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M. Kato, Y. Ishida, K. Sassa, S. Umeyama, M. Mori. MÖSSBAUER SPECTRUM OF ^{57}Fe AND ^{119}Sn ASSOCIATED WITH LATTICE DEFECTS IN ALUMINIUM. *Journal de Physique Colloques*, 1974, 35 (C6), pp.C6-309-C6-313. 10.1051/jphyscol:1974649 . jpa-00215806

HAL Id: jpa-00215806

<https://hal.science/jpa-00215806>

Submitted on 4 Feb 2008

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MÖSSBAUER SPECTRUM OF ^{57}Fe AND ^{119}Sn ASSOCIATED WITH LATTICE DEFECTS IN ALUMINIUM

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Résumé. — On a étudié par spectroscopie Mössbauer les comportements très variés d'atomes de fer et d'étain dans des alliages d'aluminium trempés ou ayant subi une trempe ultra-rapide (splat-cooling) ou implantés par des ions ou irradiés par des électrons. L'interaction de ^{119}Sn avec des lacunes est prépondérante dans des alliages trempés ou irradiés par les électrons. Dans le cas de ^{57}Fe cette interaction n'existe pas. Au cours du vieillissement ultérieur des alliages, apparaissent des phases métastables variées, riches en soluté. La stabilité de ces phases métastables dans les alliages Al-Fe est remarquable et la phase d'équilibre ne se développe qu'au-dessus de 400 °C.

Abstract. — The contrasting behavior of iron and tin atoms in quenched, splat-cooled, ion-implanted or electron-irradiated aluminium alloys were investigated by Mössbauer spectroscopy. In quenched or electron irradiated alloys the interaction of ^{119}Sn with vacancy was detected. Such an interaction was absent with ^{57}Fe . Upon subsequent aging of the alloys various solute rich metastable phases occurred. The stability of the metastable phases in Al-Fe alloy was remarkable and the equilibrium phase grew only at above 400 °C.

Interaction of ^{57}Fe and ^{119}Sn atoms with various lattice defects in (1) quenched, (2) splat-cooled, (3) ion-implanted and (4) electron-irradiated aluminium alloys were investigated by Mössbauer spectroscopy. Changes in the spectrum upon subsequent aging of the specimen were also examined to understand the kind of lattice defects evolving in the alloys during the aging process and the ways of association of iron and tin atoms with them.

1. Experiments with Al-Fe alloys. — 1.1 QUENCHED ALLOY. — Al-0.008 at % ^{57}Fe alloy foil 350 μ thick was annealed at 620 °C, quenched in alcohol at -90 °C and stored in liquid nitrogen. The Mössbauer spectrum (Fig. 1) was the same as that of fully annealed specimen. It consisted only of the solid solution peak of iron.

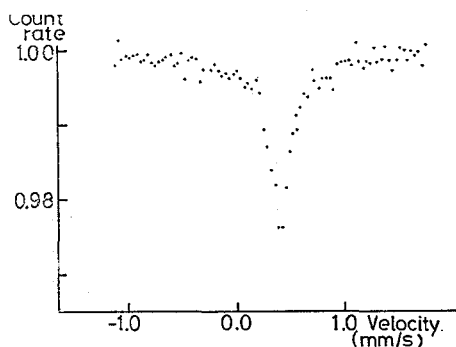


FIG. 1. — Mössbauer spectrum of Al-0.008 at % ^{57}Fe alloy annealed at 620 °C and quenched in alcohol at -90 °C. Source is ^{57}Co in Cu. Both source and absorber at liquid N_2 temperature.

No significant change in the spectrum was found after aging the foil at room temperature for 10 min. All the measurements were performed at liquid nitrogen temperature. A change in the spectrum was reported by Janot and Gibert [1] after aging the brine quenched Al-Fe alloy at above room temperatures. They concluded that the iron atom interacted with secondary defects and not simply with the vacancy since the temperature was higher than the migration temperature of vacancy. The smallness of the binding energy between vacancy and iron atom is also suggested from the present experiments.

