1. Introduction

The interest of copper precipitation in steels is currently receiving much attention, notably with respect to precipitation hardened high strength low alloy (HSLA) steels, which 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.

The model Fe–Cu system has itself received much attention, and particularly in terms of the influence of irradiation on the precipitation process and the related embrittlement of the steels, for nuclear power plants applications. Extensive studies using lately high resolution transmission electron microscopy (HRTEM) or X-ray absorption techniques such as EXAFS and XANES, have determined the precipitation sequence applicable to these alloys:

(supersaturated solid solution) → BCC copper → 9R copper → FCC

as well as the mechanisms associated with the transformation from one family into another.

Although the detailed analysis available on the Fe–Cu system has been much used to interpret the hardening observed in copper bearing steels, very little data is available which directly compares the precipitation kinetics and hardening in the two systems. The purpose of the present paper is to present a comparative experimental characterisation of the precipitation kinetics and the associated change in mechanical properties in a Fe–Cu alloy and a copper-bearing low carbon steel, both containing 0.8 wt% copper. Since HSLA steels often contain a high density of transformation-induced dislocations, the precipitation behaviour will be also investigated in the case of a pre-deformed material.

The characterisation of precipitation kinetics has been carried out by Transmission Electron Microscopy, the mechanical properties have been assessed by hardness measurements.

KEY WORDS: Fe–Cu alloy; low-carbon steel; precipitation kinetics; precipitation hardening; dislocations; strain hardening; Small-angle Scattering.

2. Materials and Methods

The compositions of both materials is shown in Table 1 (all in wt%).

The Fe–Cu alloy was received as forged bar. 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, as shown in Fig. 1(a).

The steel was received after hot rolling and coiling at 570°C. Resolutionising was carried out 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, as shown in Fig. 1(a).

The steel was received after hot rolling and coiling at 570°C. Resolutionising was carried out for 5 h at 820°C in
a vacuum furnace, which falls into the austenite/ferrite two-phase region for this steel. The samples were then air-quenched to approximately 700°C to enable the transformation of the austenitic fraction into equiaxed ferrite and then quenched into cold water. After this quench some non-equilibrium structure remained, which was annealed for 5 h at 350°C in order to avoid interference of this tempering with precipitation during the ageing treatment. Presumably, in the absence of a significant dislocation density, no precipitation should occur during this pre-ageing treatment.14) The resulting microstructure is shown in Fig. 1(b), it consists of equiaxed ferrite grains of diameter $d = 10 \mu m$, with the dark areas being coarsened bainite. 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%. Ageing treatments were conducted in a salt bath at 500°C for ageing times of up to 8 h. For longer ageing times, the samples were sealed in a quartz tube under vacuum and placed in an air furnace at 500°C.

Transmission Electron Microscopy observations were carried out on a H-800 Hitachi microscope operating at 200 kV. Samples for transmission electron microscopy were prepared by electropolishing in a 5% perchloric acid–95% acetic acid solution, held at 15°C using a voltage of 70 V.

Small-Angle X-ray Scattering experiments were conducted on the D2AM beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble. A wavelength, $\lambda$, of 1.745 Å was chosen corresponding to an energy of 7.104 keV. The beam was highly monochromatic with $\Delta\lambda/\lambda = 10^{-4}$. The X-ray energy is close to the Fe edge in order to maximise the contrast between the precipitates and the matrix while limiting the fluorescence of Fe, using the anomalous scattering behaviour. Samples for SAXS measurements were mechanically thinned to 40 μm, and then electropolished in the same conditions as the TEM foils. 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 $4 \times 10^{-3}$ and 0.25 Å$^{-1}$ could be measured. The recorded intensity was then corrected for background noise and normalised to absolute intensity $I$. Details of the experimental method can be found in Ref. 15).

Microhardness measurements were carried out with a load of 0.5 kg.

