Precipitation Kinetics and Strengthening of a Fe–0.8wt%Cu Alloy

A. DESCHAMPS, M. MILITZER1) and W. J. POOLE1)

LTPCM/ENSEEG, UMR5614, Domaine Universitaire de Grenoble, Grenoble, France.
1) The Centre for Metallurgical Process Engineering, The University of British Columbia, 309-3950 Stores Road, Vancouver, BC, V6T 1Z4 Canada.

(Received on August 28, 2000; accepted in final form on October 24, 2000)

Precipitation kinetics and strengthening have been investigated for a Fe–0.8wt%Cu alloy. Microstructure evolution during aging at 500°C has been studied by a combination of Transmission Electron Microscopy and Small-Angle X-ray Scattering to provide information on the nature and location of the precipitates as well as a quantitative estimate of their size and volume fraction. The associated mechanical properties have been studied by hardness and tensile tests.

The precipitation kinetics measured in this study are fully compatible with results reported for alloys with higher Cu levels. Nucleation of Cu precipitates is promoted by the presence of dislocations whereas coarsening rates in the later stages of aging appear to be not affected by fast diffusion paths along dislocations.

The strength of individual precipitates increases with precipitate size based on the analysis of the mechanical test results. However, the strength of the largest precipitates observed remains approximately half of the strength required for the Orowan by-passing mechanism. The Russell-Brown model for modulus strengthening has successfully been applied to the current data.

Study of the plastic behavior shows that the maximum initial hardening rate is related to the highest strength of the material. This unusual result may be explained by a dynamic strain-induced phase transformation of the precipitates from the bcc to the 9R structure. Consequently, the hardening potential of Fe–Cu alloys is associated with good plastic properties close to peak strength thereby indicating the excellent potential of copper as hardening element for the development of novel high strength interstitial free (IF) steels.

KEY WORDS: iron–copper alloy; precipitation kinetics; precipitation strengthening; strain hardening; small-angle X-ray Scattering.

1. Introduction

Precipitation of copper in iron and steels has been studied extensively in the past,1,2) particularly in reference to pressure vessel steels which are used for nuclear reactors.3,4) Further, copper bearing high strength low alloy (HSLA) steels provide a good combination of strength, toughness and weldability making them suitable for applications in natural gas pipelines, shipbuilding and offshore platforms exposed to Arctic environments.2,5) The beneficial role of Cu has recently received renewed attention due to the potential of developing post heat treatment steels which combine high strength with high formability for automotive applications.6–8) Copper alloying has the benefit of substantial strengthening due to precipitation hardening. A useful model alloy for understanding the precipitation behavior is the Fe-Cu system.3,4,9) The precipitation of copper in both iron and steels is usually observed in the temperature range 400 to 650°C. Copper precipitation has been examined with a variety of experimental techniques such as evolution of Young’s modulus,10) field ion microscopy (FIM),11,12) high resolution transmission electron microscopy (HRTEM),13,14) X-ray absorption techniques such as EXAFS and XANES.4,15) Based on these studies, it is now generally accepted that the following sequence is characteristic of precipitation in this system:

\[ \alpha(\text{supersaturated solid solution}) \rightarrow \text{BCC copper} \rightarrow \text{9R copper} \rightarrow \text{FCC} \]

Initially, metastable body centered cubic (BCC) precipitates which are fully coherent with the matrix are observed. When the precipitates reach a critical size; i.e., a radius in the range of 2.3 to 3 nm,16,17) the coherency strain energy becomes too large and a martensitic transformation to the 9R structure occurs.13) The 9R structure has a face centered cubic lattice with a high density of twins, which help to minimize the misfit with the iron matrix. Finally, at larger precipitate sizes, the twins disappear and the precipitates attain the equilibrium \( \varepsilon \) phase; i.e., face centered cubic. The solubility limit for copper at the typical aging temperatures is less well characterized. Extrapolation of higher temperature data from Salje and Feller–Kniepmeier18) gives a solubility of 0.03 at% at 500°C while recent data obtained by Atom Probe Field Ion Microscopy (APFIM) suggests a solubility of approximately 0.1 at%.12)

The contribution of the precipitates to the strength of the steels is difficult to model, because of the complicated precipitation sequence. Most researchers consider that at the peak strength the precipitates have the BCC structure.3,4,15,17) although there is some evidence that the trans-
formation to the 9R structure has been initiated.\textsuperscript{10,11,19} The strengthening is usually described by employing the approach of Russell and Brown which is based on modulus strengthening.\textsuperscript{20} This approach allows for the prediction of mechanical properties during an aging treatment assuming that the strength of the interaction between the dislocation and the precipitate increases with particle size. An alternative approach has recently been proposed by Osamura et al.,\textsuperscript{21} assuming that the hardening during the initial stage is controlled by coherency strains. The decrease in strength after the peak strength is attributed to the loss of coherency of the precipitates. Currently available experimental data do not allow to give preference to one of these two models.

