TEMPERATURE DEPENDENCE OF INTENSITIES
on Pt-rich Pt-Mn ALLOYS BY NEUTRON DIFFRACTION

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Abstract: The temperature dependence of intensities on Pt-rich Pt-Mn alloys had been measured by the in-situ neutron diffraction experiments. The diffuse maxima was found at \((\frac{1}{2}\frac{1}{2}\frac{1}{2})\), \((100)\) and their equivalent positions, so called L\(~-) and X\(~-) points of the fcc Brillouin zones, respectively, for Pt\(~-\)12 at. % Mn alloy after being quenched from 800 \(^\circ\)C. No trace of reflection at L-point was found on Pt\(~-\)25, \(~-\)30 and \(~-\)35 at. % Mn alloys, except at X-point, under the same heat treatment. From the measurements of the temperature dependence of intensities, an order-disorder transition had been observed in which two kinds of critical temperatures had been identified as \(T_c\)-low and \(T_c\)-high. The values of \(T_c\)-low and \(T_c\)-high were 665 \(^\circ\)C and 815 \(^\circ\)C for Pt\(~-\)12 at. % Mn specimen. The intensities of both L\(~-) and \(~-\)X reflections decreased as the temperatures increased until the specimen reached disordered state. The decrease of both kinds of intensities is due to Debye-Waller factors.

Keywords: Order-disorder transitions, ABC\(~6\)-type structure, neutron diffraction, Debye temperature factors.

INTRODUCTION

The most familiar effect of temperature vibration is the reduction of the intensities of the crystalline reflections by the well-known Debye temperature factors \(\exp\{-2M\}\). Except for the fact that it gives a method for obtaining the mean square amplitudes of vibration of the atoms \(\langle u_s^2 \rangle\), the reduction in intensities is a nuisance, since it weakens the reflections in which it is desired to measure and we must make adequate corrections for it in crystal structure determinations where quantitative values of the structure factors are necessary. In addition to reducing the intensities of the crystalline reflections, temperature vibrations produce a diffuse intensity. It was first shown by Laval that the frequency spectrum of the elastic waves which constitute the thermal vibrations, could be obtained from quantitative measurements of this temperature diffuse scattering.

For a crystal containing only one kind of atom, the intensities were reduced by a factor \(\exp\{-2M\}\). For the general crystal containing more than one kind of atom, the effect was to replace each \(f_n\) in the structure factor by \(f_n \exp\{-2Mn\}\). The factors \(M_n\) were expressed by

\[M_n = 8\pi^2 \langle u_s^2 \rangle \frac{(\sin^2 \theta)}{\lambda^2}\]

where \(\langle u_s^2 \rangle\) is the mean square components of displacement of atom \(n\) normal to the reflecting planes. For simple structures, values of the factors \(\exp\{-2M\}\) can be obtained directly from the measured integrated intensities, and the corresponding values of the root mean square components of the displacements \(\langle u_s^2 \rangle^{1/2}\) turns out to be of order of 0.2 Å at room temperature. Since the nearest neighbor distance in these simple structures is of the order of 3 Å, the displacements at room temperature are of the order of 5 percent of the nearest neighbor distance.

In the Pt-rich Pt-Mn alloy systems, the author and co-workers had observed a new type of ordered structure, called ABC\(~6\)-type structure, in which there are two kinds of reflections on L- and X-points of the Brillouin zones. Both reflections disappear when the temperature increases at their critical temperatures.

One of the advantages of using neutron diffraction on the present specimens is the enhancement of the intensity of the superlattice reflections due to the negative value of the nuclear scattering amplitude of Mn atoms (\(b_{Mn} = -0.36\times10^{-12}\) and \(b_{Pt} = 0.95\times10^{-12}\) cm) where \(b_{Mn}\) and \(b_{Pt}\) are scattering length for Mn and Pt, respectively. Therefore, based on structure factor the intensity for each point reflection will increases.

