Effects of the structural state of a W-Re solid solution on the Fe-57 Mössbauer spectrum


Mössbauer spectra for iron-57 are reported for alloys containing up to 27 at. % rhenum. The cobalt-57 was introduced by diffusion annealing as the parent isotope for the iron-57. Diffusion annealing at 1080°C for 16 hr causes the cobalt to diffuse mainly along lattice defects (dislocations and grain boundaries). These defects give rise to regions whose electronic structure differs from that of the matrix. The precise type of structure and the number of such regions are complex functions of the alloy composition and structural state. Results are given on the iron-57 spectra for tungsten, rhenum, the σ phase, and an alloy in the two-phase region.

It has been supposed [1] that the detailed structure of tungsten–rhenum solid solutions differs from completely disordered; we have therefore studied the Mössbauer spectra of Fe-57 in these alloys in different structural states.

The production conditions and basic characteristics for these alloys have been described in detail previously [1], and we use diffusion annealing at 1080°C for 16 hr to diffuse the Co-57 as the parent of the Fe-57. The standard absorber was a foil of austenitic EI-847 steel of thickness 0.02 mm. The Mössbauer spectra were recorded at room temperature with a constant-velocity spectrometer. The figures show the absorption spectra, the intensities are given in arbitrary units, while the error of measurement is shown on the same scale.

We first examine the spectra of Fe-57 in pure tungsten and rhenum and also alloys with 20, 32, and 45 at.% Re, whose compositions corresponded to regions representing solid solutions, the α + σ two-phase region, and the σ phase [2, 3]. The 20 at.% Re alloy was prepared by crucible-free zone melting. It has been found [1] that the fine structure corresponds to a completely disordered solid solution. The 32 at.% Re alloy was made by electron-beam melting in a water-cooled crucible; the x-ray pattern showed two groups of lines: one from a body-centered cubic solid solution and the other from the σ phase. As the state near the phase boundary was of the main interest, specimens of the 32 at.% alloy were annealed at 2200°C for 1 hr and rapidly cooled. Then only the lines from the body-centered solid solution remained. The 45 at.% Re alloy corresponded in structure to the σ phase.

The Fe-57 spectrum of W is a singlet line of Lorentz shape with an isomeric shift \( \delta = -0.27 \pm 0.015 \) mm/sec and a width at half height of \( \Gamma = 0.48 \pm 0.03 \) mm/sec (Fig. 1a). The shape of the Fe-57 spectrum in a rhenum single crystal was not of Lorentz type (Fig. 1b), and it was resolved into such lines by the method of [4] to give two lines shown dotted in Fig. 1b, which had equal widths and isomeric shifts \( \delta_1 = -0.24 \pm 0.015 \) mm/sec, \( \delta_2 = 0 \). The isomeric shift for the center of gravity of the spectrum was \( \delta = -0.12 \pm 0.015 \) mm/sec. The Fe-57 in the 20 at.% Re solid solution gave a Lorentz line whose parameters agreed within the error of measurement with those of Fe-57 in pure W (Fig. 1c). The Fe-57 spectrum for the σ phase of W + 45 at.% Re differed greatly from the spectra recorded with W, Re, and the 20 at.% Re...
Fig. 1. Fe-57 spectra for: a) tungsten; b) rhenium; c) solid solution containing 20 at.% Re; d) the σ phase; e) two-phase alloy containing 32 at.% Re.

Fig. 2. Fe-57 spectra for an alloy containing 1.8 at.% Re: a) in the deformed state; b) in the annealed state.