The effect of precipitation, coupled with the evolution of solid solution content, on the overall work hardening behavior is still poorly understood. Current knowledge derives from the pioneering contribution of Hornbogen et al.\textsuperscript{21} where a few curves of initial work hardening rates are presented. More generally, a limited theoretical framework including the effect of bypassed precipitates has been proposed recently by Estrin,\textsuperscript{22} but the complete picture is still missing.

The goal of the present study is to evaluate the precipitation process in a Fe–0.8\%Cu alloy. An in-depth understanding is sought using an investigation which includes the evolution of i) microstructure and ii) the corresponding mechanical properties using a variety of experimental techniques. The emphasis of the microstructural investigation is to combine transmission electron microscopy (TEM), which gives direct information about the type, morphology and nucleation mechanisms of the precipitates, and Small-Angle X-Ray Scattering (SAXS), which gives quantitative data on precipitate size and volume fraction. In addition, hardness and tensile tests are conducted to relate the precipitation characteristics quantitatively to the mechanical property evolution of the material. The analysis will be conducted based on aging treatments of samples after they are subjected to either i) a simple solution treatment and quench, or ii) a solution treatment followed by deformation. Deformation was used in order to study the influence of dislocations on the precipitation behavior.

2. Experimental Methods

2.1. Material and Heat Treatment

The Fe–Cu alloy was received as forged bar from Dofasco Inc. The alloy composition is shown in Table 1. Samples cut from the forged bar were cold rolled from 12 to 1 mm. The samples were then solution treated for 5 h at 820°C and quenched into cold water. This solution treatment resulted in a fully equiaxed ferritic structure with a grain size of approximately 50 μm.

Pre-deformation, when applied, was performed after the quench at a strain rate of $10^{-3}$ s\(^{-1}\) up to a true plastic strain of 10%. Aging treatments were conducted in a salt bath at 500°C for aging times of up to 8 h. For longer aging times, the samples were sealed in a quartz tube under vacuum and then placed in an air furnace at 500°C.

2.2. Transmission Electron Microscopy (TEM)

Disks for transmission electron microscopy were prepared by mechanical grinding down to 200 μm, followed by electroerosion, and final grinding down to 80 μm. The thin foils were then etched in a Tenupol jet polisher with a 5% perchloric acid–95% acetic acid solution, held at 15°C using a voltage of 70 V. Image analysis was conducted on several heat treatment conditions. In each case, the precipitate size distribution was determined from a sample of at least 700 precipitates.

2.3. Small-Angle X-rays Scattering (SAXS)

Small-Angle X-ray Scattering is a common way to study precipitation kinetics on the nanometer scale.\textsuperscript{23} However, it has been very rarely used in Fe–Cu alloys because of the poor contrast between Fe and Cu atoms.\textsuperscript{39} The development of powerful synchrotron X-ray sources enables now the use of the anomalous scattering effect in order to maximize the contrast and obtain data of high quality. In this work, SAXS experiments were conducted on the D2AM beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble. A wavelength, $\lambda$, of 0.1745 nm was chosen corresponding to an energy of 7.104 keV. The beam was highly monochromatic with $\Delta\lambda/\lambda \approx 10^{-4}$. The X-ray energy is close to the Fe edge in order to maximize the contrast between the precipitates and the matrix while limiting the fluorescence of Fe, using the anomalous scattering behavior. Thus, in this experiment the apparent difference in atomic weight, $\Delta Z_{\text{app}}$, between Fe and Cu was 8.09, as calculated by the Cromer–Liberman method.\textsuperscript{24,25} Since the intensity scales as $(\Delta Z_{\text{app}})^2$, the improvement in contrast compared to a non-anomalous scattering situation is approximately a factor of 7. Samples for SAXS measurements were mechanically thinned to 40 μm, and then electropolished to 20 to 30 μm in a 5% perchloric acid–95% acetic acid solution at a temperature of 15°C and a polishing voltage of 70 V. The scattering intensity of x-rays was recorded using a two-dimensional CCD camera located 600 mm from the sample. With this configuration, scattering vectors $(q=4\pi \sin \theta/\lambda)$ ranging between $4\times10^{-4}$ and $2.5\times10^{-2}$ nm\(^{-1}\) could be measured. The recorded intensity was then corrected for background noise and normalized to absolute intensity $I$.\textsuperscript{23}

2.4. Mechanical Property Measurements

Microhardness results were obtained using a Buehler Micromet 3 micro-hardness machine with a load of 0.5 kg. At least 5 measurements were made for each condition, and the measurements were estimated to be accurate within 2 HV. Tensile tests were conducted using a screw-driven Instron machine, with an initial strain rate of $2\times10^{-3}$ s\(^{-1}\). Load-extension data were converted to true stress and true strain data in the usual manner. Work hardening rate analysis was performed by fitting the stress–strain curve between the end of the Lüders plateau and the necking point using a polynomial function which was then analytically differentiated.