1.2 LIQUID QUENCHING. — Al-1 at % Fe and 4 at % Fe alloys were held at about 100 °C above the melting temperature and splat-cooled on copper substrate kept at liquid nitrogen temperature (gun technique). The foil thickness was 10 ~ 30 μ . The Mössbauer spectrum (Fig. 2) were completely different from that of as cast specimen. The latter coincided with that of $\text{Fe}_4\text{Al}_{13}$. Quadrupole spectrum due to FeAl_6 predominated in Al-4 at % Fe alloy while a spectrum of solid solution iron was superimposed in Al-1 at % Fe alloy. Contributions from other phases are evident to the left of these peaks indicating the occurrence of some iron rich phases. Iron rich particles were indeed observed at the cell boundary by transmission electron microscopy (Photo 1a). They are fine particles of ~ 50 Å some in BCC structure with the lattice constant 2.90 Å and the others in FCC structure with the lattice constant 3.63 Å.

The aging behaviour of the foil is shown in figure 3

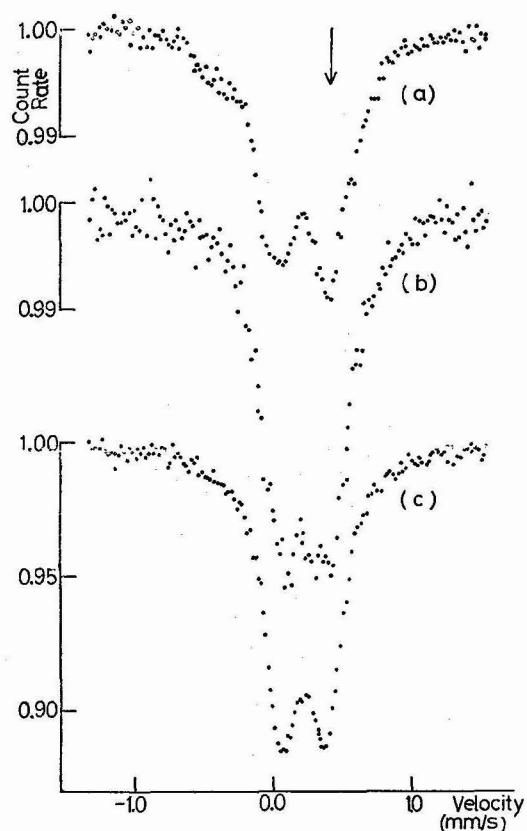
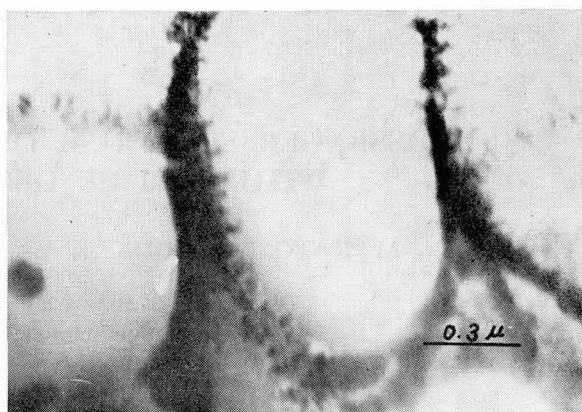


