In situ small-angle neutron scattering study of the early stages of precipitation in Fe-25at% Co-9at% Mo and Fe-1at% Cu at 500 °C

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Abstract. The early stages of precipitate formation in Fe-25at% Co-9at% Mo at 500 °C was investigated by in situ small-angle neutron scattering (SANS). The ratio of magnetic to nuclear SANS intensity, which depends on the precipitate composition, and the precipitate sizes were analyzed. The results suggest that in the Fe-Co-Mo alloy an initial stage of precipitate formation with strong compositional changes is completed after 150 s, when the full magnetic signal is established. For comparison, the well-known nucleation and growth reaction in Fe-1at% Cu was studied. Differences in the growth rate of the mean size of the developing structures could be distinguished in the two investigated alloys. While in the Fe-Co-Mo alloy the precipitate structures grow with $t^{0.15}$ to $t^{0.21}$, the mean precipitate radius in the Fe-Cu alloy grows with $t^{0.40}$ in the observed time interval.

1. Introduction

The ternary system Fe-Co-Mo has been investigated since the 1930s, where Köster and Tonn first mentioned a possible strengthening mechanism due to precipitation of intermetallic phases from a strongly supersaturated matrix [1]. Today, it is known that hardness values over 68 HRC can be achieved in this material. These alloys are promising technical materials because they also possess a high thermal microstructural stability in the hardened state [2].

The precipitates that are responsible for this hardening consist of Fe, Co, and Mo and have sizes of a few nanometers. According to literature, formation of the so-called µ-phase of the composition (Fe,Co)7Mo6 is accountable for the hardening in ternary Fe-Co-Mo alloys. This phase can be considered as a solid solution of the two intermetallic phases Fe7Mo6 and Co7Mo6 found in the binary systems Fe-Mo and Co-Mo [3, 4]. Both binary phases exhibit an ordered rhombohedral structure with almost identical lattice parameters [4]. While results on mechanical properties of Fe-Co-Mo alloys like hardness, toughness, or tensile strength can be found in the literature [1, 2], little is known about the formation mechanism of the hardening phases in these alloys (i.e. µ-phase or possible metastable precursor phases).
In order to contribute to the clarification of the precipitate formation mechanism of the $\mu$-phase, non-isothermal experiments were conducted by Leitner et al. on a Fe-25at% Co-9at% Mo alloy, employing differential scanning calorimetry and 3D atom probe microscopy (3DAP) \cite{5}. It was shown that the formation of the $\mu$-phase takes place via clustering of Mo in the matrix. The peak hardness of the alloy was reached after solution annealing, followed by quenching to room temperature, and subsequent continuous heating up to about 615 °C. However, the interpretation of the 3DAP results obtained by Leitner et al. \cite{5}, especially with regard to precipitate size and volume fraction, was difficult because of the very small analyzed volumes of $7 \times 7 \times 80$ nm$^3$. The small cross-section of the analyzed volume leads to cutting off larger particles, influencing e.g. the mean particle size.

In contrast to microscopic methods, small-angle neutron scattering (SANS) yields information from a relatively large volume and thus gives mean values over a very large number of precipitates, which makes it very sensitive to small changes in the size and volume fraction of precipitates. In the present study, SANS was used for the first time to observe the early stages of precipitate formation in Fe-25at% Co-9at% Mo at 500 °C in an in situ experiment. An Fe-1at% Cu alloy was studied for comparison because it is a simple binary system, in which Cu precipitates are formed by nucleation and growth.

2. Experimental procedure
The exact compositions of the studied samples were Fe-25.1at% Co-9.3at% Mo-0.4at% Si-0.1at% C and Fe-1.0at% Cu. A new in situ furnace for ferromagnetic samples was used for the first time for this study, allowing a heating rate of 5 K/s. The samples with a diameter of 25 mm and a thickness of 1.8–2.0 mm were heated in the furnace that was placed between the pole shoes of an electromagnet so that the ferromagnetic samples could be magnetized to saturation during the measurements. The furnace had two ceramic heating elements with direct contact to the sample. The heating elements were in a vacuum chamber with water-cooled outer walls and 1 mm thick Al windows for the neutron beam. A heat shield was not used at the moderate temperature of 500 °C for avoiding additional background. Heating up to a nominal temperature of 500 °C could be performed within about 100 s (figure 1). Temperature calibration was done in a separate run for each material with two thermocouples placed in holes drilled into the illuminated sample volume. The mean temperature within the illuminated volume was 493 °C for the Fe-Co-Mo sample and 495 °C for the Fe-Cu sample. The difference between the two materials is expected to result from different thermal conductivities.