### Table 1. Composition of the alloy (in wt%).

| Element | C  | N  | Cu | Si | Al (ASA) | S  | Mn |
|---------|----|----|----|----|----------|----|----|
| Composition | 0.0014 | 0.002 | 0.78 | 0.005 | 0.004 | 0.005 | 0.032 |
3. Study of Precipitation Kinetics

3.1. Transmission Electron Microscopy

The location, shape and size of precipitates were examined by TEM in the overaged state. These studies provided the basis for the assumptions required to analyze the SAXS data. For the case where no deformation is applied prior to aging, the precipitates show a predominantly spherical morphology and are homogeneously distributed, as shown in Fig. 1 for 100 h and 1000 h at 500°C, respectively. For samples with pre-deformation, the precipitation process is modified due to the presence of dislocations and subgrains. Figure 2a shows an example of the deformed microstructure exhibiting a fine cell structure with a size of approximately 0.5 μm, although a significant density of dislocations is observed in the cell interiors. Figures 2b and 2c clearly show that most precipitates are located on dislocations after aging of 100 and 1000 h, respectively. Precipitates on dislocations also exhibit a more elongated morphology as compared to the homogeneously distributed precipitates.

Figure 3 shows the precipitate size distribution obtained from image analysis for the samples after 100 and 1000 h of aging at 500°C with and without a pre-deformation. The precipitates size distributions are close to log-normal (see Appendix A). After 100 h, the samples with pre-deformation showed an average radius of 5.4 nm compared to 4.3 nm for the sample without pre-deformation. However, after 1000 h of aging the size difference decreases; the average precipitate radii of 9.8 and 9.5 nm for the samples with and without deformation, respectively. For 1000 h of aging, the precipitate size distribution is similar, except for the presence of some larger precipitates in the pre-deformed material. These large precipitates are responsible for the slightly higher average radius and larger standard deviation of the precipitate size distribution (2.9 nm vs. 2.6 nm) for the pre-deformed material.

3.2. Small-angle X-ray Scattering

The calculation of precipitate radii from the SAXS results was not straightforward. Frequently, SAXS results are analyzed with the Guinier approximation. In the present case, the low signal from the precipitates made it difficult to separate the scattering due to precipitates from other scattering centers such as grain boundary precipitates, dislocations or the sample surface. Therefore, the Guinier approximation could not be used. However, by plotting $I \cdot q^2$ vs. $q$ as shown in Figs. 4a and 4b, a maximum in the data could be readily observed. Appendix A shows that by conducting a simple computer simulation, the average diameter of precipitates can be correlated to the scattering angle at the maximum. Using this correlation, the precipitate size was calculated as a function of aging time for both the undeformed and the deformed material; the results are summarized in Table 2. From the area under the $I \cdot q^2$ curve, the integrated intensity ($Q_0$) may also be calculated allowing the volume fraction of precipitates be estimated as shown in
Appendix A; the experimental results are given in Table 2. Table 2 shows that both the precipitate size and volume fraction increase with aging time. Furthermore, Figures 4c and 4d compare the SAXS data for undeformed and deformed material. After 5 h at 500°C, Fig. 4c, the undeformed material shows no measurable precipitation, whereas the deformed material shows a significant amount of precipitation. Consistent with the TEM observations, Fig. 4d shows that there is very little difference between the deformed and undeformed material in the overaged state after 300 h at 500°C.

4. Mechanical Properties

4.1. Precipitation Strengthening

The strengthening resulting from this precipitation process is presented in Fig. 5 in terms of the hardness increase. The undeformed material shows a hardness increase by precipitation of 65 HV, after approximately 30 h at 500°C. The alloy shows little hardening in the two first hours of aging, however after 5 h the hardness has increased to a substantial amount (approximately 40 HV). The precipitates responsible for this initial hardening process must be very small since they were not detected in the SAXS experiments.

The deformed material shows a quite different behavior. The hardness is higher due to the dislocation hardening during the pre-deformation. Recovery of this structure during annealing can be inferred from the initial decrease in hardness during the first hour of aging. However, after 1 h, the increase in hardness due to precipitation is greater than the rate of recovery. It is also possible that the rate of recovery is reduced as precipitation proceeds. The pre-deformed material shows a well defined peak strength, with an overall hardness increase of approximately 80 HV which is significantly higher than the peak strength of the undeformed material. After the peak strength, the deformed material shows a decrease of the strength which is similar to the undeformed material.

4.2. Effect of Precipitation on the Work Hardening Behavior

Figure 6a shows the stress–strain curves for the undeformed material at selected aging times including as-quenched, under-aged, peak-aged and over-aged states. This family of stress–strain curves allows for a quantitative evaluation of the work hardening behavior as a function of precipitate state. The yield stress, $\sigma_y$, at the peak strength is approximately 200 MPa higher than the as-quenched value. Upon initial observation, the stress–strain curves appear roughly parallel to each other except for the longest aging time (1 000 h), which shows a much lower level of work hardening. In order to study the work hardening processes in more detail, the work hardening rate, $\theta$ or $d\sigma/d\varepsilon$ can be plotted as a function of the reduced flow stress, $\sigma - \sigma_y$, as shown in Fig. 6b for the different aging times. The work hardening rate is usually characterized by the initial rate and the slope of the decrease in the hardening rate. The general course of the work hardening evolution is as follows. For the as-quenched material, the initial hardening rate is observed to be high; i.e., approximately 2 500 MPa, and the slope is relatively low. After 2 h of aging at 500°C, the major change appears to be a decrease in the initial hardening rate to approximately 2 000 MPa while the slope is similar. At 7 and 40 h, the initial hardening rate returns to the high level (2 500 MPa) but the slope is now significantly increased. Finally, after 1 000 h of aging, the initial hardening rate has been reduced to substantially lower levels; i.e., below 1 500 MPa, whereas the slope reaches its highest level throughout the aging treatment.