This experiment was aimed to investigate the temperature dependence of structural changes in terms of intensity measurement and to determine two-step ordering transition temperatures by examining the evolution of the superlattice intensities on the single crystal specimens. In this experiment the intensities of
both reflections on Pt-12 at. % Mn single crystal were measured using in-situ neutron diffraction methods.

**EXPERIMENTAL PROCEDURE**

A polycrystalline specimen containing Pt-12 at. % Mn were prepared by melting 99.99 % Pt and 99.99 % Mn using an arc-melting furnace in an argon atmosphere. After that these polycrystalline specimens were prepared for single crystalline sample by using the Bridgmen technique.

A high-temperature furnace installed temporarily during neutron diffraction experiment had been employed. This furnace with a 40×40×30 cm³ in size consists of two filament heaters made of MoS₂ with 2 mm in diameter which were placed about 5 cm above and below the sample. This furnace was designed such a way that it keeps the sample from room temperature up to 1500 °C with high temperature homogeneity. During the measurements, specimen was kept in vacuumed silica tube to protect specimen from the air.

The temperature was measured by a pair of thermocouple of iron-constantan placed in contact with the quartz tube contained crystal sample. The heating rate was 5°C per minute. To prevent the experimental set up from over heating, a pipe was placed between furnace and spectrometer table for water circulation. Data collection took about 5 hours to obtain one pattern.

The following are a series of in-situ neutron experimental results taken on the Pt-12 at. % Mn alloys, after being previously annealed at 400°C and slowly cooled into room temperature. The specimen is single crystals with surface normal of <110>, making possible to observe three different reflections, i.e., Bragg, superlattice reflections at X- and L-points.

**RESULTS AND INTERPRETATIONS**

Figs. 1 to 4 show a series of neutron diffraction pattern taken on the <110> scattering plane of Pt-12 at. % Mn alloy at room temperature, 667 °C and 907 °C. In the figure, spectra were normalized with the incident neutron spectrum obtained by incoherent scattering from a vanadium specimen.

The diffraction pattern consists of the Bragg reflections, superstructure reflections at X- and L-points. The intensity distributions were also measured along (h00) and (h 0.5 0.5) directions.

For instance, scanning along (h00) axis, the intensity distributions were measurable consecutively at (100), (200), (300), (400) and (500), for which the mixed \( hkl \) indices are superlattice reflections at X-point and the even \( hkl \) indices are belong to Bragg reflections.
Meanwhile scanning along \((h \ 0.5 \ 0.5)\) direction shows, in sequence, the superlattice peak at \(\left(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}\right)\), Bragg peak at \((311)\), superlattice peak at \(\left(\frac{3}{2} \ \frac{1}{2} \ \frac{1}{2}\right)\) and finally Bragg peak at \((622)\). The superlattice peaks at lower order reflections on both directions are clearly sharp and narrow. But for higher order reflections the widths of the superlattice intensity look broader possibly due to effect of instrumental broadening from the Bragg reflection. Fig. 2 shows diffraction pattern taken at temperature 667 °C after scanning for about 5 hours. Drastic change was taken place at this temperature in which one observes a broad diffuse maxima at \(\left(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}\right)\) (L-point) as presented in diffraction pattern as well as in the intensity peak profile.

On the other hand, the measured intensity shows that the superlattice reflection at X-point still clearly appeared though the intensity decreased by about 50 % compared to one taken at room temperature, see Fig. 1.

By increasing temperature to 907 °C, the superlattice at L-point completely disappeared as shown in diffraction pattern of Fig. 3. A small peak seen along \((h \ 0.5 \ 0.5)\) direction is actually the Bragg \((311)\) rather than the peak at \(\left(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}\right)\) position.

It is shifted from its original position due to the effect of thermal motion during the heating. Superlattice peak intensity at \((100)\) position decreased and broadened in width as shown in Fig. 2 (top). At this temperature, the specimen became in disordered state.

