# The Structure of Molten Nickel-Phosphorus Alloys

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Detailed analyses of the x-ray scattering intensities of molten nickel-phosphorus alloys ranging from 0 to 30 at.% phosphorus have been carried out. The three partial structures required to characterize the binary alloys have been estimated. The interatomic distance of P—P pairs was found to be about 3.2 Å, and thus phosphorus atoms cannot exist as nearest neighbours in molten Ni—P alloys, at least within the present experimental composition range. It was confirmed that this arrangement of atoms contributed to the characterisic structure in which the expansion of the Ni—Ni distance was unavoidable. Calculations have also been carried out in terms of the dense random-packing model of binary spheres. The calculations were consistent with the experimental results.

## I. Introduction

Information on the structure of molten transition metal-metalloid systems, such as Ni — P alloys, is limited. From both fundamental and metallurgical points of view, knowledge of the structure of these systems is of interest. For example, the justification of the interstitial model [1–3] as the basis for the calculation of the activity coefficients of these systems has not been confirmed by diffraction experiments.

The main purpose of this paper is to provide information about the structure of molten Ni — P alloys obtained by means of a high temperature x-ray diffraction technique.

## II. Experimental

The experimental arrangements, operating procedures for the x-ray intensity measurements of high temperature melts, correction of the observed intensity data and their analysis were almost identical to those described in detail in the previous studies on liquid transition metals and alloys [4, 5]. For this reason, only the modifications required for the present work are described.

The purity of the materials used were 99.92% Ni and 99.99% P. A master alloy containing 34 at.% P, as determined by chemical analysis, was used to prepare alloys of lower phosphorus compositions. The required sample was placed in the high temperature x-ray cell and melted to the desired temperature within ± 5 deg. under a purified argon gas of 3 atmospheres pressure. Before and after each run, the composition of the sample was determined by chemical analysis. If the phosphorus content differed by more than 2 at.%, the measurements were repeated. The values of the composition shown in this paper are those evaluated for the samples after the x-ray measurements.

All x-ray data were obtained using a goniometer with a stationary horizontal sample. Mo, Cu and Co radiations were used applying the step scan mode operation. Fe and Cr radiations were also used to determine the intensity patterns. This type of analysis of using several radiations has been described in detail earlier for some binary disordered systems such as liquid Fe — Si [6] and amorphous Ni — P alloys [7]. The generalized Krogh-Moe-Norman's method was used to convert the observed intensity into electron units with the atomic scattering factors calculated by Cromer and Waber [8].

## III. Analysis of Intensity Patterns

The analysis of the measured x-ray intensity was made in the same manner as that described previously [5, 9]. The essential features of this procedure are based on the following principles:

The total structure factor $S(Q)$, in terms of the experimentally obtained coherent x-ray scattering intensity $I_{\mathrm{eu}}^{\mathrm{coh}}(Q)$ can be expressed by

$$S(Q) = [I_{\mathrm{eu}}^{\mathrm{coh}}(Q) - (\langle f^2 \rangle - \langle f \rangle^2)]/\langle f \rangle^2 \tag{1}$$

$$= w_{ii}\,S_{ii}(Q) + w_{jj}\,S_{jj}(Q) + 2\,w_{ij}\,S_{ij}(Q) \tag{2}$$

were $\langle f^2 \rangle = \Sigma\, c_i\, f_i^2$, $\langle f \rangle = \Sigma\, c_i\, f_i$, $w_{ij} = c_i\, c_j\, f_i\, f_j / \langle f \rangle^2$, $Q = 4\,\pi \sin\Theta/\lambda$ and $c_i$ and $f_i$ are the atomic concentration and the atomic scattering factor of $i$-kind of atoms, respectively. The partial structure factor $S_{ij}(Q)$ is defined by the generalized equation:

$$S_{ij}(Q) = 1 + (4\,\pi\,\varrho_0/Q) \int_0^\infty r[g_{ij}(r) - 1]\,\sin(Q \cdot r)\,\mathrm{d}r \tag{3}$$

