this can be performed by measuring the whole pattern of the ring without the slit before and after the experiments.

Another factor determining the time resolution is the scanning speed. Once the slit width is determined, the scanning speed can be determined so as to collect enough intensity for analysis. Typical values of slit width and scanning speed are about 3 mm and 0.5 mm s^{-1} , respectively, in the case of *in situ* observation of Fe–Zn described hereafter.

The curvature, r , of the IP holder determines the resolution of the scattering angle 2θ , where the specimen is placed at the centre of a circle with a radius of r (Fig. 1). A larger r gives good resolution, but the recorded intensities become weak because of air

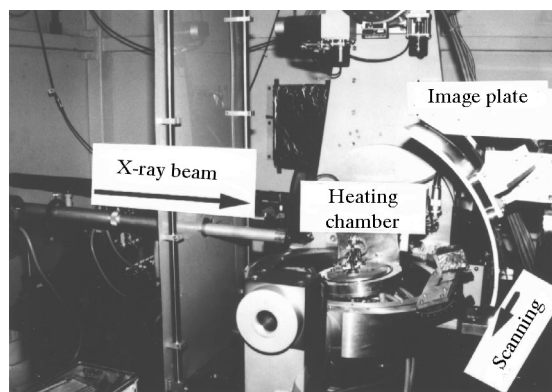


Figure 2 Photograph of the new system.

Table 1

Atomic concentrations of specimens (in wt%).

	P	C	Si	Mn	S	Al	Fe
FE	<0.001	0.0024	<0.001	<0.001	0.0002	0.04	Matrix
FEP	0.09	0.0016	<0.001	<0.001	0.0002	0.04	Matrix

absorption. A typical value in the following application is $r = 310$ mm. When an IP with a size of 400×200 mm is used, the diffraction in the range $\Delta 2\theta = 74^\circ$ can be measured.

For the following application, this system was set up at PF-BL3A (Sasaki *et al.*, 1992) at the Photon Factory, Tsukuba, Japan. The X-ray wavelength, λ , was selected by considering the thickness of the specimen and the necessary resolution of the scattering vector, \mathbf{q} . Typical values are $\lambda = 0.0800$ and 0.1541 nm.

2.2. Heating system

A heating system was designed for a sheet specimen ($\sim 5 \times 6$ mm); it can heat the specimen up to 1100 K at a rate up to 160 K s^{-1} . Both ends of the heater (a Pt strip) are supported by Cu holders, and one of them can slide only in the length direction of the heater. This minimizes the effects of thermal expansion of the heater during heating.

The temperature of the specimen was monitored with a thermocouple attached to the back of the heater. The temperature difference between the specimen and the heater was checked; a reference material the same as that of the specimen was placed on the heater and heated under the same conditions as in the experiments. Another thermocouple was attached to the reference material, and the temperature difference between the reference material and the heater was monitored as a function of the temperature of the heater, giving correction data for experiments. The temperature difference within the specimen was also checked and was found to be less than 5 K at about 800 K.

2.3. Analysis of IP data

Diffacted intensities recorded on an IP were read with a resolution of $100 \times 100 \mu\text{m}$. The x and y directions in the IP correspond to the time evolution and the scattering angle 2θ ,

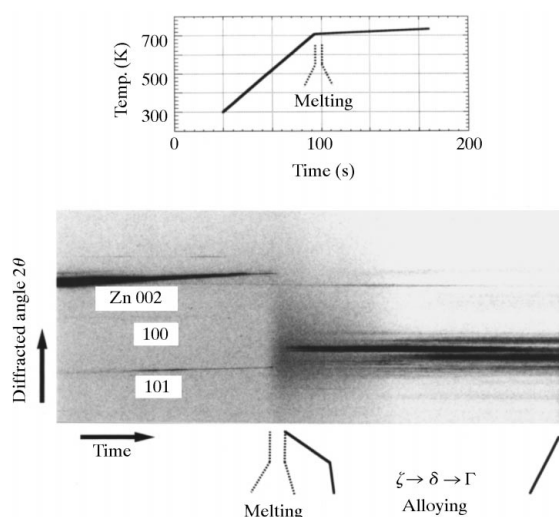


Figure 3 Heating pattern and intensity data recorded in the IP for the specimen FE. Darker areas mean stronger intensity at a point.