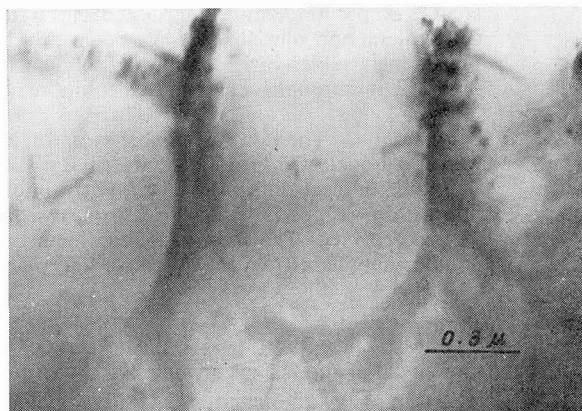
FIG. 2. — Mössbauer spectrum of a) splat cooled Al-1 at % Fe, b) cast Al-1 at % Fe and c) splat cooled Al-4 at % Fe. Source is ^{57}Co in Cu. Both source and absorber at room temperature.

for Al-1 at % Fe alloy. The specimen was aged isochronally at 50 °C intervals from 100 °C \times 30 min to 450 °C \times 30 min. Little change was noticed in the spectrum after aging below 350 °C except a decrease in the solid solution peak. An increase in the lattice constant of the alloy from 4.01 Å in as splat-cooled state to 4.05 Å after 300 °C aging corresponds to the precipitation of iron atoms from the supersaturated matrix. Only a small but continuous shift occurred in the left peak until 350 °C suggesting a gradual change in the structure. A drastic change occurred at 400 °C and a broad spectrum corresponding to $\text{Fe}_4\text{Al}_{13}$ grew. *In situ* observations by high voltage electron microscopy showed the nucleation of needle like precipitate at the cell wall and the concurrent dissolution of the fine iron rich precipitates at the temperature (Photo 1b). After aging at 450 °C \times 3 h the spectrum became, identical with that of $\text{Fe}_4\text{Al}_{13}$. The aging behavior was very much the same in Al-4 at % Fe.

The experiment confirmed the conclusion of Tonejc and Bonefacic [2] that the apparent solubility increase of iron in splat cooled aluminium-iron alloy up to 4.4 at % Fe was not correct and some iron rich phase formed during splat cooling. The occurrence of fine iron rich particles reported by Blank [3] Furrer and Warlimont [4] was also confirmed. The Mössbauer spectrum detected gradual changes in the iron rich



(a)



(b)

PHOTO 1. — Transmission electron micrograph of Al-1 at % Fe alloy. a) as splat cooled and b) annealed *in situ* at 480 °C.

phase up to 400 °C but couldn't identify the proposed transformations [3, 4].

1.3 ION-IMPLANTATION. — $^{57}\text{Fe}^+$ dose about $3 \times 10^{15} \text{ cm}^{-2}$ was implanted to aluminium foil in an isotope separator unit operated at 40 kV. The foil was 99.999 % pure aluminium 15 μm thick mounted on a copper plate kept at liquid nitrogen temperature. The Mössbauer spectrum (Fig. 4) was taken from a specimen consisting of 40 foils. Broad peaks occurred in as implanted specimen centered at 0.44 mm/s (peak 1) and 0.00 mm/s (peak 2). The peak 1 coincided with that of solid solution iron which is shown in figure 1. Specimens ion-implanted at room temperature showed about the same spectrum.

The specimens were aged isochronally at 100 °C intervals from room temperature \times 5 min to 500 °C \times 5 min in vacuum. The peak 1 decreased with increasing aging temperature but remained sharp while the peak 2 broadened after aging the specimen at room temperature. Consequently, the two peaks can not be a quadrupole pair as considered by Sawicka *et al.* [4]. They implanted ^{57}Fe at room temperature and obtained a spectrum with two peaks whose centers are in agreement with our peaks 1 and 2. The width of our