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where the partial pair distribution function $g_{ij}(r)$ is the average distribution of type $j$ atoms at a radial distance $r$ from atom $i$ at the origin and $\varrho_0$ is the average number density of atoms. It is well known that when the anomalous scattering of x-rays occurs the total scattering factor of Eq. (1) becomes complex in the following form:

$$f_i = f_i^0 + \Delta f_i' + i\,\Delta f_i'',\quad f_j = f_j^0 + \Delta f_j' + i\,\Delta f_j'' \tag{4}$$

where $f_i^0$ and $f_j^0$ correspond to the atomic scattering factor for radiation with a frequency much higher than the absorption edge. $\Delta f'$ and $\Delta f''$ are the real and imaginary components of the anomalous dispersion term. Using this relation, the Laue monotonic scattering term, $(\langle f^2\rangle - \langle f\rangle^2)$, and the weighting factor $w_{ij}$ in Eqs. (1) and (2) may be written as follows:

$$(\langle f^2\rangle - \langle f\rangle^2) = c_i(1-c_i)\,f_i^*\,f_i + c_j(1-c_j)\,f_j^*\,f_j - 2\,c_i\,c_j\,[\,(f_i^0+\Delta f_i')\,(f_j^0+\Delta f_j') + \Delta f_i''\,\Delta f_j''\,]\,, \tag{5}$$

$$w_{ii} = c_i^2\,f_i^*\,f_i/\langle f\rangle^2 \quad\text{and}\quad w_{jj} = c_j^2\,f_j^*\,f_j/\langle f\rangle^2\,, \tag{6}$$

$$w_{ij} = c_i\,c_j\,[\,(f_i^0+\Delta f_i')\,(f_j^0+\Delta f_j') + \Delta f_i''\,\Delta f_j''\,]/\langle f\rangle^2\,. \tag{7}$$

The anomalous dispersion terms $\Delta f'$ and $\Delta f''$ are dependent on the wavelength of the incident radiation. Consequently, measurements made with several radiations give additional items of the structural information of the binary alloys which lead to a separation of the partial structure factors. The anomalous dispersion terms used in this study were the values calculated by Cromer [10].

## IV. Results and Discussion

### 1. Errors

The accumulated counts, varying from $1\times10^5$ at low angles to $3\times10^5$ at high angles, were chosen in this work in order to keep the counting statistics approximately uniform. The errors in the measurements also depend on the experimental difficulties associated when dealing with temperatures in excess of 1000 °C. In addition, a source of systematic error in x-ray diffraction arises from the procedure in normalizing the measured intensity. For this reason, an independent check was carried out according to the method proposed by Rahman [11]. This method has been used frequently [5, 12]. Applying Rahman's method to the present study, the error in the normalization performed to obtain the total structure factor $S(Q)$ is less than 1.0%. Another source of systematic error in x-ray diffraction is the uncertainty of the atomic scattering factor and the Compton scattering intensity. On the basis of the detailed discussion by Greenfield, Wellendorf and Wiser [12], the maximum error in the value of these scattering factors does not exceed 1.0%. Thus, the total error in the structure factor is estimated to be less than 2.0%. The problems associated with the estimation of the partial structure factors $S_{ij}(Q)$, such as the reliability of the numerical solution of Eq. (2), have already been discussed [5, 13]. By using these results, the error bars in the partial structure factors are of the order of ±0.2 for the first peak and ±0.1 beyond the second peak. As the computation errors have been reduced to a minimum, the uncertainty in the value of the partial pair distribution function $g_{ij}(r)$ estimated using Eq. (3) is expected to be similar to that of the partial structure factor.