3. Microstructure Evolution

The aim of the microstructural investigation was to compare the precipitation nature and kinetics in the two materials, namely:

- Morphology and size evolution of the precipitates.
- Response of the precipitation reaction to the presence of structural defects (dislocations).

3.1. Undeformed Material

The microstructure was first investigated by means of TEM in the over-aged state. Figure 2 shows the microstructures of the steel and the Fe–Cu alloy after 1000 h at 500°C, where all precipitates are expected to be of the equilibrium $\varepsilon$ phase. Both materials show a comparable homogeneous distribution of somewhat faceted precipitates. However, it appears immediately that the precipitate sizes are different: precipitates are much smaller in the Fe–Cu alloy.

This effect was quantified by image analysis of the TEM micrographs in the case of the 1000 h ageing treatment. Figure 2 shows the precipitate size distributions for both materials. Although the two distributions are quite similar in shape (close to a log-normal distribution law), the average diameter of the Fe–Cu alloy is much smaller (19 nm) than for the steel (24 nm).

The difference in kinetics between the steel and the iron–copper alloy has been further investigated by SAXS. Figure 3 shows the SAXS spectra for the two alloys as a function of ageing time between 5 h and 300 h at 500°C. In this type of plots ($I \cdot q^2$ vs. $q$), a given precipitate population gives a maximum in the scattering signal. The scattering vector at which this maximum occurs is related to the average radius of the precipitates by an inverse relationship:

$$ R = \frac{1}{q_{\text{max}}} $$

Moreover, the volume fraction of precipitates is proportional to the integrated intensity $Q_o$ of the spectrum, which is the area under the curve in the plots of Fig. 4:
However, the first ageing time (5 h at 500°C), does not show any visible scattering signal related to fine-scale precipitates, either in the case of the Fe–Cu alloy of in the case of the steel. Thus the existing scattering signal (leading to the substantial integrated intensity 0.024 Å\(^2\)/H11061 in the case of the Fe–Cu and 0.04 Å\(^2\)/H11061 in the case of the steel) is related to the presence of other scattering centres, such as dislocations, grain boundary precipitates, and possibly the presence of double Bragg diffraction in the detector. In consequence, we will subtract this initial integrated intensity for the calculation of the precipitate volume fraction, leading to the following calculation:

\[
Q_u = \sum q^2 dq
\]

Where \(\Delta \rho\) is the difference in apparent electronic density between the precipitate and matrix (taking into account the anomalous scattering effect).

The data in Table 2 is graphically represented in Fig. 4. At the shortest ageing time where a signal was recorded (15 h), the precipitate radius in both materials is similar (about 2.5 nm). Although some precipitation may have occurred before 15 h (as will be seen by hardness measurements), it is quite safe to assume that this size is close to the nucleation radius of precipitates. However, for longer ageing times the growth rate of precipitates is markedly different in both materials, namely much faster in the steel, corresponding to the above TEM measurements. Moreover, the increase of the integrated intensity is much faster in the steel as compared to the iron–copper alloy, which shows that the equilibrium volume fraction is attained earlier. However, the final value of this integrated intensity is similar in the two materials, confirming that the copper solubility is not very different. Taking the volume fraction attained after the longest ageing time as close to equilibrium (namely 0.6%), one can estimate the solubility of copper at 500°C to close to 0.1%. However, the precision of this figure, related with large sensitivity to the precision of the SAXS intensity calibration, is quite low.

It has to be pointed out that the calculation of the precipitate sizes and of the integrated intensity is much more reliable in the Fe–Cu system as compared to the steel: in the steel some extra scattering centres such as other precipitates (e.g., AlN, cementite, ...), which have high contrast with the matrix (because of very different average atomic number), disturb the signal from copper precipitates.