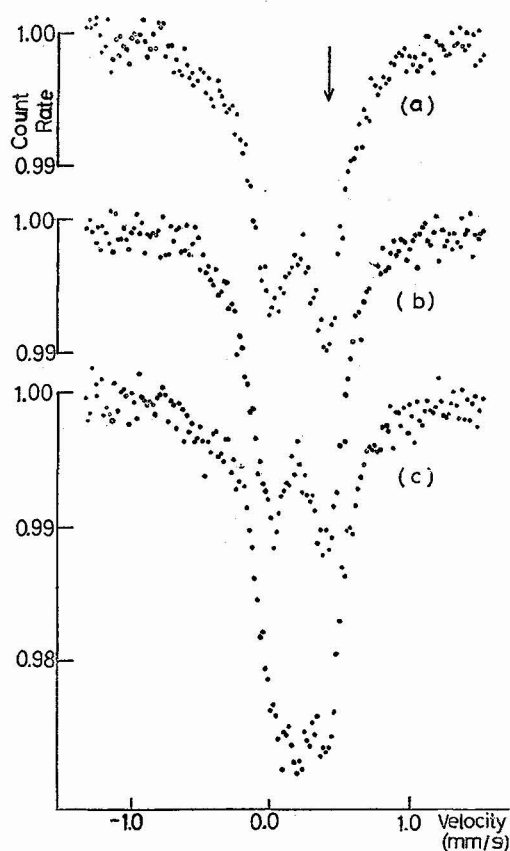


FIG. 3. — Absorber; Al-1 at % Fe at room temperature source; ^{57}Co in Cu at room temperature Specimen aged at a) 200 °C, b) 300 °C and c) 450 °C for 30 min.

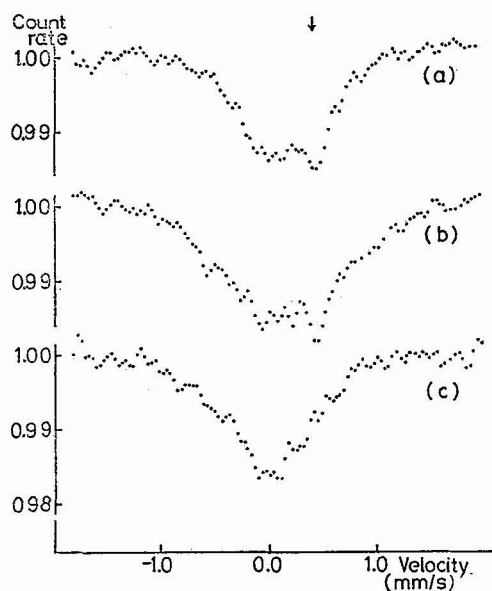


FIG. 4. — Absorber; 99.99 % pure Al foil implanted by $^{57}\text{Fe}^+$ at 40 keV and 3×10^{15} ions/cm² source; ^{57}Co in Cu at liquid nitrogen temperature a) as implanted, b) annealed at 200 °C for 5 min and c) annealed at 500 °C for 5 min. Data are smoothed.

peak 2, however, was broader and became even broader after aging at 100 °C. Peak 1 remained sharp even after aging at 400 °C, but disappeared after aging at 500 °C. Transmission electron microscopy (Photo 2) of the foil aged at room temperature showed dense black dots corresponding to the secondary defect. The defect remained stable and disappeared only after aging at 500 °C \times 5 min.

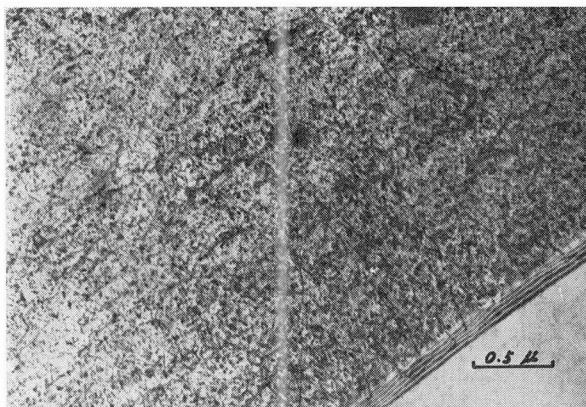


PHOTO 2. — Transmission electron micrograph of Al-Fe alloy. Implanted by ^{57}Fe and aged at room temperature.

