Modulus and Mössbauer Studies of Precipitation in Fe-1.67 At. pct Cu

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Comparison of the yield stress and Young's modulus behavior on aging at 475° and 500°C confirms Hornbogen's suggestion that a two-stage aging process occurs in solution treated Fe-Cu alloys. While the yield stress increases rapidly with initial aging, Young's modulus does not. It increases rapidly at longer aging times corresponding to the appearance of the fcc copper phase. Dissolved copper broadens the Mössbauer effect lines of iron and causes a small isomer shift. Aging for a short time (30 min at 475°C) corresponding to the yield stress increase but before the modulus increase, sharpens the lines and reduces the isomer shift proving that clustering of the copper atoms has occurred. Since there is little change in modulus, there is probably no change in structure supporting Hornbogen's postulate that bcc copper clusters form during the first aging stage. After extended aging, the Mössbauer effect pattern is identical to that of pure iron showing that nearly all of the copper has precipitated from solution.

While the yield stress of solution treated Fe-Cu alloys increases rapidly with aging, a precipitate has only been directly observed in overaged samples. This precipitate is essentially pure fcc copper, the ε phase. Hornbogen suggested that the initial hardening is due to clustering of copper atoms in a bcc iron matrix. Hornbogen was not able to obtain direct confirmation for such bcc clusters by either X-ray diffraction or electron microscopy; however, he did observe analogous clustering in Fe-Au alloys where the scattering factor difference between iron and gold is more favorable than that for iron and copper.

Fujii, Nemoto, Suto, and Momma recently observed diffuse electron diffraction scattering in a 2.5 pct Cu alloy aged at 500°C for 30 hr. They suggested that part of the diffuse scattering was due to a modulated structure of 25 to 42Å wavelength parallel to the (110) matrix plane. This disappeared with further aging. However, 30 hr at 500°C is well beyond the peak strengthening in this alloy which occurred at less than 1 hr at 500°C. By transmission electron microscopy they could not distinguish between quenched samples and samples aged to maximum strength.

The purpose of the present investigation was to try to obtain further confirming evidence for a precipitation stage preceding the formation of the fcc ε phase. Change in Young's modulus was selected for study because clustering of copper might be expected to give only a relatively small change in modulus compared to formation of the fcc ε phase. Mössbauer effect measurements give information concerning the local environment about the iron atoms. The Mössbauer effect characteristics are expected to change on precipitation of the copper ions whether they are in bcc or fcc precipitates because the probability for neighboring Fe-Cu atoms is reduced.

EXPERIMENTAL PROCEDURE

The Fe-1.67 at. pct Cu alloy was supplied by the U.S. Steel Corporation in the form of a hot forged rectangular bar. The carbon and nitrogen contents of this alloy were 70 ppm and less than 10 ppm, respectively. The samples for Young's modulus measurements were made by cold swaging to 1/8 in. diam and cutting to 2 in. lengths. Tensile test samples 1 in. long were prepared by cold rolling to a thickness of 0.012 in. and then machining to gage dimensions of 0.5 by 0.012 in.

For Mössbauer studies, foils 1 mil thick were prepared by cold rolling. During fabrication the alloy was given intermediate anneals at 845°C followed by quenching.

The specimens after preparation were solution treated at 1000°C (γ field) or 845°C (α field) for 1 to 2 and 5 to 6 hr, respectively, in a dynamic vacuum of about 2 × 10⁻⁶ torr. The tensile and modulus specimens were drop-quenched into iced brine through an aluminum foil which vacuum-sealed the bottom of the furnace tube. The Mössbauer foils were drop-quenched into helium gas cooled by passing through N₂ (liq) in a copper coil. The grain diameter of the modulus and tensile specimens was between 0.025 and 0.035 mm. The samples were aged from 400° to 500°C in a dynamic vacuum of 2 × 10⁻⁶ torr and cooled by pulling into a water-cooled portion of the vacuum system.

The dynamic Young's modulus was measured at room temperature using electrostatic excitation and detection of longitudinal vibrations. Neglecting any length change during the aging, (this is expected to be comparatively small), the fractional change of Young's modulus (ΔE_t)/E_av is equal to twice the fractional change of the resonant frequency (Δf_t)/f_av .

