

Effect of carbon on copper precipitation in deformed Fe-based alloys studied by positron annihilation spectroscopy

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Abstract. The role of deformation-induced defects and carbon addition on the copper precipitation during aging at 550 °C is investigated in high-purity Fe-Cu-B-N-C alloy samples by Coincidence Doppler Broadening. In samples with 0% and 8% cold pre-strain, the influence of tensile pre-deformation on the precipitation kinetics of copper is studied. The deformation-induced defects are found to enhance the Cu precipitation kinetics. A sharp reduction in open volume defects is accompanied with a strong increase of Cu signature during the initial stage of aging, implying that the open defects (mainly dislocations) act as nucleation sites for Cu precipitates. A comparison of the time evolution of *S-W* plots between Fe-Cu, Fe-Cu-B-N, and Fe-Cu-B-N-C alloys indicates that the addition of carbon does not alter the Cu precipitation mechanism but decelerates the kinetics.

1. Introduction

Recently, we studied the copper precipitation behavior in Fe-Cu and Fe-Cu-B-N alloys during aging by positron annihilation spectroscopy and neutron scattering to evaluate the potential contribution of Cu precipitation to self-healing of open volume defects created by prior plastic deformation [1,2]. Carbon, being the primary alloying element in steel, is widely used to raise the mechanical properties of the steel, such as tensile strength, hardness and resistance to wear and abrasion. For copper containing iron-based alloys, it is therefore of importance to clarify the influence of carbon on the Cu precipitation behavior in iron-based alloys. In earlier studies the carbon content was found to affect the activation energy of Cu diffusion in steel [3]. Positron annihilation has successfully been utilized to study the interaction of irradiation-induced vacancies and carbon in the Fe matrix [4,5]. Carbon was demonstrated to act as trapping site for vacancies and to form carbon-vacancy pairs, which favor the formation of precipitates. The effect of carbon on the deformation-induced Cu precipitation, however, has attracted limited attention. It is therefore desirable to investigate the influence of carbon on the



copper precipitation behavior, which is assumed to lead to self-healing in Fe-Cu and Fe-Cu-B-N alloys under higher temperature loading conditions. In the present paper, we investigate the influence of carbon on the copper precipitation during thermal aging in deformed and un-deformed Fe-Cu-B-N-C alloys using positron annihilation spectroscopy.

2. Experimental

The composition of the Fe-Cu-B-N-C alloy produced by Goodfellow Ltd is in Table 1. The Ce was added to prevent S segregation at grain boundaries. Dog-bone shaped samples with a thickness of 0.5 mm were machined by spark erosion from the rolled sheet material. The samples were solution treated at 800 °C for 3 h in evacuated silica tubes filled with 200 mbar ultrahigh purity argon, and subsequently quenched into water at room temperature. Some samples were tensile pre-deformed at room temperature using a 2 kN microtensile tester (Deben). Vickers microhardness testing was carried out using a load of 500 g.

Table 1. The chemical composition of Fe-Cu-B-N-C alloy (in wt. %) with balance iron. The Ce concentration amounts to the nominal concentration.

Cu	B	N	C	S	Ce
1.00	0.050	0.019	0.087	0.002	0.015

The coincidence Doppler broadening (CDB) measurements were carried out by using a sandwich of two samples with a ^{22}Na positron source in between. By measuring the Doppler shift in the energy of the two 511 keV annihilation γ -ray, one obtains the information on the momentum distribution of the electrons involved in the positron annihilation. In comparison with the conventional 1-detector measurement, the 2-detector technique results in a significant improvement in the peak-to-background ratio, with better energy resolution. The overall energy resolution was 1 keV at 511 keV, corresponding to a momentum resolution of $4 \times 10^{-3} m_0c$ (full width at half maximum, FWHM).

3. Results and discussion

Figures 1 and 2 show the time evolution of the CDB ratio curves of the Fe-Cu-B-N-C alloy with 0% and 8% pre-strain, respectively. The momentum distribution is represented in relative terms as $(\rho - \rho_{Fe})/\rho_{Fe}$, where ρ is the momentum spectrum for the positron annihilation in the samples and ρ_{Fe} is the momentum spectrum measured on annealed (defect-free) pure iron. The CDB ratio curve for a pure bulk copper sample shows a broad peak at around $24 \times 10^{-3} m_0c$, which is the characteristic feature for the 3d electrons of Cu. In the low momentum region ($< 5 \times 10^{-3} m_0c$), the presence of open-volume defects as positron trapping sites is the dominant contribution to the variation in the momentum distribution [6].