It appears that iron atoms implanted by that dose do not remain in solid solution but cluster each other due perhaps to the repeated local heating during the subsequent implantation.

2. Experiments with Al-Sn alloys. — **2.1 QUENCHED ALLOY.** — Al-0.014 at % ^{119}Sn alloy was produced from aluminium 99.999 % pure and tin enriched by 90 % ^{119}Sn . Sheet specimens 1.2 mm thick was annealed at 620 °C and either cooled in air or quenched in iced water. The latter specimens were then aged isochronally at 50 °C and 150 °C for 5 min. Figure 5 shows the Mössbauer spectra of the specimen. The spectrum of the air cooled specimen consisted of a single peak of solid solution tin centered at + 2.3 mm/s. The half width was 0.90 mm/s. The half width of as quenched specimen was larger by about 20 % and the spectrum was asymmetrical. The spectrum can be decomposed into four peak as shown in figure 5 (b) ~ (d). The width of each peak was taken equal to that of air cooled specimen. Changes in the spectrum upon aging the specimen was described successfully by the change in the peak intensities. The new peak to the left of the main solid solution peak is probably that of tin atoms trapped by vacancies. The peak position indicates that the electron density at the tin nucleus is lower than that of the solid solution tin, which is likely to be so with tin atoms trapped by vacancies. According to Ceresara *et al.* [6] tin detraps the vacancy at 30 °C. Consequently the observed decrease in the peak intensity during the aging process may be explained by the detrapping. Two peaks to the right of the solid solution

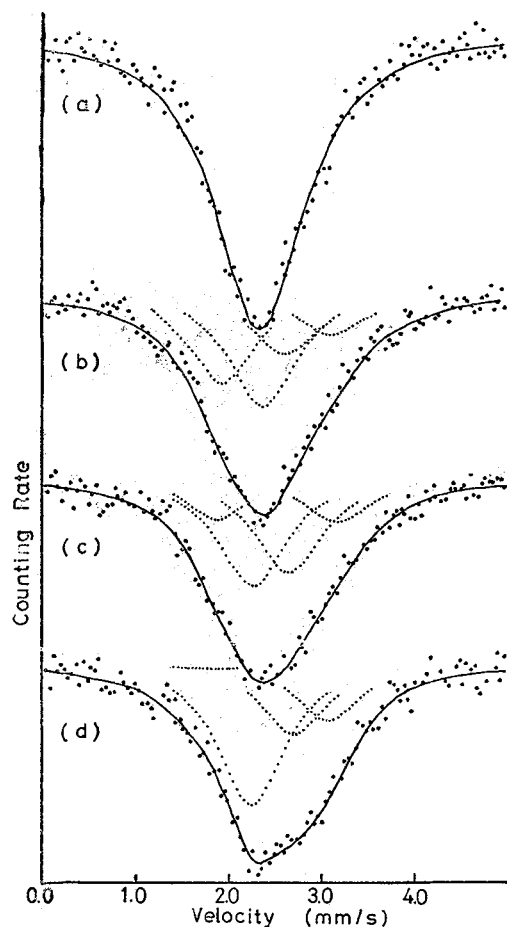


FIG. 5. — Absorber ; Al-0.014 at % Sn at liquid N₂ temperature. Source ; ^{119m}Sn in BaSnO₃ at room temperature : a) air cooled ; b) as quenched ; c) quenched and annealed at 50 °C, 5 min ; d) quenched and annealed at 150 °C, 5 min.

peak increased instead during the aging processes. They may be the peaks of tin cluster or metastable precipitate phases rich in tin concentration, since the peak positions are near that of β -Sn.