### 3.2. Pre-deformed Material

The influence of a pre-deformation (and thus of the introduction of dislocations prior to the precipitation process) on the precipitation state is shown in Fig. 5, both after a 100 h and a 1800 h ageing treatment. Qualitatively, the effect of predeformation on both alloys is similar on the microstructural viewpoint. After 100 h, a majority of particles are located on dislocations, although some homogeneous particles are also present. The homogeneous particles are more equiaxed than the particles located on dislocations, which...
are elongated when the dislocation line is favourably orient-
ed with respect to a preferential growth direction of the pre-
cipitate. In the coarsened state (1 000 h at 500°C), the pro-
portion of particles not located on dislocations is further re-
duced, showing that particles on dislocations are both ener-
geetically and kinetically favoured.

For the Fe–Cu alloy, the influence of predeformation on
the precipitation kinetics has been quantitatively assessed
by SAXS measurements. Results are shown in Fig. 4, in
parallel with the kinetics of the undeformed material. The
nucleation radius is not much affected by the predeforma-
tion, however the nucleation rate is much larger, leading to
significantly larger volume fractions at low ageing times.
However, at long ageing times, the coarsening stage does
not seem to be affected by the presence of the residual dis-
locations, and both size and volume fractions are similar in
the deformed and undeformed materials.

4. Precipitation Strengthening

The ageing curves for the Fe–Cu alloy and the Cu-con-
taining steel are shown in Fig. 6. The general shapes of the
two ageing curves are similar: one can observe an incuba-
tion time, followed by a rapid increase in hardness, and
then a peak strength and over-ageing regime. However, im-
portant differences arise: the Fe–Cu alloy shows significant-
ly higher peak strength (65 HV vs. 50 HV), and longer time
to reach this peak strength (30 h vs. 10 h).

The strengthening response of the two materials to a pre-
deformation is very similar, as shown in Fig. 7:
(i) both materials retain their pre-deformed strength in
the first stages of ageing;
(ii) although the precipitation strengthening of the pre-
deformed state, compared to the as-deformed hardness, is
smaller when compared to the undeformed materials, the
overall peak strength is increased by pre-deformation;
(iii) in both materials the time to peak strength is re-
duced by the presence of dislocations;
(iv) in the over-aged state, both pre-deformed materials
loose most of their advantage as compared to the unde-
formed materials. This observation, together with the slight
initial decrease of yield strength during the first hour of ageing (whereas the undeformed material hardens) demonstrates that significant static recovery occurs during the ageing treatment.

5. Discussion

From the present results we can conclude that the precip-

![Fig. 5. Precipitate microstructures in the pre-deformed materials aged at 500°C: (a) Fe–Cu, 100 h; (b) Fe–Cu, 1000 h; (c) steel, 100 h; (d) steel, 1000 h.](image)

![Fig. 6. Change in hardness during the 500°C ageing treatment in the steel and the Fe–Cu alloy. Note that the initial hardness of the steel (118 HV) is larger than that of the Fe–Cu alloy (89 HV).](image)

Fig. 7. Influence of pre-deformation on the change in hardness during a 500°C ageing treatment on the Fe–Cu alloy and the steel. In both cases the reference hardness corresponds to the undeformed material.
The nucleation size of precipitates is identical in both materials (namely about 2.5 nm). The effect of precipitates on the mechanical properties is also similar.

However, despite this identical qualitative behaviour, important quantitative differences are shown in the present study, which can be summarised in the following points:

(i) Although the nucleation size is identical in the two alloys, the growth rate of the particles are vastly different: after 100 h at 500°C, we measure a factor of 2 in the precipitate size. Accordingly, the evolution of the volume fraction is also much faster in the steel as compared to the Fe–Cu alloy.

(ii) Concerning the hardness (or yield stress) evolution, the net precipitation hardening $\Delta H_{\text{net}}$ is much smaller in the steel as compared to the Fe–Cu alloy, and occurs at a much earlier ageing time (10 h vs. 30 h at 500°C). Only in the first hours of ageing is the precipitation hardening of the steel larger in magnitude, corresponding to the faster precipitation kinetics.