As shown in figure 1, for the as-quenched Fe-Cu-B-N-C alloy, the Cu peak intensity continuously grows with aging time up to 1 h, followed by gradual decrease at longer aging times. Simultaneously, a continuous rise is observed in the low-momentum region, suggesting that the formation of new open-volume defects is associated with the formation of Cu precipitates. For the deformed Fe-Cu-B-N-C alloy (figure 2), a similar evolution of the CDB curves is observed. The broad peak in the low p_L region before aging is attributed to the positron trapping at open-volume defects introduced by cold deformation (8% pre-strain). During the subsequent initial aging up to 1 h, the peak obviously decreases while the copper peak gradually increases, implying a simultaneous reduction of the open-volume defects with the formation of copper precipitates.

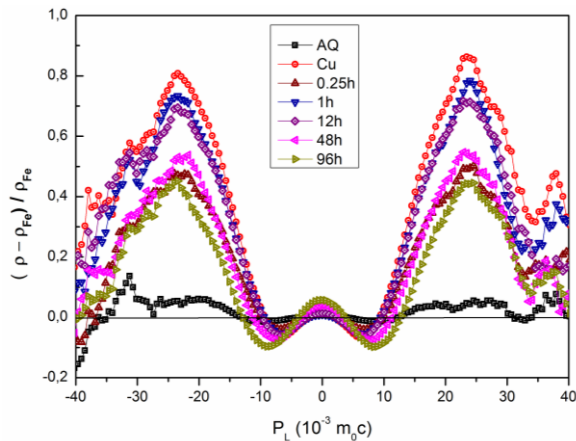


Figure 1. Coincidence Doppler Broadening relative to annealed iron $(\rho - \rho_{Fe})/\rho_{Fe}$, as a function of the electron momentum p_L for the Fe-Cu-B-N-C alloy with 0% pre-strain.

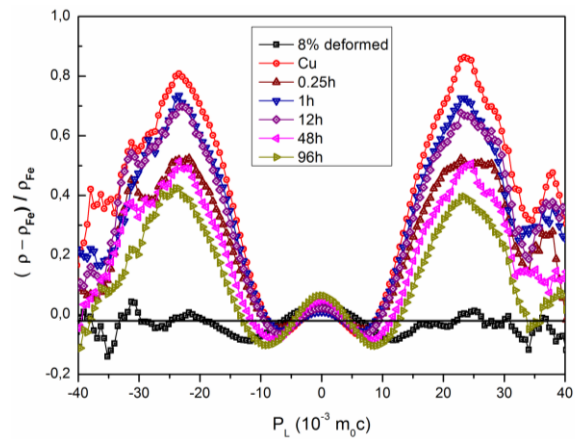


Figure 2. Coincidence Doppler Broadening relative to annealed iron $(\rho - \rho_{Fe})/\rho_{Fe}$, as a function of the electron momentum p_L for the Fe-Cu-B-N-C alloy with 8% pre-strain.

Figure 3 shows the evolution of the S - W points for the as-quenched and the 8% deformed sample for ageing at 550 °C and times up to 96 h. The parameters S and W are defined as the ratio of low-momentum ($|p_L| < 3.1 \times 10^{-3} m_0c$) and high-momentum ($9.2 \times 10^{-3} m_0c < |p_L| < 24.3 \times 10^{-3} m_0c$) regions to the total region, respectively. All S - W points are normalized to those for annealed pure iron ($S_{Fe} = 0.461$, $W_{Fe} = 0.120$). The S - W points approach the value of the annealed pure Cu after an aging time of 2-4 h for the Fe-Cu-B-N-C alloy without deformation and after 1-2 h for the Fe-Cu-B-N-C alloy with 8% pre-strain. For longer aging times, a shift is observed towards a high S and a low W value, indicating that the interface between the copper precipitates and the matrix gradually loses coherency when the Cu precipitates grow during further aging [1,2]. For aging times from 4 to 96 h the evolution of the S and W parameters follows the same trajectory for the deformed and undeformed samples, where the undeformed sample lags behind with respect to the deformed sample. The faster evolution for the deformed sample indicates that the nucleation of the Cu precipitates is promoted by the open volume defects (mainly dislocations) introduced by the pre-strain. The subsequent coarsening shows a similar behavior for both alloys, while the overall precipitation kinetics is promoted by deformation.