### 2. Atomic Distributions in Molten Ni – P Alloys

Figure 1 shows the total structure factor using Mo radiation for molten Ni – P alloys at temperatures about 50 °C above the liquidus. The position of the first peak gradually decreases with the addition of phosphorus from 3.10 Å$^{-1}$ for pure Ni to 2.96 Å$^{-1}$ for a Ni – 20.2 at.% P alloy. Further addition of phosphorus, beyond 20.2 at.%, does not change the position of the first peak, as shown in Fig. 1 for Ni – 25.1 and 30.2 at.% alloys. The general form of the total structure factor for molten Ni – P alloys is relatively insensitive to the phosphorus composition because of the larger scattering power of the nickel atoms in these alloys. However, it was found that the total structure factor beyond a phosphorus concentration of 14.7 at.%, toward the phosphorus rich side, is asymmetric. That is, the low angle side of the first peak near the region of about 2.1 Å$^{-1}$ is less steep than that of the high angle side. This behaviour was also confirmed on using Cu and Co radiations. In this analysis, the spectrum of the scattered intensity from the primary beam in the low angle region ($Q$ 2.5 < Å$^{-1}$), the corrections for air scattering and absorption, and the elimination of the Laue monotonic scattering [see Eq. (5)] were carefully taken into account. Thus, the observed asymmetry of the first peak must be related to the characteristic structure of molten Ni – P alloys.

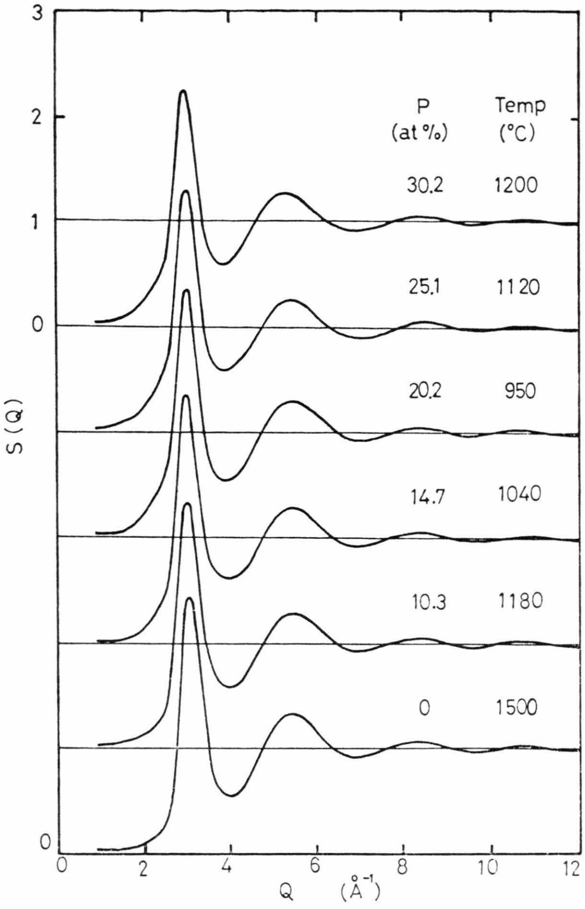

Fig. 1. Total structure factor for molten Ni-P alloys obtained with Mo-K$_\alpha$.

Figure 2 A shows the partial structure factors $S_{ij}(Q)$ evaluated from the measured intensity data of liquid Ni – 25.1 at.% P alloy using three types of radiation, namely Mo, Cu and Co. The general form of the curve is similar to that of other molten metals and alloys, i. e., the structure factor is characterized by the presence of the usual principal peaks followed by small oscillations about unity. The estimated values represented by solid dots, crosses and circles are scattered due to the experimental uncertainty, as previously discussed[5].

A similar analysis of the measured intensity data of molten Ni – 14.7, 20.2 and 30.2 at.% P alloys were also carried out using the same procedure. In all cases, the resultant three partial structure factors were similar to those of the molten Ni – 25.1 at.% P alloy. In order to demonstrate the effect of alloy concentration on the partial structure factors, all the values for the three partials derived from the data of these molten Ni – P alloys are displayed in Figure 2 B. The vertical lines in this figure correspond to the differences due to both alloy concentration and to the experimental uncertainty. They are of the order of ±0.2, so that in molten Ni – P alloys the partial structure factors are not critically dependent on alloy concentration, at least within the present experimental composition range.