The SANS measurements were carried out at the SANS-2 instrument of GKSS Research Centre, Geesthacht, Germany. Selector-monochromated neutrons with a mean wavelength of 0.58 nm and a wavelength spread of 10% were used. The distance between sample and detector was 1 m. The used area detector had a size of $500 \times 500$ mm and a pixel size of $2.2 \times 2.2$ mm. The data acquisition time at the beginning of the reaction was 30 s. After 30 minutes it was increased to 60 s, after additional 60 minutes it was increased to 120 s. An empty image without a sample in the beam was subtracted from all detector images. Scattering curves were corrected for sample transmission.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Temperatures measured directly at the two samples in two different runs.}
\end{figure}
Absolute cross sections were obtained by calibration with a Vanadium sample.
Details about the small-angle scattering technique can be found e.g. in [6, 7, 8]. When matrix and precipitates have different magnetizations there is a magnetic scattering contrast \( \Delta \eta_m \) in addition to the nuclear scattering contrast \( \Delta \eta_n \). \( \eta \) is the scattering length density, which is the mean coherent scattering length per volume. While nuclear scattering is isotropic, magnetic scattering depends on the angle \( \alpha \) between scattering vector and magnetization. The total contrast can be written as the sum
\[
(\Delta \eta)^2 = (\Delta \eta_n)^2 + \sin^2 \alpha (\Delta \eta_m)^2.
\]

Scattering curves of the nuclear and magnetic cross sections were calculated as azimuthal mean values within sectors parallel and perpendicular to the external field. The sector size was increased as much as possible to improve the statistics without significant smearing. The smearing effect is large for \( \alpha = 0^\circ \) where large intensity gradients are present in azimuthal direction. Finally, 20° wide sectors were used.

3. Results

3.1. Scattering curves

Selected nuclear and magnetic scattering curves for both materials are shown in figures 2 and 3. Already after 66 s, a strong intensity increase is observed in the Fe-Co-Mo alloy (figure 2). A maximum is observed in these scattering curves, resulting from a high precipitate number density. In general, Fe-Co-Mo shows stronger scattering intensity than Fe-Cu. However, in the very early stages, both intensities are quite low; therefore, integrated intensities will be discussed in the following.
3.2. Integrated intensity

The integrated small-angle scattering intensity is defined as [6]

\[ Q = 4\pi \int_0^{\infty} \frac{d\Sigma(q)}{d\Omega} q^2 dq = (2\pi)^3 f (1 - f) (\Delta\eta)^2 \]  

(2)

and is a measure for the product of particle volume fraction \( f \) and square of scattering contrast \( \Delta\eta \). The baseline of \( Q \), given by its value before precipitation starts, was subtracted for both alloys since only the contribution of newly formed precipitates was of interest. It is thus assumed that the scattering contributions to the baseline do not change significantly during decomposition.

The ratio \( R \) of integrated intensities calculated from magnetic and nuclear scattering curves,

\[ R = \frac{Q_m}{Q_n} = \frac{(\Delta\eta_m)^2}{(\Delta\eta_n)^2}, \]

(3)

reflects the ratio of scattering length density differences squared, \((\Delta\eta_m)^2\) and \((\Delta\eta_n)^2\), as long as both scattering contributions originate from the same structure with the same volume fraction \( f \). In general, \( \Delta\eta_m \) is given by the mean magnetic moments per atom in matrix and precipitate. It does not change with the chemical composition of the precipitates as long as they are not ferromagnetic. \( \Delta\eta_n \), on the other hand, changes with chemical composition. Thus, \( R \) is an indicator for chemical changes in the precipitate composition leading to changes in \( \Delta\eta_n \) and also \( \Delta\eta_m \). The hardening precipitates in the Fe-Co-Mo alloy are expected to be non-ferromagnetic with an approximate composition in later decomposition stages of 35at% Fe-41at% Mo-18at% Co-6at% Si, which was observed in a recent 3DAP study in a sample that was heated up to 615 °C [9]. In the case of ferromagnetic precipitates, the quantitative interpretation of \( R \) is more complicated because changes in the mean magnetic moment per atom also lead to changes in \( R \).