2.2 ELECTRON-IRRADIATED ALLOY. — Al-0.005 at % ¹¹⁹Sn alloy sheet 1.2 mm in thickness was annealed at 620 °C, cooled in air and electron-irradiated at liquid nitrogen temperature. The electron dose was 10^{17} cm⁻² at 1 MeV. The Mössbauer spectra of the irradiated specimens are shown in figure 6. The half-width of solid solution peak in as air cooled alloy was 0.85 mm/s about the same as that of 0.014 % Sn alloy. Only a slight change occurred in the spectrum upon irradiation of the specimen at liquid nitrogen temperature and the half width didn't change. Aging of the specimen at 0 °C, however, increased the width by about 15 %. Since the vacancy is considered to migrate at about -40 °C, the width increase may be attributed to the formation of Sn-vacancy pair. A small peak was resolved to the left of the solid solution peak as shown in figure 6c and d. The peak position, however differed from that of quenched and aged specimen. The position of the two peaks

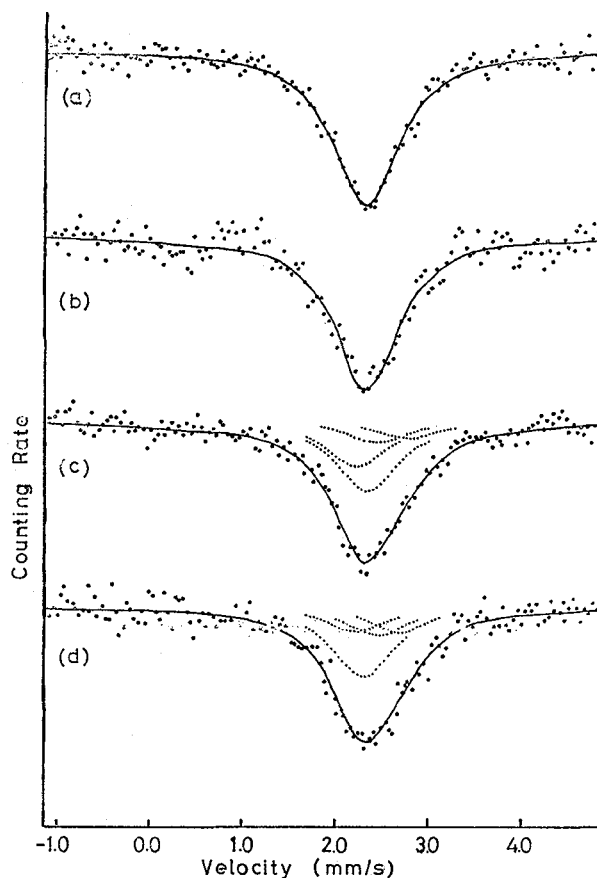


FIG. 6. — Absorber ; Al-0.005 at % Sn at liquid N₂ temperature. Source ; ^{119m}Sn in BaSnO₃ at room temperature : a) before electron irradiation ; b) as irradiated ; c) irradiated and annealed 0 °C, 5 min ; d) irradiated and annealed 50 °C, 5 min.

to the right of the main solid solution peak also varied from those of quenched and aged specimen. It appears that the smallness of the secondary peaks reflected the smallness of the amount of the lattice defects produced by the present electron irradiation.

3. Comparison of the two alloys. — The association of iron and tin nuclei with the lattice defects in quenched, splat-cooled, ion-implanted and electron-irradiated aluminium was by no means similar. A peak associated with Al interstitial-solute pair was reported by Mansel *et al.* [7] on aging a neutron-irradiated Al-⁵⁷Co alloy. No such peak was found in the present electron-irradiated Al-¹¹⁹Sn alloy, although a peak corresponding to the vacancy-solute pair was observed on aging the alloy, while a peak corresponding to the vacancy-solute pair was absent in quenched and aged Al-⁵⁷Fe alloy. More than one metastable phases co-existed in most of the alloys on aging. No clear identification of a metastable phase common to the alloys has been successful, which must be reflecting the difference in the defect structure and the solute distribution in the alloys and shows their strong effects on the evolution of the solute rich metastable phases.

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