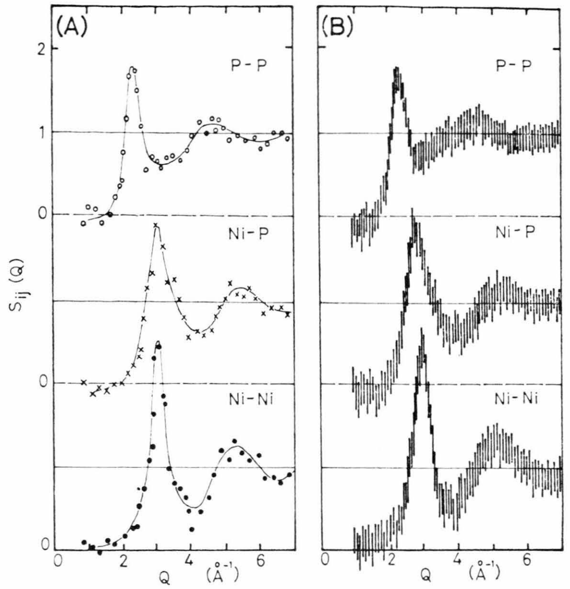

Fig. 2. Partial structure factor for molten Ni-P alloys; (A) Ni—25.1 at.% P alloy, (B) Ni—14.7, 22.2, 25.1 and 30.2 at.% P alloys.

The evaluation of the partial pair distribution functions $g_{ij}(r)$ was carried out by using Eq. (3), along with the measured density[14]. For this purpose, the profile of $S_{ij}(Q)$ was assumed to be a smooth function; thus, the average value of the respective partial structure factor was used. The calculated partial pair distribution functions for the molten Ni – 25.1 at.% P are shown in Figure 3. In order to demonstrate the changes in $g_{ij}(r)$ derived from the different curve fitting of $S_{ij}(Q)$, the functions $g_{ij}(r)$ were calculated from several smooth curves of $S_{ij}(Q)$. As an example, for $g_{\mathrm{Ni-Ni}}(r)$ the results of the different calculation are also shown in Figure 3. This result implies that the distribution function does not critically depend on the procedure of the curve fitting of $S_{ij}(Q)$.

On the other hand, the analysis of the x-ray anomalous scattering is restricted to about $Q_{\max} =$

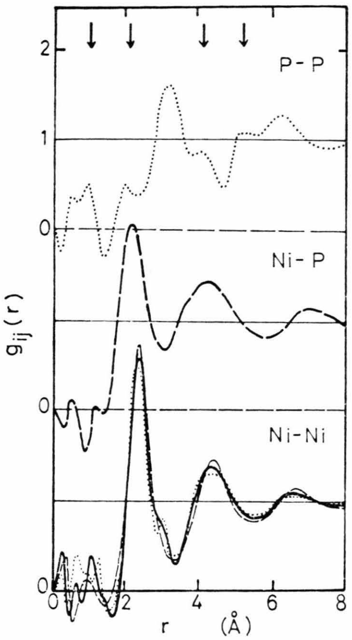

Fig. 3. Partial pair distribution functions of molten Ni—25.1 at.% P alloy.

7.0 Å$^{-1}$. Consequently, the spurious ripples in $g_{ij}(r)$ due to the finite termination of the Fourier transformation of Eq. (3) frequently appear. However, it is relatively easy to trace the position where the spurious ripples occur significantly. This trace is important in the case of the P – P pairs. According to the methods proposed by Finbak [15], Sugawara [16] and Furukawa [17], some spurious ripples appear at positions of $\Delta r \cong \pm 5\pi/2\,Q_{\max}$ and $\cong 9\pi/2\,Q_{\max}$ from the principal peak position, where $Q_{\max}$ is the upper limit of the experimentally observed $Q$. The arrows in Fig. 3 indicate the expected positions of these spurious ripples derived from the relation $\Delta r = \pm 5\pi/2\,Q_{\max}$. The peak found at 0.5 Å also corresponds to one of the positions derived from the relation $\Delta r = \pm 9\pi/2\,Q_{\max}$. On the basis of this trace, the peaks at about 0.5, 1, 2, 4 and 5 Å found in the partial pair distribution function of the P – P pairs possibly correspond to the spurious ripples; thus, the first peak of the P – P pair distribution function at 3.2 Å is significant. This value is larger than the predicted value (2.20 Å) from the size factor of P atoms, and thus it appears unlikely for phosphorus atoms to occupy positions of nearest neighbours in molten Ni – P alloys within the present experimental composition range (up to 30 at.% P).