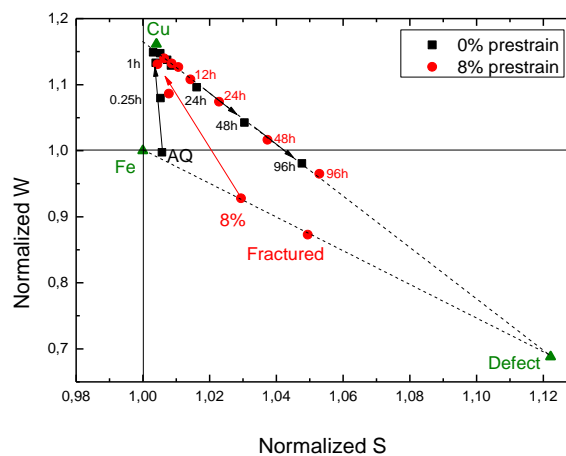


Figure 3. Time evolution of S and W parameters for the as-quenched Fe-Cu-B-N-C alloy with 0% and 8% pre-strain.

To clarify the role of carbon on the copper precipitation during aging, we compare the S - W plot of the deformed Fe-Cu-B-N-C alloy with that of the deformed Fe-Cu and the deformed Fe-Cu-B-N. It is interesting to note that the addition of carbon decelerates the Cu precipitation, which is opposite to the effect of boron and nitrogen. The S - W point of the deformed Fe-Cu-B-N-C alloy annealed for 1 h overlaps with that of the Fe-Cu alloy annealed for 1 h (figure 4), whereas the S - W point of the Fe-Cu-B-N alloy after 1 h annealing is quite close to that of the Fe-Cu-B-N-C alloy annealed for 12 h (figure 5). The shift of the S - W points for the Fe-Cu-B-N-C alloy is observed to be less than that of the Fe-Cu alloy and the Fe-Cu-B-N alloy for the aging time longer than 1 h. A possible explanation for the observation is that carbon reduces the solubility of B and N in the alloy via the precipitation of boron carbides. According to Kim and co-workers [7], in boron-containing low carbon steels, $\text{Fe}_{23}(\text{B,C})_6$ particles containing N are found to precipitate at around 700 to 900 °C, which may reduce the levels of solute B and N in the matrix. Further study is required to clarify the structure of the carbides formed during the solution treatment and the following quench process.

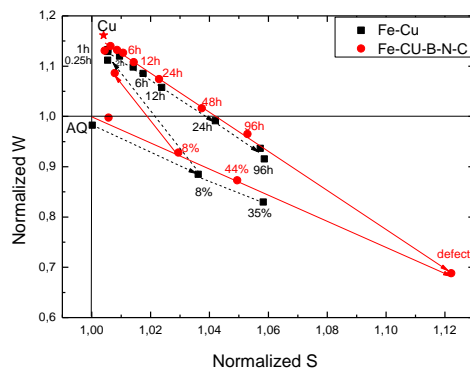


Figure 4. S - W plots of Fe-Cu and Fe-Cu-B-N-C alloys with 8% pre-strain during aging at 550 °C for 96 h.

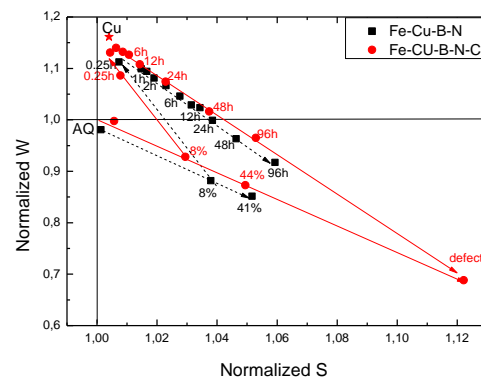


Figure 5. S - W plots of Fe-Cu-B-N and Fe-Cu-B-N-C alloys with 8% pre-strain during aging at 550 °C for 96 h.

3. Conclusions

Positron annihilation spectroscopy is a powerful technique to monitor the fine details of the Cu precipitation in a cold rolled Fe-Cu-B-N-C alloy during aging at 550 °C. During the initial aging stage, the deformed sample exhibits a sharp reduction in the defects accompanied with a strong copper signature, implying that the open defects act as nucleation sites for Cu precipitates and accelerate the precipitation. A comparison between the S - W plots for Fe-Cu, Fe-Cu-B-N, and Fe-Cu-B-N-C alloys indicates that the addition of carbon decelerates the kinetics of Cu precipitation but does not change the mechanism.

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