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Letter

Determination of the solid solubility of cerium in α-Fe by the positron annihilation technique

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Abstract

The line shape parameters S of a series of Fe–Ce alloys of different composition at 700 °C were measured at room temperature by the Doppler broadening method using the positron annihilation technique. The solid solubility of cerium in α-Fe at 700 °C was found to be 0.082 wt.%. The same result was obtained using electron probe microanalysis.

1. Introduction

It is well known that the metallurgical properties of steel can be changed by the addition of rare earths. The alloying and solid solubility of rare earths in steel have been investigated for some time. It is useful to determine the solid solubility of rare earths in iron accurately in order to study the function of rare earths in steel.

Although the atomic radii of rare earths are much larger than that of iron, they can still be partially dissolved in iron. Many workers have used various methods to study the solid solubility of cerium in iron, such as the metallographic method [1], the X-ray method [2] and the electric resistance technique. However, the results obtained are different [1–3]. The solid solubility is so small that it can only be determined by a sensitive experimental technique. The metallographic and X-ray methods cannot demonstrate the appearance of a new phase because it is required that the particle size of the new phase should be larger than 0.1 μm and the amount of new phase correspondingly larger. The accuracy of the electric resistance method is limited because of the strict demand of sample size. Electron microprobe analysis is thought to be an accurate method [2].

The positron annihilation technique is a new and sensitive measurement method [4]. The annihilation process occurs after a positron meets an electron, and a signal is emitted which contains information about the electronic structure. In this paper, the solid solubility of cerium in α-Fe is determined by the Doppler broadening method using the positron annihilation technique.

2. Methods

The purity of the iron used was 99.98%, containing 0.0005% sulphur and 0.02% oxygen. Dry hydrogen, which was filtered through a molecular sieve, was used in the deoxidation of the sample at 850 °C for 80 h. After this process, the oxygen content had decreased to 0.0004%. The purity of the rare earth cerium was 99.9%. The impurities were removed by refining twice in a vacuum furnace. The iron and cerium were then smelted in a tungsten arc furnace with magnetic control to prepare a series of samples with different compositions. After heating at 700 °C for 720 h the samples were quenched. In order to remove the vacancies caused by quenching, the samples were furnace cooled after heating at 200 °C for 1 h. After the heat treatment, the chemical composition of each sample was measured and these are given in Table 1. Two specimens (thickness, 1 mm; area, 2 cm^2) were cut from each sample.

The apparent energy distribution of the photons was measured by the Doppler broadening method using

TABLE 1. Ce content of the specimens

Sample No.	Ce content (wt.%)
1	0.000
2	0.010
3	0.019
4	0.029
5	0.057
6	0.076
7	0.095
8	0.114
9	0.143
10	0.286
11	0.477
12	0.953

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positron annihilation radiation. The information on the electronic structure was studied by measuring the line shape parameter S, which is defined as the ratio C/A, where C is the area under the central channels and A is the total area under the curve.

All samples were electrolytically polished using an electrolyte ($HClO_4$–alcohol–glycerine, 2:7:1) before the positron annihilation measurements. The measurements were made using a high-purity germanium detector with a resolution (full width at half maximum (FWHM)) of less than 1.3 keV at 514 keV. A positron source of about 3.7×10^5 Bq of ^{22}Na, deposited from an aqueous solution of the chloride onto a Kapton foil, was used in the measurements. The source enclosed by the foil was sandwiched between duplicated specimens. More than 10^6 events were accumulated in the full energy peak in a measurement time of 1 h.

3. Results and discussion

The relationship between the line shape parameter S of the Doppler broadening measurements and the cerium content is shown in Fig. 1. The curve in Fig. 1 is composed of three stages. The points in each stage are almost on a straight line. Three straight line equations for the three stages were obtained using the least-squares method

$$S = -0.0458X_{Ce} + 0.3970 \qquad (X_{Ce} < 0.082\%\ \mathrm{Ce})$$
$$S = 0.0950X_{Ce} + 0.3855 \qquad (0.082\%\ \mathrm{Ce} < X_{Ce} < 0.140\%\ \mathrm{Ce})$$
$$S = 0.0036X_{Ce} + 0.3983 \qquad (X_{Ce} > 0.140\%\mathrm{Ce})$$

where X_{Ce} is the cerium content in weight per cent. From the three equations, the cerium contents of the two turning points of the curve can be obtained as 0.082% and 0.140%.