5. Discussion

5.1. Microstructure Evolution

Most of the existing studies on Fe–Cu alloys have been carried out on higher Cu levels in the range of 1.3 to 1.5 wt%\textsuperscript{3,9}. It is of interest to evaluate whether the same characteristics of the precipitation process can be applied to lower Cu alloying such as the present 0.8 wt%. The first ob-
Fig. 4. Results from small angle x-ray scattering experiments plotted as $I \cdot q^2$ vs. $q$. a) evolution of scattering with aging time for the undeformed material, b) scattering curves as a function of aging for the 10% predeformed sample, c) effect of predeformation on scattering for 5 h at 500°C and d) effect of predeformation on scattering for 300 h at 500°C.

Table 2. Radii (in nm) and volume fraction of precipitates calculated from the SAXS data.

|        | 5h  | 15h | 30h  | 110h | 300h |
|--------|-----|-----|------|------|------|
| Undeformed | $Q_{\text{max}}$ (nm$^2$) | 0.66 | 0.53 | 0.35 | 0.16 |
|         | R   | 2.6 | 3.2  | 4.9  | 10.4 |
| 10% Predeformed | $Q_{\text{max}}$ (nm$^2$) | 0.66 | 0.55 | 0.47 | 0.25 | 0.16 |
|         | R   | 2.6 | 3.1  | 3.6  | 6.8  | 10.4 |
|         | $f_r$ (%) | 0.05 | 0.06 | 0.06 | 0.09 | 0.07 |
|         | $f_r$ (%) | 0.54 | 0.65 | 0.69 | 0.97 | 0.75 |

Fig. 5. Change in microhardness during aging at 500°C for the undeformed and 10% predeformed samples with reference to the as-quenched hardness of the undeformed material.

Fig. 6. Tensile test results for the undeformed materials for different aging times, a) stress–strain curves, b) work hardening rate vs. reduced flow stress.
ervation of significance from the present work is that the precipitate sizes measured with SAXS and TEM are consistent. For example at the longest aging times, both techniques measure a precipitate radius of approximately 10 nm. Furthermore, the precipitate radius at the peak strength determined from the SAXS measurements is 3 nm which is consistent with the results for higher Cu contents reported in the literature.\textsuperscript{4,9,16,17} This finding suggests that the peak strength is related to a critical size of the copper precipitates, regardless of the total concentration in copper.

Table 2 shows the volume fractions calculated from the SAXS data for various aging times. It appears that at peak strength no complete precipitation has occurred, e.g. in the undeformed material the volume fraction at the peak (30 h at 500°C) is 0.44%, only approximately half of 0.85% measured after 300 h. This is consistent with previous studies\textsuperscript{11} and can be related to the fact that at peak strength precipitates are still metastable; i.e. BCC precipitates are dominant. The volume fraction of precipitates at long aging times is expected to approach the equilibrium value. In the overaged state the SAXS results suggests a volume fraction times is expected to approach the equilibrium value. In the

In the pre-deformed material, the presence of dislocations affects the precipitation process. It has been observed by several authors\textsuperscript{4,25} that introducing dislocations prior to aging changes some characteristics of the copper precipitation reaction. It was observed by EXAFS and XANES that a cold-rolled material contained a higher proportion of FCC precipitates than the undeformed material for the same aging time.\textsuperscript{4} Furthermore, it has also been observed that precipitation occurs at a much lower temperature; i.e., 350°C, in the presence of dislocations.\textsuperscript{28} This is consistent with the present observations where, compared to the undeformed material, the pre-deformed material shows a significant acceleration of the precipitation process at the shorter aging times. This suggests that the effect of dislocations is to decrease the activation energy for nucleation of the copper precipitates, most probably by a relief of the coherency strains.

It appears from the present study that the faster precipitation rates observed in the first stages of aging do not continue to very long aging times. During overaging, the precipitate size distribution is similar in undeformed and pre-deformed materials, as confirmed by the SAXS results after 300 h of aging and the TEM micrographs after 1 000 h of aging. This suggests that dislocations do not play a significant role as fast diffusion paths at the later stages of the precipitation process.