In Table I, the correlations of the near neighbour distances derived from the partial pair distribution functions are listed. These correlations were obtained by using the same approach as that of Sadoc and Dixmier [18]. The present results imply that the near neighbour region in molten Ni – P alloys is very close to that of the $Ni_3P$ structure [19], but it should be kept in mind that molten Ni – P alloys are not composed of small $Ni_3P$ crystallites. If species having such definite bonds and angles exist, a correlation between the experiments and calculations should also exist in a similar manner, as found in molten $CS_2$ and $CSe_2$ [20], but such correlation has not been confirmed in molten Ni – P alloys. These experimental results suggest that the fundamental configuration of atoms in the near neighbour distance in molten Ni – P alloys is similar to that of $Ni_3P$ (see Table I), but the atomic configuration in molten Ni – P alloys mainly depends on a disordered distribution of Ni atoms, like that in the dense random packing model proposed by Bernal [21] based on tetrahedral units. This is consistent with the fact that short-range order in close-packed structures such as liquids and metallic glasses are also composed of tetrahedrons.

From the size factor of Ni and P atoms (Ni: 2.52 Å, P: 2.20 Å) it can be predicted that the expansion of the Ni – Ni distance is unavoidable in configurations of the above type. This inference

Table I. Comparison between the correlation of near-neighbour distance in molten Ni—25.1 at.% P alloy and crystalline $Ni_3P$.

| | Origin atom | r (Å) | Ni<br>n (atoms) | P<br>r (Å) | n (atoms) |
|---|---|---|---|---|---|
| Molten Ni—25.1 at.% P alloy | Ni | 2.60 | 10.6 | 2.33 | 2.6 |
| | P | 2.33 | 8.1 | 3.20 | 3.4 |
| Crystalline $Ni_3P$ * | Ni | 2.68 | 10 | 2.28 | 3 |
| | P | 2.28 | 9 | 3.44 | 4 |

* Rundqvist et al. [1962] [19].

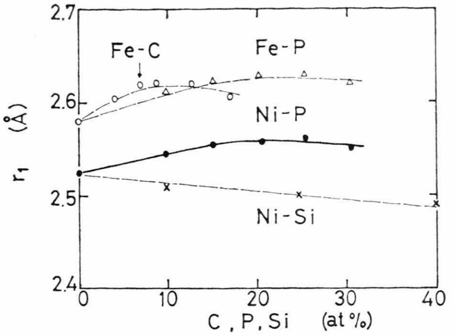

Fig. 4. Concentration dependence of the metal-metal distance in molten transition metal-metalloid alloys; Fe-C[4, 22]; Fe-P[23]; Ni-Si[5]; and Ni-P: present work.

is supported by the results given in Figure 4. A similar behaviour was also found in molten Fe – C alloys[4, 22] and Fe – P alloys[23]. In molten alloy systems, where the difference in size factor of the constituent elements is larger than approximately 15%, an increase in the liquid volume on melting appears to contribute to the formation of these atomic configurations. Such configurations cannot exist in the normal solid state for alloys of this system. In contrast to the Ni – P, Fe – P and Fe – C systems, the molten Ni – Si alloys[5] do not exhibit such expansion. The size factor difference of the constituent elements in this system is only 7%.

It is of interest to note that the atomic distributions in molten Ni – P alloys within the near neighbour regions, where expansion of the Ni – Ni distance results, are quite similar to the interstitial model for crystals. The present results thus support the application of the interstitial model for the estimation of the properties of molten Ni – P alloys, at least within the present experimental composition range. As a first approximation, this is a useful approach; however, there is a need for a more rigorous theoretical treatment[24].

### *3. Calculation Based on the Binary Dense Random Packing Hard Spheres Model*

Recently, structure calculations of disordered systems have shown that the model, based on the dense random packing of hard spheres (DRPHS model), in particular the extended DRPHS model proposed by Ichikawa[25], gives good agreement with the experimental data. For this reason, the binary DRPHS model was applied to the present system to attempt to reproduce the characteristic structure of molten Ni – P alloys.

