Metastable fcc Fe-Rh Alloys and the Fe-Rh Phase Diagram*

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Single-phase metastable fcc Fe-Rh alloys have been obtained by rapid quenching from the liquid state over a wider range of compositions than formerly reported. Lattice spacings and Mössbauer spectra of Fe⁵⁷ of these alloys have been measured at room temperature. Both lattice parameters and isomer shifts are found to vary smoothly with rhodium concentration. These experimental findings suggest the existence of a continuous γ field at high temperatures. A tentative phase diagram based on the results of the present investigation is proposed.

I. INTRODUCTION

Among the transition-metal binary alloys, the ironrhodium system is of particular interest due to its unusual magnetic properties. Many previous investigators have contributed to the present understanding of this system. Fallot first reported that the mean magnetic moment increases as rhodium is added to iron and reaches a maximum at approximately 25 at. % Rh. It has also been well established that a first-order low-temperature phase transition from ferromagnetic to antiferromagnetic state occurs in alloys containing between approximately 48 and 52 at. % Rh. ²⁻⁵ This phase transition is accompanied by a 1% volume decrease. 3 An additional interesting feature of the Fe-Rh system is the existence of a fcc γ phase in alloys containing 25 at. % Rh quenched from 1000 °C, 6 in mechanically deformed FeRh 7 and in equilibrium alloys containing 70 and more at. % Rh.

In view of the fact that the system exhibits rather interesting magnetic properties, it is surprising that

the phase diagram of the iron-rhodium system has not been well established. Only portions of this diagram have been worked out by Fallot, ¹ Gibson and Hume-Rothery, ⁸ and de Bergevin and Muldawer. ³ Shirane *et al.* ⁶ proposed a tentative phase diagram which unfortunately does not satisfy Gibb's phase rule near 20 at. % Rh. Furthermore, the diagram does not extend above 1000 °C and therefore it is not clear whether or not the γ field extends from 0 to 100% Rh. Several attempts ⁶, ⁹ to retain the γ phase from high temperatures by quenching were somewhat unsuccessful, and this presumably is the reason why the γ Fe-Rh alloys have not been studied in detail.

In this investigation, it was possible to retain the γ phase from 27.5 to 40 and at 60 at.% Rh by the technique of rapid quenching from the liquid state. The lattice parameter measurements and the Mössbauer studies were also performed.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Alloys were prepared by induction melting of appro-

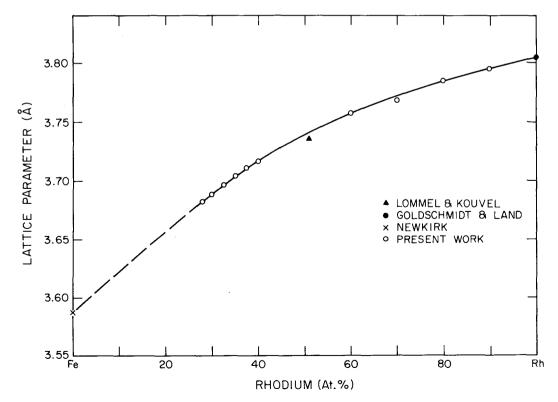


FIG. 1. Lattice parameter of fcc Fe-Rh alloys.

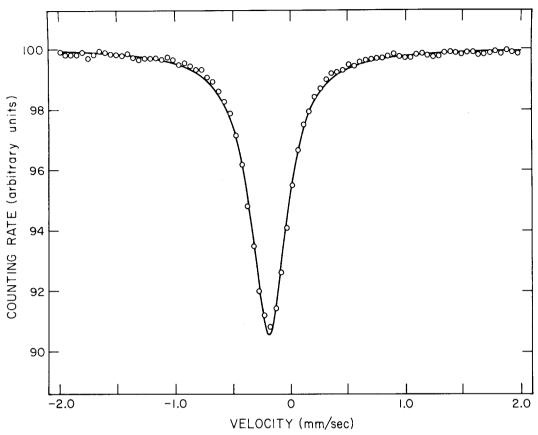


FIG. 2. Room-temperature Mössbauer spectrum of metastable fcc Fe_{62.5}Rh_{37.5} alloy obtained by liquid quenching.

priate quantities of the constituents (99.99%-pure Fe and 99.9%-pure Rh) on a water-cooled silver boat on an argon atmosphere. The weight losses were less than 0.1% and the nominal compositions of the alloys were taken as the actual ones. The single metastable phase was obtained by quenching small amounts (~40 mg) of the alloy from the liquid state. The samples obtained by this technique are foils of irregular dimensions about 10 mm long, 5 mm wide, and 50 μ m thick. Since the rate of quenching is not reproducible, the structure of each foil is checked by taking x-ray diffraction patterns with a diffractometer (nickel-filtered copper $K\alpha$ radiation).

X-ray diffraction patterns were also obtained with cobalt $K\alpha$ radiation in a 114.6-mm-diam Debye-Scherrer camera. The lattice parameters were determined by using the Nelson-Riley extrapolation function. The metastable γ phase was obtained in the concentration range from 27.5 to 40 and in alloys containing more than 60 at. % Rh. The lattice-parameter results are plotted against rhodium concentration in Fig. 1. The average atomic volume is found to be constant in spite of the change in crystal structure.

The Mössbauer spectra were measured at room temperature by using a standard spectrometer in the constant acceleration mode with a 10-mCi source of Co^{57} in Cu. A typical single-peak spectrum is shown in Fig. 2. Figure 3 shows the isomer shifts of the γ

phase corrected relative to Fe, as a function of Rh concentration.

The results of this investigation show that, by rapid quenching from the liquid state, the γ phase can be retained in Fe-Rh alloys, except for compositions from 40 to 60 at. % Rh. A possible reason for the difficulties in retaining the γ phase within this range of compositions is that the limits of the solid-state immiscibility gap in the binary diagram are at relatively high temperatures. Previous investigators have reported that at 50 at. % Rh, the γ field might be stable only above 1450 °C. ³ It is therefore possible

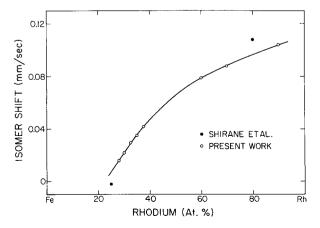


FIG. 3. Isomer shift relative to iron of fcc Fe-Rh alloys.

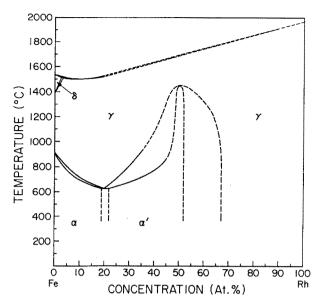


FIG. 4. Tentative Fe-Rh phase diagram.

that, in spite of the high rate of cooling achieved by quenching from the liquid state, the reaction from γ to $\alpha' + \gamma$ still occurs during cooling. If this is so, the results of this investigation do not contradict the tentative diagram shown in Fig. 4, in which the top of the two-phase field around 50 at. % Rh is located at 1450 °C. The fact that the lattice parameters and isomer shifts of the γ phase vs Rh concentration vary very smoothly (see Figs. 1 and 3) seems to conconfirm the existence of a solid-solution field across

the diagram. The Fe-rich side of the suggested diagram shown in Fig. 4 is essentially the same as that reported in Ref. 6, except that a very narrow two-phase region has been added between the single-phase field α and α' . This is based on the assumption that instead of a minimum in the γ field boundaries around 20 at. % Rh, a eutectoid reaction takes place and this leads to a phase diagram which satisfies the phase rule.

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