Problems on the Diffraction Study of Liquid Metals†

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Abstract

The effect of melting temperature on the X-ray diffraction profiles in iron and nickel were investigated. The intensity correction for high curvature of the specimens was emphasized. It was shown that it is necessitated to raise temperature 200°C above melting point to disappear solid-like reflection.

Introduction

With the development of technology, the demand for the study of high temperature materials has increased. Studies of physical properties, reactivity and structure are triplet poles in material science.

It has been a long time since Bockris and his coworkers published the brilliant works about physical properties of high temperature melts.[1] However, recently many investigators are trying to pursue physical properties from their own fields.

The studies about reactivity and structure of materials are still inadequate because of the experimental difficulties involved at high temperatures. More work is needed, in the future, concerning studies about structure at temperatures above 1500°C.

In this paper, the issues about high temperature X-ray diffraction studies are briefly discussed.

Experimental Procedures

Diffraction was operated with a spectrometer in which the specimen was horizontal and the source and detector moved in such a way as to hold focusing conditions. A continuous drive was also mounted inside the housing and allowed for selection of speeds 1/32° to 4°/min in 2θ. The standard distance of 185 mm between X-ray target and the centre of diffractometer was used. The specimen was contained in a vessel of 18 X 13 mm inside a housing filled with H_2 or He-10 %H_2 gas.

It was possible to raise the temperature up to 2500°C with the small specimen used. The experimental temperature was measured with Pt-Pt·13 % Rh or W·5 %Re-W·26 %Re thermo-couples or two-colored optical pyrometer. The accuracy of the temperature measurement was within ±10°C. Most of data were obtained with Mo k_α radiation using a curved graphite crystal as monochromator in the diffracted beam. Experimental data were obtained on iron (99.99 %) and nickel (99.95 %) in the temperature range from 1550 to 1750°C.

Experimental apparatus is shown in **Photo. 1.**

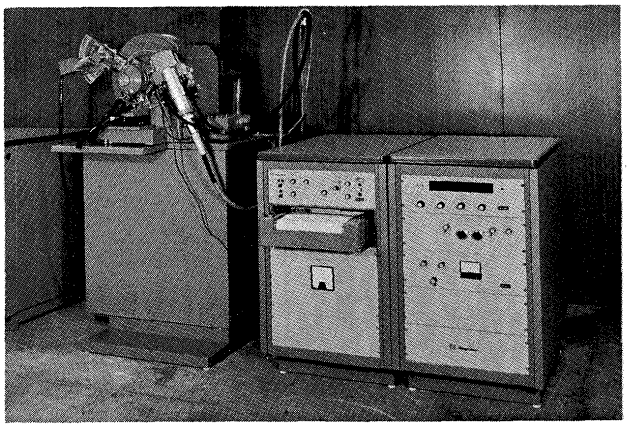

Photo. 1. Experimental apparatus

Experimental Results and Discussions

Figs. 1 and **2** show the intensity curves observed for liquid iron and nickel at various temperatures. The results obtained were as follows:

1) It was verified that the absorption correction for their curvature was necessary in order to proceed with further accurate analysis. Especially, the curvature of liquid nickel was found to be extraordinarily high.
2) It was shown that solid-like reflection did not disappear without raising the temperature about 200°C above the melting point.

   An abrupt change of surface tension was observed in a certain range.
3) Both solid iron and nickel showed the unexpected diffraction peak besides the original reflection induced from α or γ structure.
4) It was difficult to accept the previous statement

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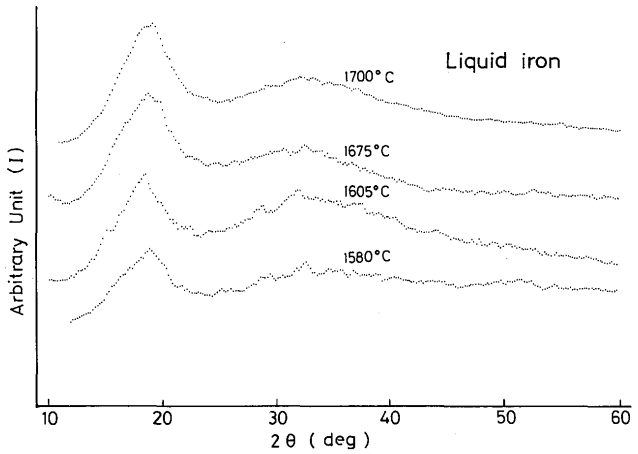

Fig. 1. X-ray diffraction pattern of liquid iron.