5.2. Precipitation Hardening

The prediction of precipitation strengthening requires knowledge on precipitate spacing and the obstacle strength of precipitates. Based on the investigations by Pyhtian et al.\textsuperscript{13} and Osamura et al.\textsuperscript{19} it can be assumed that the Cu precipitates are weak obstacles. Thus, the Friedel assumption applies where the critically resolved shear stress is given by\textsuperscript{29}:

$$\tau_c = \frac{2}{bLT^{1/2}} \left( \frac{F}{2} \right)^{3/2}$$  \hspace{1cm} (1)

Here, $F$ is the strength of the precipitate as an obstacle, $T$ is the line tension of the dislocation, $b$ is the magnitude of the Burgers vector. For spherical precipitates, the average spacing on the glide plane is given by:

$$L = \sqrt[3]{\frac{2\pi}{3f_v}} \bar{R}$$  \hspace{1cm} (2)

where $f_v$ is the volume fraction of precipitates and $R$ is the average precipitate radius.\textsuperscript{30} Substituting (2) into (1) and converting from a resolved shear stress to tensile stress using the Taylor factor, $M$, gives:

$$\Delta \sigma_p = \frac{M}{\sqrt{2Tb}} \sqrt[3]{\frac{3f_v}{2\pi}} \frac{F^{3/2}}{R}$$  \hspace{1cm} (3)

Figure 7 shows the evolution of yield stress with aging time for the undeformed material. The precipitation contribution to the yield stress can be estimated by simply subtracting the yield stress of the as-quenched material. This assumes that the base strength (i.e. grain size and intrinsic strength) and precipitate strengthening are linearly additive and that solid solution strengthening due to copper is negligible. The volume fraction and radius of precipitates have been estimated from the SAXS results. The only unknown in Eq. (3) is the average obstacle strength of the precipitates. It is useful to normalize the strength of the precipitates relative to the maximum strength that the precipitates could attain, i.e. the Orowan condition where $F=2T$:

$$k = \frac{F}{2T}$$  \hspace{1cm} (4)

The normalized strength, $k$ can range from 0 to 1, with
the latter case corresponding to the strength for by-passing the precipitates. The value of $k$ can also be related to the critical breaking angle, $\phi_c$, (i.e. the angle between the dislocation segments when the particle can no longer resist shearing by the dislocation) by

$$k = \frac{F}{2 \tau} = \cos \frac{\phi_c}{2} \quad \text{............................}(5)$$

The value of $k$ can now simply be estimated by rearranging Eq. (5) and assuming a line tension of $G b^2 / 2; \ i.e.,$

$$k = \left( \frac{2 \pi}{3} \frac{R}{M y b f_i} \right)^{2/3} \quad \text{............................}(6)$$

Taking a Taylor factor of approximately 3, the shear modulus of iron; \ i.e. 80 GPa, and the magnitude of the Burgers vector of 0.25 nm, the values of normalized precipitate strength, $k$, or the critical breaking angle, $\phi_c$, have been calculated as a function of the aging time; the results are summarized in Table 3. The normalized strength is plotted in Fig. 8 as a function of the normalized precipitate radius, $R/R_p$, where $R_p$ is the precipitate radius at the peak strength. Clearly, at all the conditions examined, the strength of the precipitates is far below the strength for non-shearable precipitates. The calculated critical breaking angles are consistent with the observations of Pyhtian et al.,$^{33}$ who measured a breaking angle at the peak strength of 120°, and with the breaking angle results of 140–170° reported by Osamura et al.$^{33}$

The Russell and Brown model$^{20}$ for strengthening due to the modulus effect can be applied to the present results. In this approach, the critical breaking angle between the arms of the dislocation, is related to the relative moduli, $E_1$ and $E_2$, of the precipitates and the matrix as:

$$\phi_c = 2 \sin^{-1} \left( \frac{E_1}{E_2} \right) \quad \text{............................}(7)$$

Using Eqs. (5) and (7), it can be shown that:

$$k = \left[ 1 - \frac{E_1^2}{E_2^2} \right]^{3/2} \quad \text{............................}(8)$$

where the relative line energy of the dislocation $T_1/T_2$ in the precipitate and the matrix is related to the ratio $E_1/E_2$. This ratio is size dependent and Russell and Brown suggest the following form:

$$\frac{E_1}{E_2} = \frac{\log \frac{r_{\text{in}}}{R_{\text{in}}}}{\log \frac{r_{\text{out}}}{R_{\text{out}}}} + \log \frac{r_{\text{out}}}{r_{\text{in}}} \quad \text{............................}(9)$$

where $E_1^*$ is the modulus of the precipitate (i.e. 130 GPa), $E_2^*$ is the modulus of the matrix (i.e. 210 GPa for iron), $r_{\text{in}}$ is the inner cutoff radius and $r_{\text{out}}$ is the outer cutoff radius. The inner and outer cutoff radii can be taken as adjustable parameters but must be in the ranges of the dislocation core radius and the distance between dislocations, respectively. In Fig. 8, the Russell–Brown model is compared with the experimental data assuming reasonable values for the adjustable parameters; i.e., an inner cutoff radius of 1.2 nm and an outer cutoff radius of 1 000 nm. The agreement with the experiments is very good considering that the Russell–Brown model neglects the complexities of the precipitation sequence.