respectively. The diffracted pattern for a certain time was obtained by processing IP data; background intensities were subtracted and diffracted intensities were averaged over five pixels in the x direction. Under the geometry described here, resolutions are about 0.02° in 2θ and 6 s in time.

The volume fraction of each phase was determined from the intensity of the diffracted pattern. Because the peaks are convoluted, the peak intensity of the main peak, which is strongest in the case of an ideal powder, was used for calculation. The validity of this procedure was checked by measuring the whole Debye–Scherrer ring before and after each experiment; it is confirmed that a reasonable number of grains are involved in diffraction which is measured through the slit.

3. Application to Zn-coated steel

This system was applied to *in situ* observation of the alloying phenomena of Zn-coated steel. During the galvanizing process, a Zn-coated steel is drawn through a furnace at around 800 K, where the molten zinc layer diffuses into the substrate iron and reacts with it to form several intermetallic Fe–Zn phases. As seen from the Fe–Zn phase diagram (Massalski, 1990), three phases may be formed in the process: ζ , δ and Γ phases in the order of increasing Fe content. The control of this alloying process is one of the keys for high performance of the products, because these phases have different properties, such as ductility. As this reaction occurs in a short period of less than half a minute, *in situ* observation with a time scale of less than 10 s is essential to understand the phenomena; little work has been performed on this (Rizzo *et al.*, 1995; Gomi *et al.*, 1995).

Two kinds of steel were prepared to elucidate the effects of an addition of P into the substrate iron on the alloying process (Table 1). The samples were immersed in a molten Zn (with 0.15 wt% Al) bath and removed after a certain time; the excess Zn was wiped off as they were being removed. Specimens were cut from these sheets of Zn-coated steel.

Fig. 3 shows a heating pattern and the intensity data recorded in the IP for the specimen FE. Specimens were heated to 713 K at a rate of 4.4 K s^{-1} , and to 733 K at a rate of 0.2 K s^{-1} . The time evolution of the diffraction pattern during the alloying process is shown in Fig. 4. The change of relative intensity of the main peak of each phase for the specimens FE and FEP, obtained by processing the IP data, is shown in Fig. 5. The curves in Fig. 5 interpolate points smoothly.

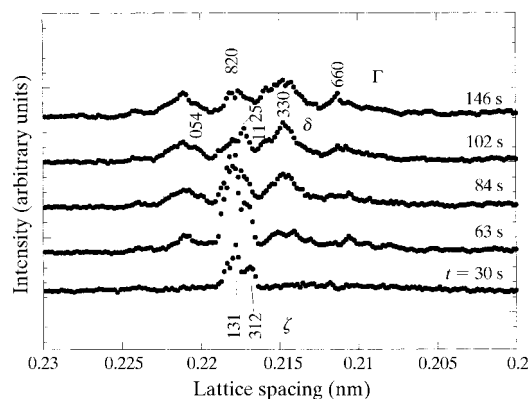
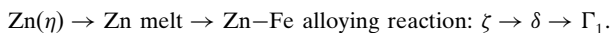


Figure 4 Time evolution of a diffraction pattern during the alloying process.

The moment of melting of the Zn layer is clearly observed in Fig. 3, where there is no clear diffraction observed. The alloying process begins about 5 s after the melting of the Zn layer. The ζ phase was formed first, and the δ and Γ_1 phases followed. The change in volume fraction of the three phases is clearly determined with a time scale of a few seconds. The reaction can be summarized as



This can be understood by interdiffusion between Zn and Fe. The most conspicuous effect of P addition was the delay in formation of the ζ phase. The rate of increase of volume fractions is also suppressed for the δ phase and especially for the Γ_1 phase.