The temperature dependence of the integrated intensities for the superlattice reflections at \((100)\) and \(\left(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}\right)\) are plotted respectively in Fig. 5 and 6. Similar plot for the Bragg reflections at \((200)\) is presented in Fig. 7. The nature of temperature dependence of superlattice peaks is quite similar, being decreased monotonically up to about 550°C then drastically dropped down to a certain temperature, defined as critical temperature, Tc-
low for L-point curve and Tc-high for X-point curve.

Whereas, the Bragg peaks slowly decreased without drastic change as temperature increased. To determine the order-disorder transition temperatures, both curves of Fig. 4 are extrapolated from peaks where the intensities start to decrease down to the zero in intensity. The extrapolated curves are approached zero in intensity at 665°C and 815°C for the superlattice intensity at \( \frac{2}{3} \) and (100), respectively, as shown by arrows.

The temperature dependence of the full-width at half maximum (FWHM) can also be obtained using a resolution convoluted Gaussian fits of the profiles, for the superlattice intensities at \( \frac{2}{3} \) and (100) positions. The tendency of these curves also show similar in nature without a significant change in FWHM’s values below 600°C and 700°C for superlattice at L- and X-points, respectively. Above these temperatures both curves increase drastically due to the effect of thermal diffuse scattering.

In contrast to the value of FWHM for superlattice reflections, in fact as temperature increase, no significant changes are shown for the Bragg reflections at (200) positions as shown in Fig. 7. At room temperature the widths of both peak intensities are quit broad due to the experimental broadening. In this experiment, monochromator or energy analyzer was not used for the TOF method with white neutron beam, so that the observed intensities include both elastic and inelastic components.

Variations of temperature dependence of peak positions are presented in Fig.6. for superstructure reflection at \( \frac{1}{2} \), and Fig. 7 for fundamental reflection at (200) and Generally speaking, all peaks slightly shifted from their original positions at a given temperature, due to thermal motion of atoms. The intensity ratio between superlattice reflections at L-and X-points is about 0.275. Similar procedure was employed on Pt-14 at. % Mn specimen as previous experiment on Pt-12 at. % Mn. This specimen shows more spots consisting of the Bragg and superstructure reflections on X- and L-points compared to Pt-12 at. % Mn alloy. The intensity ratio between superlattice reflections L-and X-points whose value is directly proportional to the degree of order, is about 0.675 at room temperature, being greater that that for Pt-12 at. % Mn alloy.

From these experiment, we have seen clearly that a double transition took place at different temperature on both specimens. The nature of reduced intensity can be explained physically by following a general approach on binary alloy systems as follows. Due to the increase of temperature, the atoms vibrate with larger amplitudes. This affects the intensity of diffuse reflection in two opposite ways. One of them is that the increased atomic vibration diminishes the structure amplitude of reflecting plane owing to the lessening of its truly planar character.

The diminution will be much more important for the higher orders of reflections, since the phase difference introduced by any displacement from the plane is proportional to the order. This qualitative description is in agreement with the present in-situ experimental results. The effect of thermal vibration was first explained by Debye and Waller which is known as the Debye–Waller factor, B, can be expressed mathematically as 

\[
I(T) = I_0 \exp(-2M) 
\]

\[
2M = 2B \frac{\sin^2 \theta}{\lambda^2} \quad \text{and} \quad B = 8\pi <u^2> 
\]

where \(<u^2>\) is the mean fluctuation of atoms.

Similar results of the temperature dependence of intensities have been reported by many workers on various crystalline alloys.

**CONCLUSION**

Based on the experimental results using in-situ neutron diffraction method, it can be drawn some conclusions as following:

a. The intensities of both superstructures on L- and X-points are dependent on increasing temperatures. The higher temperature the weaker the intensities.

b. The critical temperatures for both reflections were identified as Tc-low and Tc-high whose values are 665°C and 815°C, respectively for Pt-12 at. % Mn specimen.

c. Intensities for specimen with higher Mn concentration (Pt-14 at. % Mn) are higher than that with lower Mn concentration (Pt-12 at. % Mn).

**REFERENCES**


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