Based on the above information regarding precipitation, the combined strengthening response of precipitates and dislocations can be discussed. Onodera and Mizui$^{28}$ found a much lower hardening potential in the predeformed Fe–1.4%Cu alloy as compared to the undeformed material. However, they considered the age hardening relative to the hardness after deformation thereby removing the dislocation strengthening contribution from their analysis. Comparing the hardness to the initial hardness, as illustrated in Fig. 5, the maximum hardening in the presence of dislocations is substantially higher than in the undeformed material. This maximum hardening can be adequately described by adopting a square-root addition law for the strength contributions from the precipitates and the dislocations which are both obstacles with similar strength and density.$^{31,32}$

$$\sigma_{\text{tot}} = \sqrt{\sigma_{\text{precipitates}}^2 + \sigma_{\text{dislocations}}^2} \quad \text{............................}(10)$$

With $\sigma_{\text{precipitates}} = 62 \text{ HV}$ and $\sigma_{\text{dislocations}} = 45 \text{ HV}$, the calculated strength contribution is 76 HV, which is very close to the experimental value of 78 HV.

### 5.3. Work Hardening Behavior

In the classic framework developed by Kocks, Mecking and Estrin,$^{22,26,27}$ work hardening is seen as a competition between dislocation storage and dynamic recovery (dislocation loss) mechanisms. There are a number of ways in which these two processes can be affected by the solid solu-

| Table 3. Microstructural and mechanical parameters for the undeformed Fe–Cu alloy. |
|-----------------|----------|------------|-------|-----|-----------|
| $R$ (nm)        | $f_i$ (%)| $\Delta \sigma$ (MPa) | $k$   |       | breaking angle |
| 15 h            | 2.6     | 0.58       | 175   | 0.27 | 150°      |
| 30 h            | 3.2     | 0.44       | 185   | 0.35 | 140°      |
| 110 h           | 4.9     | 0.64       | 162   | 0.38 | 135°      |
| 300 h           | 10.4    | 0.85       | 125   | 0.48 | 120°      |

Fig. 8. The effective normalized precipitate strength vs. normalized precipitate radius calculated from the SAXS data (symbols) and predicted from the Russell–Brown model (line).
Fig. 9. The evolution of mechanical property parameters as a function of aging time, a) initial work hardening rate, b) slope of the work hardening rate vs. stress and c) the ductility in tension.

As can be seen in Eq. (11), when the flow stress is raised the necking condition is reached at a lower strain resulting in the usual observation that uniform elongation decreases with strength level. However, if, as in the present case, the work hardening rate increases as the flow stress increases, these two factors can offset each other resulting in large uniform elongation. The high work hardening rate associated with the peak strength in the present alloy is very beneficial for combining high values of ductility with high strength. Finally, as the material is overaged, there is little change in the ductility even though the flow stress is much lower. This is a consequence of the low work hardening rate in the overaged condition.
6. Conclusions

This study has used a combination of experimental techniques to quantitatively characterize the nature and kinetics of precipitation, in conjunction with mechanical tests which describe the resulting yield strength and work hardening behavior. The kinetics of precipitation in Fe–0.8wt%Cu are consistent with previously reported studies, which had been obtained for higher Cu contents. Notably, it appears that the precipitate radius for peak strength is 3 nm independently of the solute content. The presence of dislocations appears to promote the nucleation of precipitates with the SAXS technique being particularly useful for detecting precipitates early in the aging process. However, the characterization of the early precipitation stages is challenging. In particular, a significant strengthening contribution has been observed before recording precipitates by SAXS in the present investigation. Additional studies on alloys with higher Cu alloying may be useful to gain further insight into detail of precipitation and associated strengthening in these early stages.

Based on the quantitative microstructural data, the influence of precipitates on the yield stress has been examined using the classical framework for precipitation hardening summarized by Brown and Ham.29) The strength of precipitates as obstacles has been back calculated from the yield stress, precipitate size and the volume fraction of precipitates. These calculations show that the precipitates stay shearable throughout the aging process, and that the highest strength the precipitates achieve is only approximately one half of that necessary for the precipitates to be non-shearable. Further, the current investigation confirms the Russell–Brown approach to reduce the complexity of the precipitate-dislocations interactions in the Fe–Cu system to simple modulus strengthening. When considering the overall strength of the alloy in the presence of pre-deformation, the age hardening response can be adequately described in terms of a square root addition law between the hardening contributions from precipitates and dislocations, as again is expected from theoretical considerations.

The plastic response of the material in the presence of precipitates show unusual characteristics for an age-hardenning material. Notably, the peak strength is associated with a high work hardening rate, whereas the overaged state shows the lowest work hardening response. The consequence is a relatively mild decrease of the ductility up to the peak strength, and a lack of increase of ductility from the peak strength to the overaged state. The relatively high work hardening rate of the alloy at the peak strength may be associated with a stress or strain assisted transformation of the precipitates from the BCC to the 9R crystal structure. Further investigations are necessary to examine this hypothesis.