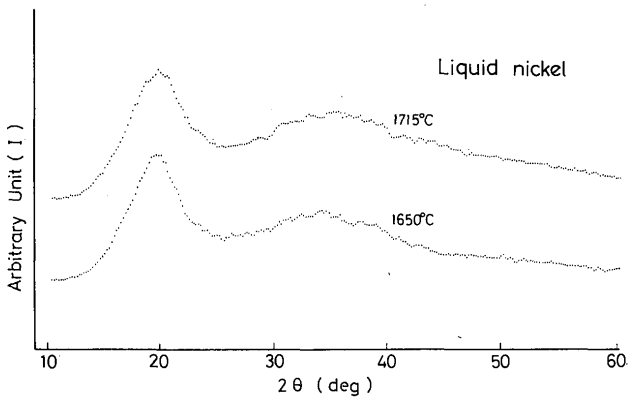

Fig. 2. X-ray diffraction pattern of liquid nickel.

obtained by low melting metals, i. e. the higher the melting temperature, the lower and the broader the first diffraction peak became and the diffraction peak shift appeared.

Although there are a few works[2),3)] concerning the structure of liquid iron by X-ray diffraction, the experimental details are not clear and many questionable points exist. Furthermore, the variation of the experimental results with the temperature has been uncleared. Ruppersbeng and Seemann[3)] have reported that reasonable results were obtained when a vessel having a size of 15 × 10 mm and containing a little CaO was used.

According to the present results, it was difficult to obtain reasonable results even when the vessel of 18 × 13 mm was used and the impurity effect was kept in mind. Even if the impurities have a lower atomic scattering factor which do not contribute to X-ray reflection, they would have an important influence on the subsequent result, since the surface tension of the specimen is impurity sensitive. To clarify this effect, the distribution of impurities from the vessel used (high grade Al_2O_3) were investigated by means of an Ion Micro-Analyzer (Hitachi Co. Ltd). Two examples are shown in **Figs. 3** and **4.** Although the absolute value

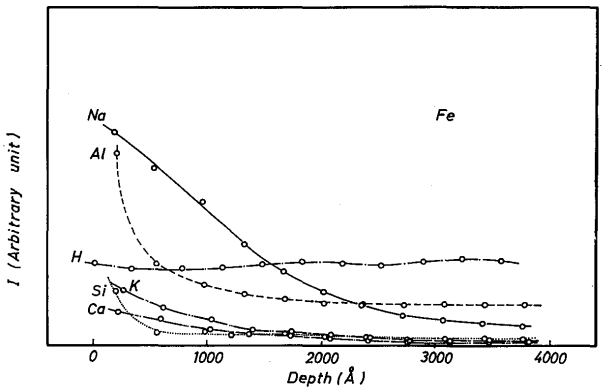

Fig. 3. Impurities distribution in iron solidified.

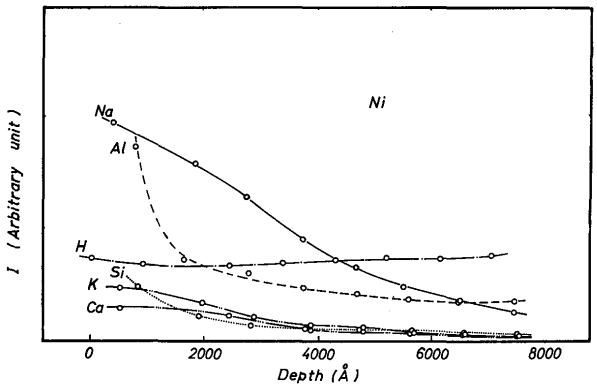

Fig. 4. Impurities distribution in nickel solidified.

are now in experiment, the solution of hydrogen and solution of calcium were found to be remarkable as shown in **Figs. 3** and **4.**

Especially, the distributions of hydrogen and Aluminum being close to surface of the specimens were investigated in detail. These results are shown in **Figs. 5** and **6.** It will be seen that the concentration of hydrogen near surface about 10 Å is remarkable in opposition to aluminum.