The method of calculation was almost similar to that previously reported[25–27]. Only a few additional details which are preculiar to the present calculation are given below. The sphere sizes were assumed to be 2.52 Å for Ni atoms and 2.20 Å for P atoms. According to the results of Ichikawa[25], the parameter for the tetrahedral perfection was assumed to be 2.0 and an assembly of 250 spheres was considered from which the tetrahedron of Ni atoms was first constructed. Ni and P atoms were then arranged according to a growth process of tetrahedral clusters. In this process, the probability is proportional to the alloy concentration. In addition, the distance of P – P pairs is larger than 2.67 Å, based on the experimental data obtained in the previous section.

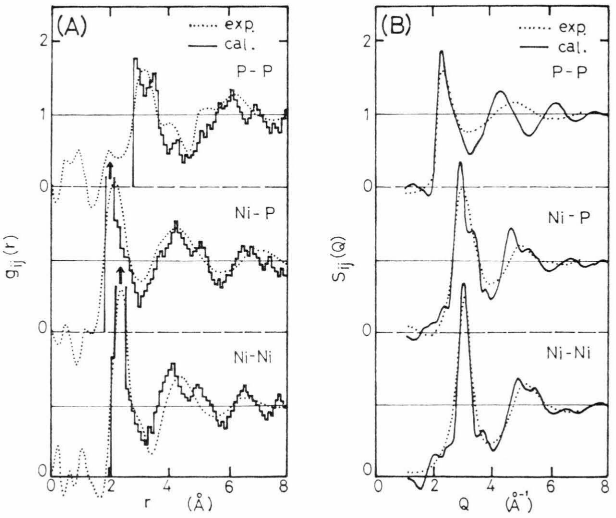

Fig. 5. Partial structural information of molten Ni—25.1 at.% P alloy calculated from the binary DRPHS model.

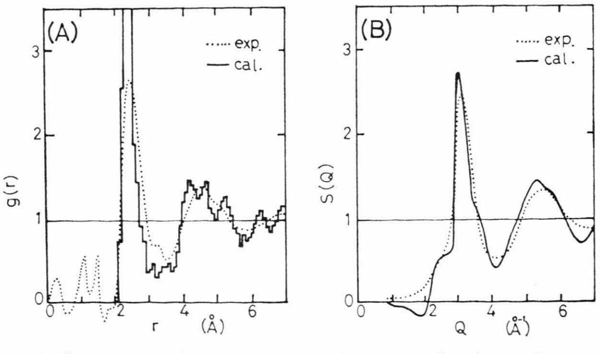

Fig. 6. Comparison between the total structural information calculated from the binary DRPHS model and from the experimental data for molten Ni—25.1 at.% P alloy.

The calculated partial and total structural information on liquid Ni – 25.1 at.% P alloy are compared to the experimental values in Figs. 5 and 6. A coincidence between the calculations and experiments is found in both the partial and total structural information. Consequently, it can be concluded that the model structure qualitatively explains the experimental data. In order to obtain a better agreement between the calculations and experiments, the following factors could be considered in the calculation [26, 28]: the relaxation effect through energy minimization by the assumed pair potential; the softening effect, in which the model distribution function is broadened in a Gaussian way to have approximately the same near-neighbour peak widths as those observed experimentally; and finally, the use of more than two kinds of parameters for the tetrahedral perfection used in the assemblies of spheres so as to better fit the experimental data. In addition, it is desirable that the number of spheres used to construct the model structure be larger than 250 as selected in this work, but the above factors seem somewhat artificial, and the resulting modifications would give only a small quantitative improvement with respect to the original DRPHS model.

The intention of the present work was not the construction of a detailed model structure of molten Ni – P alloys. However, the present calculations suggest that the binary DRPHS model is a satisfactory model which has successfully reproduced the characteristics of the structure of molten Ni – P alloys. Thus, the atomic configurations in molten Ni – P alloys, at least within the present experimental composition range, mainly, depend on disorderly distributed Ni atoms, as described in terms of the DRPHS model based on the tetrahedral units. The P atoms occupy the vacant space in the dense random-packing structure formed by the Ni atoms, which results in the expansion of the Ni – Ni distance.

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