Δf_t = f_t - f_0 where f_0 and f_t are the resonant frequencies of a specimen before aging and after aging to time t. The measured Δf's, approximately 51,000 cps, were corrected to 25°C for any variation in the ambient temperature.

The tensile tests reported were carried out at room temperature in an Instron with a 1000 lb full scale load cell. The flow stress reported herein corresponds to a strain of 0.002.

The Mössbauer spectra were taken in a constant acceleration model AM-1 NSEC spectrometer. The
RESULTS AND DISCUSSION

The change in modulus and flow stress on aging at 475° and 500°C are compared in Fig. 1. While the flow stress \( \sigma \) increases rapidly at small aging time at these temperatures, Young's modulus \( E \) does not. The \( \Delta E/E \) curve is sigmoidal in shape. The flow stress is near its maximum value before the region of most rapid change in modulus. Comparison of the two properties gives a clear indication of a two-stage precipitation process.

The fractional change in modulus is plotted vs log aging time, \( t_A \), at 425°, 475°, and 500°C in Figs. 2 and 3. Two solution treating temperatures were used, 845°C which is in the \( \alpha \) field and 1000°C which is in the \( \gamma \) field. Before an appreciable increase in modulus, there is an incubation time of about 200 min duration for \( t_A = 425°C \) and about 30 min for \( t_A = 500°C \). The final change in Young's modulus \( \Delta E/E \) is about 15 pct larger after aging at the higher solution treating temperature. This point will be discussed later.

Fig. 2—Fractional change in Young's modulus vs log aging time at 425°, 475°, and 500°C. Sample was solution treated at 845°C.

Fig. 3—Fractional change in Young's modulus vs log aging time at 425°, 475°, and 500°C. Sample was solution treated at 1000°C.
whether the solution treating was carried out at 845°C or 1000°C. Aging 11 hr at 550°C gives a half-width indistinguishable from that of pure iron. The alloy line has a 25 pct higher flow stress than that of pure iron. Any difference between samples solution treated above (1000°C) or below (845°C) the γ-to-α transformation. Fujii et al. observed similar behavior for the increase in yield strength on aging. Thus the defect structure produced by the γ-to-α transformation has little effect on the transformation kinetics. The vacancy concentration for the γ-to-α transformation is probably determined by the temperature of the γ-to-α transformation and thus there is probably little difference in the vacancy concentration between the two solution treating temperatures. On the other hand, when the Møssbauer effect foils were accidentally bent during quenching, the outside lines were only about 15 pct broader than in pure iron. Thus, precipitation seems to have been accelerated by the deformation.

If the modulus data is fit to an empirical equation of the form 1 − x' = (E_f − E_t)/(E_f − E_o) = e−(kT/E_f)[m], after an initial transient m is equal to about 2.5 over most of the curve. If 1 − x' is related to the fraction untransformed (1 − x) through a power function, then the slope of a ln ln(1 − x') vs ln t line gives the same m as a ln ln(1 − x) vs ln t line. An m of 2.5 may arise from simultaneous nucleation and diffusion controlled growth. If simultaneous nucleation and growth is occurring, then the rate of nucleation appears in k. The rate of nucleation will be a function of temperature as well as the particle growth rate and thus an activation energy for growth of the e particles may not be determined from the data by simply measuring the time to a given 1 − x' vs temperature.

On aging at 475°C or 500°C the yield stress increases very rapidly during the initial clustering stage; there
is no evidence for an incubation time in the yield stress data plotted in Fig. 1. For example, the value for 5 min of aging at 475°C is clearly above the as quenched value, Fig. 1(b). The yield stress does not drop when the ε-fcc-copper phase forms as both the initial clustering and the ε precipitate give strengthening.

The behavior at 400°C appears different. Fujii et al. observed a rather long incubation time at 400°C before any increase in yield strength was observed. In a 1.8 pct alloy the incubation time was about 10 hr and the time to peak yield strength, \( t_p \), was not reached until about 300 hr of aging at 400°C. Aging one of the present samples for 5 hr at 400°C gave a Mössbauer pattern identical to the as quenched sample within experimental error.

CONCLUSION

The Mössbauer and modulus measurements give good support to Hornbogen’s postulate that bcc copper clusters precede precipitation of the bcc copper phase, ε.

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REFERENCES

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