It should be considered the effect of the efficiency of secondary emission of nickel.

It was necessary to do X-ray diffraction study in the solid region because, with this information about transition between the solid and the liquid phase, it was possible to get the linear lattice parameter was measured and compared with the result by Basinski, Hume-Rothery and Sutton.[4)] The result is shown in **Fig. 7.** The temperature distribution in the specimen should be considered in the study at high temperatures.

Summary

It was shown how the diffraction pattern of liquid iron and nickel could be changed with the variation of temperature.

It was verified that the absorption correction of X-ray intensity was necessitated because they showed

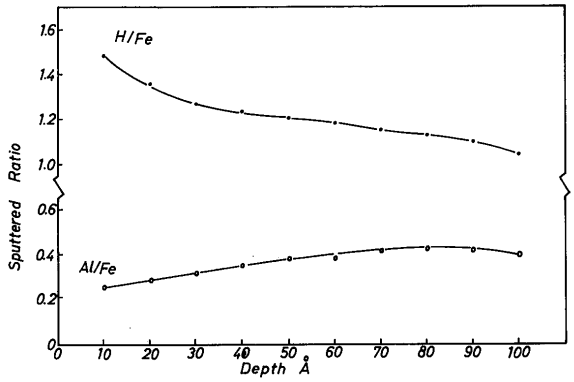

Fig. 5. Existing condition near surface of hydrogen and aluminum ion in iron.

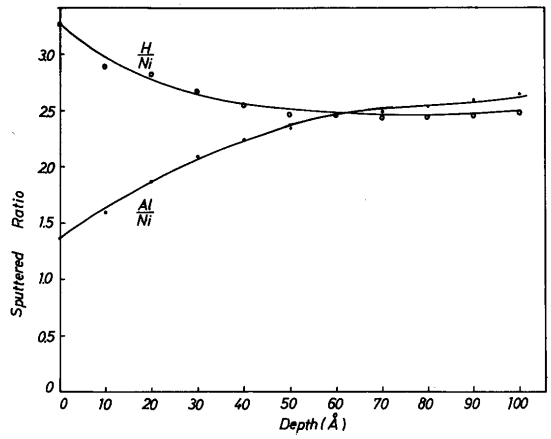

Fig. 6. Existing condition near surface of hydrogen and aluminum ion in nickel.

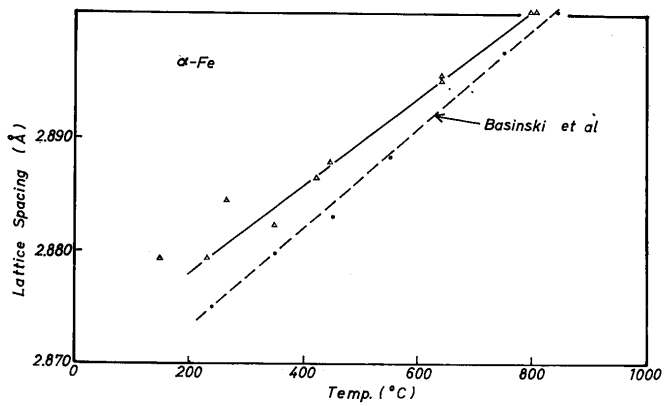

Fig. 7. Lattice parameter change of iron.

a high curvature. Furthermore, the impurity distribution in specimens was studied because it has great influence on the surface tension. As one merit, result of high temperature X-ray studies, we can get the thermal linear expansion coefficient of various substances. For example, the variation of lattice parameter of iron was studied and compared with the result by Basinski and et al.[4]

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References

1) J. O'M. Bockris: "Physical Chemistry of Melts" *Inst. Min. Met.*, London (1953).
2) **Е. З. Спектор: Докл. Акад. Наук.** CCCP, **190** (1970), p. 1322.
3) H. Ruppersberg and H. J. Seemann: *Z. Naturfor.*, **21a** (1966), p. 320.
4) Z. S. Basinski, W. Hume-Rothery and A. L. Sutton: *Proc. Roy. Soc.*, **A229** (1955), p. 459.