solid solution (Fig. 1d). Resolution as above revealed three lines with the parameters \( \delta_1 = -0.48 \pm 0.015 \) mm/sec, \( \delta_2 = -0.30 \pm 0.015 \) mm/sec, \( \delta_3 = +0.48 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.48 \pm 0.03 \) mm/sec, \( \Gamma_2 = 0.36 \pm 0.3 \) mm/sec, \( \Gamma_3 = 0.54 \pm 0.03 \) mm/sec. The ratios of the areas of the lines were \( S_1:S_2:S_3 = 4.6:2.3:1 \). The Fe-57 spectrum for 32 at.% Re was similar to that for the σ phase (Fig. 1e); the line parameters were \( \delta_1 = -0.48 \pm 0.015 \) mm/sec, \( \delta_2 = -0.30 \pm 0.015 \) mm/sec, \( \delta_3 = 0.42 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.48 \pm 0.03 \) mm/sec, \( \Gamma_2 = 0.60 \pm 0.03 \) mm/sec, \( \Gamma_3 = 0.60 \pm 0.03 \) mm/sec, while the area ratios were \( S_3:S_1:S_2 = 1.6:0.8:1 \). The Fe-57 shifts for the σ phase and 32 at.% Re alloy showed that the values for the first and second lines are unchanged, whereas \( \delta_3 \) is reduced in the 32 at.% Re alloy, which indicates that the spectrum of Fe-57 in the σ phase consists of three lines arising from differences in electronic structure of atoms that take up nonequivalent positions in the σ-phase lattice.

It is considered [5] that the excess charge is screened in systems with bonds of metallic type at distances of the order of the lattice constant, so the three lines are to be reckoned as anomalous. We therefore conclude that the bonds between the atoms in the σ phase are of nonmetallic type, at least as regards the atoms in the nonequivalent positions.

The Fe-57 spectrum for 1.8 at.% Re alloy in the deformed state differed from Lorentz shape and was due to two lines (Fig. 2a): \( \delta_1 = -0.255 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.48 \pm 0.03 \) mm/sec, \( S_1 = 0.70 \), \( \delta_2 = 0.24 \pm 0.015 \) mm/sec, \( \Gamma_2 = 0.66 \pm 0.03 \) mm/sec, \( S_2 = 0.30 \), where \( S_i \) is the specific area under the corresponding line. The Fe-57 spectrum for the same alloy after annealing differed considerably from the previous (Fig. 2b). The line parameters were \( \delta_1 = -0.60 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.42 \pm 0.03 \) mm/sec, \( S_1 = 0.14 \), \( \delta_2 = -0.27 \pm 0.015 \) mm/sec, \( \Gamma_2 = 0.48 \pm 0.03 \) mm/sec, \( S_2 = 0.59 \), \( \delta_3 = -0.12 \pm 0.015 \) mm/sec, \( \Gamma_3 = 0.42 \pm 0.03 \) mm/sec, \( S_3 = 0.27 \). The Fe-57 parameters for 4.8 at.% Re alloy in the deformed state were the same as those for the annealed state within the errors of measurement, and were as for Fe-57 in pure W, which applies also to an alloy with 6 at.% Re in the deformed state. However, the Fe-57 spectrum in 6 at.% Re alloy in the annealed state again shows a shape different from the Lorentz form, with two lines: \( \delta_1 = -0.30 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.40 \pm 0.03 \) mm/sec, \( S_1 = 0.75 \), \( \delta_2 = -0.12 \pm 0.015 \) mm/sec, \( \Gamma_2 = 0.36 \pm 0.03 \) mm/sec, \( S_2 = 0.25 \).

The Fe-57 lines in 12.5 at.% Re alloy in the deformed state differ considerably from the Lorentz shape (Fig. 3a) representing three lines: \( \delta_1 = -0.465 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.50 \pm 0.03 \) mm/sec, \( S_1 = 0.26 \), \( \delta_2 = -0.27 \pm 0.015 \) mm/sec, \( \Gamma_2 = 0.48 \pm 0.03 \) mm/sec, \( S_2 = 0.57 \), \( \delta_3 = 0.42 \pm 0.015 \) mm/sec, \( \Gamma_3 = 0.42 \pm 0.03 \) mm/sec, \( S_3 = 0.17 \).

In the annealed state, this alloy has a spectrum of the same form (Fig. 3b): \( \delta_1 = -0.48 \pm 0.015 \) mm/sec, \( \Gamma_1 = 0.36 \pm 0.03 \) mm/sec, \( S_1 = 0.11 \), \( \delta_2 = -0.27 \pm 0.015 \) mm/sec, \( \Gamma_2 = 0.48 \pm 0.03 \) mm/sec, \( S_2 = 0.77 \), \( \delta_3 = 0.24 \pm 0.015 \) mm/sec, \( \Gamma_3 = 0.48 \pm 0.03 \) mm/sec, \( S_3 = 0.12 \).