The existence of rare earth inclusion is not considered in this paper because of the high purity of the samples.

In stage 1 (0–0.082% Ce), the parameter S decreases with an increase in cerium content. A negative charge which can attract positrons is introduced when an iron atom is replaced by a cerium atom in the Fe–Ce alloy, because the ionic valence of cerium is less than that of iron. The electron number of the cerium core is higher than that of iron, so that the positron annihilation rate with electrons in the core increases and the parameter S decreases. The introduction of cerium also causes a reduction in the valence electron density and hence in the parameter S.

In stage 2 (0.082–0.140% Ce), the parameter S increases with increasing cerium content. The second phase starts to appear in the Fe–Ce alloy when the segregation of cerium atoms occurs. This induces many lattice defects, and so the parameter S becomes large.

In stage 3 (more than 0.140% Ce), parameter S varies slowly with the variation in cerium content. In this stage, the second phase increases in volume, the defect density reaches an equilibrium and the parameter S hardly varies.

From these results, it can be concluded that, at low cerium concentrations, the cerium is dissolved in α-Fe. The second phase starts to appear when the cerium content becomes larger than the solid solubility of cerium in α-Fe. Therefore the cerium content (0.082%) relating to one of the turning points of the curve represents the solid solubility limit of cerium in α-Fe at 700 °C.

The solid solubility of cerium in α-Fe can also be determined using the electron microprobe method [2]. The sample with a cerium content of 0.953% was chosen

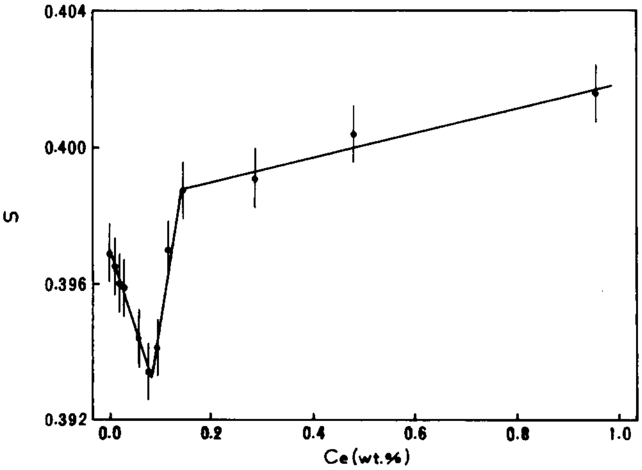

Fig. 1. Line shape parameter S of Doppler broadening *vs.* cerium content for Fe–Ce alloys exposed at 700 °C for 720 h.

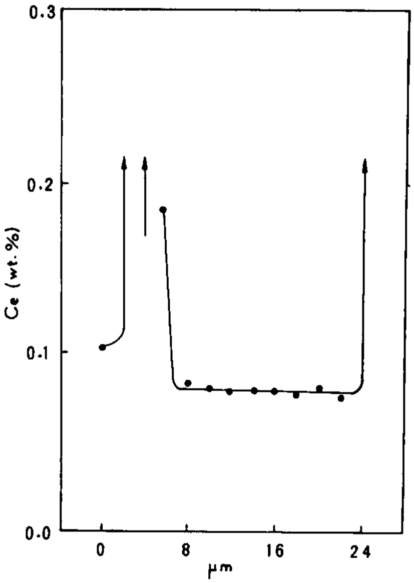

Fig. 2. Distribution of cerium in Fe–0.953 wt.%Ce alloy.

and the scanning line was chosen between two large Ce_2Fe_{17} phases. The distribution of cerium between the two phases is shown in Fig. 2. The solid solubility of cerium was derived from the mean value of all the measurement points in five scanning lines and corresponds to 0.082%. It agrees well with the positron annihilation measurements, and so the result from the positron annihilation technique can be considered to be reliable.

4. Conclusions

The solid solubility of rare earths in α-Fe can be accurately determined with the aid of the positron annihilation method. From our experiments, the solid solubility of cerium in α-Fe at 700 °C is 0.082 wt.%.

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