The excellent combination of high strength and comparatively high formability in the peak aged material further fuels the idea of developing a new class of high strength Cu bearing steels with superior properties. It is suggested to confirm these findings for Cu-bearing IF steels which appear to be candidates for an appropriate industrial material.

Acknowledgements

This work was conducted as part of the Dofasco Chair program in Advanced Steel Processing. The authors would like to thank Dofasco Inc. for financial support and for providing the material for this study. Financial support has also been received from Natural Sciences and Engineering Research Council of Canada (NSERC) and the French ministry of foreign affairs. The help of Dr. F. Bley, F. Livet and J-P. Simon with the Small-Angle X-Ray Scattering experiments is gratefully acknowledged. Professor E. Gauthier is also thanked for fruitful discussions.

REFERENCES

1) D. T. Llewellyn: Ironmaking Steelmaking, 22 (1995), No. 1, 25.
2) A. K. Lis, M. Mujahid, C. I. Garcia and A. J. DeArdo: Proc. of the Gilbert R. Speich Symp. Fundamentals of Aging and Tempering in Bainitic and Martensitic Steel Products, ISS, Warrendale, PA, (1992), 129.
3) W. J. Phythian, A. J. E. Foreman, C. A. English, J. T. Buswell, M. Hetherington, K. Roberts and S. Pizzini: Proc. of the 15th Int. Symp. on the Effect of Radiation on Materials, ASTM, West Conshohocken, PA, (1992), 131.
4) M. Charleux, F. Livet, F. Bley, F. Louchet and Y. Brechet: Philos. Mag. A, 73 (1996), No. 4, 885.
5) S. K. Lahiri, D. Chandra, L. H. Schwartz and M. E. Fine: Trans. AIME, 245 (1969), 1865.
6) S. R. Goodman, S. S. Brenner and J. R. Low: Metall. Trans., 4 (1973), 2363.
7) M. K. Miller, K. F. Russell, P. Pareige, M. J. Starink and R. C. Thomson: Mater. Sci. Eng., A250 (1998), 49.
8) P. J. Othen, M. L. Jenkins, G. D. W. Smith and W. J. Pythian: Philos. Mag. Lett., 64 (1991), No. 6, 383.
9) N. Maruyama, M. Sugiyama, T. Harada and H. Tamehiro: Mater. Trans., JIM, 40 (1999), No. 4, 268.
10) K. Osamura, H. Okuda, S. Ochiai, M. Takashima, K. Asano, M. Furusaka, K. Kishida and F. Kurosawa: ISIJ Int., 34 (1994), No. 4, 359.
11) E. Hornbogen, G. Lütjering and M. Roth: Arch. Eisenhüttenwes., 37 (1966), 523.
12) Y. Estrin: in Unified Constitutive Laws for Plastic Deformation, Academic Press, London, (1996), 1.
13) A. K. Lis, M. Mujahid, C. I. Garcia and A. J. DeArdo: Proc. of the Gilbert R. Speich Symp. Fundamentals of Aging and Tempering in Bainitic and Martensitic Steel Products, ISS, Warrendale, PA, (1992), 129.
14) W. J. Phythian, A. J. E. Foreman, C. A. English, J. T. Buswell, M. Hetherington, K. Roberts and S. Pizzini: Proc. of the 15th Int. Symp. on the Effect of Radiation on Materials, ASTM, West Conshohocken, PA, (1992), 131.
15) M. Charleux, F. Livet, F. Bley, F. Louchet and Y. Brechet: Philos. Mag. A, 73 (1996), No. 4, 885.
16) S. K. Lahiri, D. Chandra, L. H. Schwartz and M. E. Fine: Trans. AIME, 245 (1969), 1865.
17) M. K. Miller, K. F. Russell, P. Pareige, M. J. Starink and R. C. Thomson: Mater. Sci. Eng., A250 (1998), 49.
18) P. J. Othen, M. L. Jenkins, G. D. W. Smith and W. J. Pythian: Philos. Mag. Lett., 64 (1991), No. 6, 383.
19) N. Maruyama, M. Sugiyama, T. Harada and H. Tamehiro: Mater. Trans., JIM, 40 (1999), No. 4, 268.
20) K. Osamura, H. Okuda, S. Ochiai, M. Takashima, K. Asano, M. Furusaka, K. Kishida and F. Kurosawa: ISIJ Int., 34 (1994), No. 4, 359.
21) E. Hornbogen, G. Lütjering and M. Roth: Arch. Eisenhüttenwes., 37 (1966), 523.
22) Y. Estrin: in Unified Constitutive Laws for Plastic Deformation, Academic Press, London, (1996), 1.
23) O. Glatter and O. Kratky: Small Angle X-ray Scattering, Academic Press, London, (1982).
24) D. T. Cromer and D. A. Liberman: J. Chem. Phys., 53 (1970), 1891.
25) D. T. Cromer and D. A. Liberman: Acta Crystallogr., A37 (1981), 267.
26) U. F. Kocks: J. Eng. Mater. Technol., 98 (1976), 76.
27) H. Mecking and U. F. Kocks: Acta Metall., 29 (1981), 1865.
28) R. Onodera and N. Mizui: Tetsu-to-Hagané, 79 (1993), No. 6, 53.
29) L. M. Brown and R. K. Ham: Strengthening Methods in Crystals, ed. by A. Kelly and R. B. Nicholson, Applied Science Publishers, London, (1965), 10.
30) A. J. Ardell: Metall. Trans., 16A (1985), 21.
The scattering per unit volume of precipitate is given by

\[ \text{SAXS} \propto \text{radius of a precipitate and the scatter} \]