It is suggested that a metastable Fe-Al(-Zn) phase is formed when a steel sheet is dipped into molten Zn containing a small amount of Al (Guttman, 1994). It is considered that this phase disappears before the alloying reaction (*i.e.* the formation of the ζ phase). *In situ* observation has shown that P addition changes this incubation time of the alloying process.

The process of the disappearance of the Fe-Al(-Zn) phase was not clearly observed in these experiments. This may be because the Fe-Al(-Zn) phase exists near the interface between the Zn layer and Fe substrate; further experiments with different conditions, such as thickness of the Zn layer and λ , will provide additional information (Kimura *et al.*, 1997).

4. Conclusions

A new system has been developed for *in situ* observation of phase transformation at high temperatures. It was applied to the observation of the alloying process in Zn-coated steel. The change of volume fraction of the Fe-Zn intermetallic phases is clearly observed with a time scale of a few seconds.

The advantages of this system compared with other *in situ* methods using a scintillation counter or a position-sensitive proportional counter (see, for example, Fujii *et al.*, 1979) are: (i) even a slight change of diffraction pattern can be detected because of its continuous recording, (ii) the effects of preferred orientation are easily checked with the same specimen and

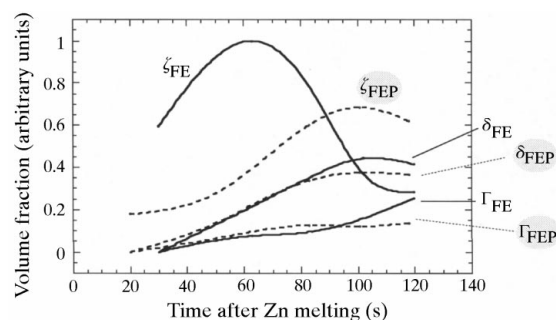


Figure 5
Change of relative intensity of the main peak of each phase for the specimens FE and FEP.

geometry, and (iii) the time and the angle resolutions can be easily varied. Therefore this system has enough potential for application to *in situ* observation of various surface reactions, especially in the cases where grain growth and/or preferred orientation are expected.

References

- Clarke, R., Passos, W. D., Lowe, W., Rodricks, B. G. & Bizard, C. (1991). *Phys. Rev. Lett.* **66**, 317–320.
- Fujii, Y., Shimomura, O., Takemura, K., Hoshino, S. & Minomura, S. (1979). *J. Appl. Cryst.* **13**, 284–289.
- Gomi, S., Fujimura, R., Simomura, J., Kato, C., Mochizuki, K. & Katayama, M. (1995). *Curr. Adv. Mater. Process.* **8**, 1545. (In Japanese.)
- Guttman, M. (1994). *Mater. Sci. Forum.* **155**, 527–548.
- Kimura, M. *et al.* (1997). In preparation.
- Massalski, T. B. (1990). *Binary Alloy Phase Diagrams*, 2nd ed. ASM International.
- Miyahara, J., Takahashi, K., Amemiya, Y., Kamiya, N. & Satow, Y. (1986). *Nucl. Instrum. Methods Phys. Res. A*, **246**, 572–578.
- Rizzo, F., Doyle, S. & Wroblewski, T. (1995). *Nucl. Instrum. Methods Phys. Res. B*, **97**, 479–482.
- Sasaki, S., Mori, T., Mikuni, A., Iwasaki, H., Kawasaki, K., Takagi, Y. & Nose, K. (1992). *Rev. Sci. Instrum.* **63**, 1047–1050.
- Shimomura, O., Takemura, K., Fujihisa, H., Fujii, Y., Ohishi, Y., Kikegawa, T., Amemiya, Y. & Matsushita, T. (1992). *Rev. Sci. Instrum.* **63**, 967–973.