In terms of chemical composition, the Fe–Cu alloy and the steel are mainly different through their carbon content (650 and 14 ppm respectively), and the Mn composition (0.35 vs. 0.03 wt%). The influence of carbon and manganese on the precipitation of copper has been investigated by a few authors. The effect can be summarised as follows:

- Wada and co-workers$^{16}$ have compared the hardness increase due to copper precipitation as a function of the carbon content (Cu content was 1.5 wt%). No influence of carbon on the time for the peak hardness was recorded, and the peak hardness was observed to increase with increased carbon content. However, the net increase in hardness due to precipitation $\Delta H_{\text{Cu}}$ was observed to decrease with increased carbon content. More recently, Kohji and co-workers$^{17}$ found by resistivity measurements an interaction energy between Cu and C atoms of approximately 0.3 eV.

- Wada and co-workers$^{16}$ investigated as well the effect of Mn on the copper precipitation process. The addition of 1.3% Mn was observed to decrease significantly the time to peak hardness, but to leave unchanged the net hardness increase due to precipitation. This was confirmed in terms of precipitation kinetics by Maury and co-workers,$^{10}$ who found that the precipitate size in a Fe–Cu–Mn alloy were larger than in a Fe–Cu alloy of same copper content (namely 1.3%). The same authors did not find however any evidence of the presence of Mn inside the copper precipitates (as determined by X-ray absorption methods).$^{16,10}$ This is in contradiction with the results of Maruyama,$^{9}$ who found from FIM measurements evidence for Mn segregation at the iron/copper interface. However, this author found as well an acceleration of the precipitation kinetics with the addition of manganese.

Our present results are in general agreement with these former studies. Having directly access to the precipitation kinetics, we can confirm that the growth rate of precipitates in the steel is much larger than in the iron–copper alloy.

This does not seem to be related to the carbon content: the binding energy between carbon and copper atoms would slow down the diffusion process rather than accelerate it. Thus it seems that the Mn addition should explain the difference in precipitation kinetics. If this interpretation is correct, then the effect of Mn for accelerating the precipitation kinetics is effective at much lower concentrations that what was observed earlier: in the above-mentioned studies, Mn concentration was always approximately 1.3 wt%.

In terms of precipitation strengthening, we have observed simultaneously a decrease in the time to peak strength, and a decrease in the net strengthening related to precipitation. The first point is coherent with the effect of Mn. As discussed above, many authors have observed this effect, even though it has been for higher Mn contents. However, the decrease in the net hardening ability is more likely to be related to the carbon content. This is in agreement with the results of Wada et al., and is most probably related to the initial strength of the steel as compared to the Fe–Cu alloy.

In our case, the yield strength of the Fe–Cu alloy in the as-quenched condition is 170 MPa, whereas the yield stress of the steel is 300 MPa. A large part of this difference can be attributed to the difference in grain size and solute content, which can be estimated using the empirical relationship by Choquet et al.,$^{19}$ established for plain carbon steels:

$$\sigma_{\text{YS}} = \sigma_{\text{YS}} + \left\{ \begin{array}{l}
15.4 - 30C + \frac{6.094}{0.8 + \text{Mn}} \\
\end{array} \right\} d^{-1/2}
$$

with $\sigma_{\text{YS}} = 63 + 23\text{Mn} + 53\text{Si} + 700\text{P}$

all concentrations being in wt%, and the ferrite grain size $d$ in mm.

This relationship gives 166 MPa for the Fe–Cu alloy, in excellent agreement with the experimental value, and 258 MPa for the steel, which is substantially lower than the value experimentally measured. The difference is related to the islands of high carbon concentration, containing the hard cementite phase (which we estimate as 8% in volume fraction from image analysis of optical micrographs), which have a much higher hardness.