The intensity of scattering in the experimental distribution was 0.25. Starting from this distribution is then given by

\[ \text{Fig. A1.} \]

Simulated scattering curve for a log-normal distribution of spherical precipitates. \[ \text{Fig. A2.} \]

The resulting simulated scattering curve can be represented in a Guinier plot, as shown in Fig. A2 for an average radius of 4 nm. The Guinier plot shows a linear portion from which the Guinier radius can be calculated. However, it is frequently difficult to choose a linear portion from experimental data, particularly when scattering is weak, as in the present case. Alternatively, the plot of \( I \cdot q^2 \) vs. \( q \) can be used for further analysis. As shown in Fig. A2, this curve shows a maximum as a function of \( q \) for the simulated precipitate distribution. This maximum which is also clearly observed in the experimental spectra is closely related to the average precipitate radius. A series of simulations were carried out in order to calibrate the relationship between the average precipitate radius and the scattering vector \( q_{\text{max}} \) at which the maximum of \( I \cdot q^2 \) occurs. In all the simulations the width of the log-normal distribution was taken as 0.25. A nearly perfect linear relationship was found between the Guinier radius \( R_g \) and the reciprocal of \( q_{\text{max}} \) such that

\[ R_g = \frac{1.7}{q_{\text{max}} (I \cdot q^2)} \] .................(A-4)

This relationship has been used to access the precipitate sizes.

From the area under the \( I \cdot q^2 \) curve, i.e. the integrated intensity, \( Q_{\text{v}} \) may be calculated; i.e.,

\[ Q_{\text{v}} = \int_0^{q_{\text{max}}} I(q)q^2dq \] .................(A-5)

The value of \( Q_{\text{v}} \) has been shown to only depend on the volume fraction and composition of the precipitates

\[ Q_{\text{v}} = 2\pi\rho(\rho_f,\Delta\rho)(1-f_c)(\Delta \rho)^2 \] .................(A-6)

where \( \Delta \rho = \Delta Z_{\text{app}}/\Omega \) is the difference in electronic density between the matrix and the precipitate. \( \Delta Z_{\text{app}} \) is 8.09 (see Sec. 2.3), \( \Omega \) is the atomic volume of copper (11.8 Å³) and \( f_c \) is the volume fraction of the precipitates. This equation can be used for the determination of the precipitated volume fraction, provided that the composition of the precipitates is known. It will be assumed that the precipitates only contain copper and this remains constant throughout the aging process.

Appendix

In order to relate the scattering curves of the SAXS experiments to radius and volume fraction of precipitates, assumptions have to be made regarding shape and size distribution of the precipitates. Based on the TEM observations, the precipitate distribution can be approximated with a log-normal distribution of spheres. Figure A1 shows the comparison of the experimental distribution measured by image analysis for the 110 h aged un-deformed material and a log-normal distribution defined as:

\[ f(R) = \frac{1}{\alpha R^2 2\pi} \exp\left(-\frac{1}{2} \left( \frac{\ln(R/R_0)}{\alpha} \right)^2 \right) \] .................(A-1)

with \( R = 4.5 \) nm is the average radius and \( \alpha \) is the dimensionless parameter describing the width of the size distribution. The value of \( \alpha \) chosen to obtain good agreement with the experimental distribution was 0.25. Starting from this log-normal distribution, it is now possible to calculate theoretically the scattering curve. The intensity of scattering in SAXS is related to the radius of a precipitate and the scattering vector, \( q = 4\pi \sin\theta/\lambda \). For a single sphere of radius, \( R \), the scattering per unit volume of precipitate is given by [17]:

\[ I_k(q) = A \frac{\sin(q \cdot R) - q \cdot R \cdot \cos(q \cdot R)}{q^2 R^2} \] .................(A-2)

The total scattering from the entire precipitate size distribution is then given by

\[ I(q) = \int_0^{\infty} I_k(q)f(R)dR \] .................(A-3)

\[ \text{Log-normal law} \]
\[ \text{Image analysis} \]
\[ \text{Undeformed material} \]
\[ \text{100h aging} \]

![Fig. A1. Best fit of a log-normal law to the TEM-determined precipitate size distribution. Average radius was 4 nm and the width of the distribution, \( \alpha \), was 0.25.](image)

![Fig. A2. Simulated scattering curve for a log-normal distribution of spherical precipitates. Average radius was chosen to be 4 nm, and the width of the distribution, \( \alpha \) was 0.25.](image)