Both the solid solution hardening and the grain size contributions of the steel yield strength are expected to add linearly to the precipitation hardening. However, the hard regions of the steel can lead to a decreased apparent precipitation strengthening, either by some recovery of this strength during the ageing at 500°C (even though tempering at 350°C has been carried out prior to the precipitation ageing treatment), either simply by an effect of the mixing law between the hardening contributions of these regions and of the precipitated ferrite grains. A last explanation would be a reduced copper concentration inside the ferrite grains due to segregation of copper in the carbon-rich zones; however this is unlikely, since a reduced amount of copper would tend to slow down the precipitation kinetics,$^{20}$ as well as reduce the precipitated volume fraction, both effects being contradictory with the present results.

6. Conclusion

(i) The precipitation behaviour of copper in pure Iron
and in the low-carbon steel are qualitatively identical. The nucleation size at 500°C are similar, the effect of the presence of dislocations is similar both in terms of precipitation location and resultant hardening. In both materials a minimum in strain hardening capability is encountered in the over-aged material.

(ii) Important quantitative differences in the precipitation kinetics of the two materials are observed. The precipitate growth is much faster in the steel as compared to the iron alloy. In consequence, the time to peak hardness is much reduced in the steel. The net hardening capability of the steel is however much smaller than the hardening capability of the Fe–Cu alloy, although in absolute value it has a higher strength due to solute and grain size hardening. These differences are most probably related to the influence of Mn, which accelerates the precipitation kinetics, and of carbon, which reduces the hardening potential due to the mixing law between the hard cementite-containing regions and the precipitation-hardened ferrite.

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REFERENCES

1) M. T. Miglin, J. P. Hirth, A. R. Rosenfield and W. A. T. Clark: Metall. Trans. A, 17A (1986), 791.
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, Warrensdale, PA, (1992), 129.
3) G. Banadkouki, D. Yu and D. P. Dunne: ISIJ Int., 36 (1996), 61.
4) M. K. Banerjee, P. S. Banerjee and S. Datta: ISIJ Int., 41 (2001), 257.
5) S. K. Dhua, A. Ray and D. S. Sarma: Mater. Sci. Eng. A, 318 (2001) 197.
6) S. K. Dhua, D. Mukerjee, D. S. Sarma: Metall Mater. Trans. A, 32A (2001) 2259.
7) T. Llewellyn: Ironmaking Steelmaking, 22 (1995), No. 1, 25.
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. Hara and H. Tamehiro: Mater. Trans., JIM, 40 (1999), No. 4, 268.
10) F. Maary, N. Lorenzelli, M. H. Mathon, C. H. De Novion and P. Lagarde: J Phys. Condens. Matter, 6 (1994), 569.
11) S. Pizzini, K. J. Roberts, W. J. Pythian, C. A. English and G. N. Grevaxes: Philos. Mag. Lett., 61 (1990), No. 4, 223.
12) R. Monzen, M. L. Jenkins and A. P. Sutton: Philos. Mag. A, 80 (2000), 711.
13) Y. Le Bouar: Acta Mater., 49 (2001), 2661.
14) R. Onodera and N. Mizui: Tetsu-to-Hagané, 79 (1993), 671.
15) A. Deschamps, M. Militzer and W. J. Poole: ISIJ Int., 41 (2001), 196.
16) H. Wada, Y. Houbaert, J. Penning and J. Dibvija: ATB Metall., 23 (1983), 31.
17) K. Takazawa, S. Noto and K. Tagashira: Tetsu-to-Hagané, 83 (1997), 760.
18) F. Maary, N. Lorenzelli, Ch. de Novion and P. Lagarde: Scr. Metall. Mater., 25, (1991), 1839.
19) P. Choquet, P. Fabrége, J. Giusti, B. Chamont, J. N. Pezant and F. Blanchet: Mathematical Modelling of Hot Rolling of Steels, ed. by S. Yue, The Metall. Soc. of CIM, Montreal, (1990), 34.
20) J. Liu, D. Xue, D. Wang, L. Gao, M. Wen, S. Luo, P. Li, J. Gui and R. Wang: ISIJ Int., 39 (1999), 614.