Integrated magnetic and nuclear intensities as well as the ratio \( R \) is shown for both alloys in figures 4 and 5. Figure 6 shows a comparison of \( Q_m \) and measured hardness (HV10) for both alloys.

3.3. Mean precipitate size

The interference maximum in the scattering curves of the Fe-Co-Mo alloy results from the combination of precipitate volume fraction, precipitate size and morphology, and concentration gradients between precipitate and matrix phase. While the precipitates are growing, the maximum
shifts to smaller $q$. The inverse of $q_{\text{max}}$ can be used as a measure that is proportional to the precipitate size [10]. Even if there were no particles with a sharp interface, but rather an interconnected structure of two phases [9], the inverse of $q_{\text{max}}$ still describes a characteristic length of the system. The maximum of each scattering curve was fitted by a Gaussian curve and $q_{\text{max}}^{-1}$ plotted as a function of ageing time (figure 7).

In the case of Fe-Cu, the Guinier approximation was used for determining the Guinier radius $R_G$ [7]. In a plot of $\ln(d\Sigma/d\Omega)$ over $q^2$, there is a linear part for $qR_G \leq 2$. As in the calculation of $Q$, the scattering curve of the reference state before precipitation starts was subtracted for the Guinier plot. From the slope $s$ of the linear part, $R_G$ is calculated as $\sqrt{-3s}$. The Guinier radius is a mean size of the scattering particles. In the case of spherical particles, the sphere radius is $R_S = \sqrt{5/3} R_G$. $R_S$ is plotted as a function of ageing time (figure 7).

4. Discussion

In the Fe-Co-Mo system, $Q$ was found to increase from the very beginning of heating (figure 4). After a temperature of 493 °C is reached, the increase of $R$ from 0 to 13 takes 150 s. During this period, $Q_m$ has a higher slope than in later stages, while $Q_n$ does not show this change in slope. This means that the magnetic contrast is building up during the first 150 s. As was observed with the atom probe [5], precipitate formation starts with a simultaneous enrichment of Mo and depletion of Fe and Co. With the exchange of these elements, the magnetic moment per atom decreases in the precipitate region and $\Delta \eta_m$ increases. After 150 s $\Delta \eta_m$ reaches a plateau. Thus, from this data it is concluded that there are strong compositional changes in the newly formed precipitates during the first 150 s. In the following, $R$ decreases slowly due to smaller changes that can occur in the matrix as well as in the precipitate composition while $Q$ still increases.

The initial behavior of the Fe-Cu system is different: An incubation period of about 800 s is observed after the aging temperature of 495 °C is reached, during which the intensity is close to zero (figure 5). This behavior is typical for the nucleation mechanism where a nucleus of critical size that is stable and can grow must be formed by statistical diffusion processes. One must keep in mind,
however, that there is a detection limit for small numbers of very small particles; the true incubation time could thus be smaller than 800 s. At the end of the incubation time $R$ increases and reaches a value of about 3.2 after 1300 s. It continues to increase slower up to about 3.8 after 10000 s (figure 5). The initial relatively fast increase of $R$ fits to the picture of classical nucleation, in which overcritical clusters already have the final equilibrium concentration; in the Fe-Cu case from the equilibrium phase diagram it is usually expected to be almost pure Cu. However, the increase in $R$ afterwards hints to a further change in precipitate composition. In addition, the apparent maximum value of $R$ of about 3.8 is significantly smaller than expected for pure non-ferromagnetic Cu precipitates in Fe ($R \approx 12$). Recent studies have suggested that the Cu precipitates can reach their equilibrium composition only slowly [11], and can contain significant amounts of Fe. It is, however, not yet fully clear if this is an explanation for the observed $R$-behavior. In general, due to the definition of the scattering length density $\eta$ changes in $R$ can be due to changes either in the composition or in the mean volume per atom, but also due to changes in the mean magnetic moment per atom in matrix and precipitate. As a consequence, the small precipitates in Fe-Cu also would have to be tested for a significant magnetic moment.

Comparing the results for both materials, they seem to behave similar as far as the initial compositional changes in the precipitates are concerned. Also in the Fe-Co-Mo system, the compositional changes producing precipitates are very fast, resembling classical nucleation. Nevertheless, the actual decomposition mechanism in this highly supersaturated system is expected to deviate significantly from classical nucleation. Such deviations in highly supersaturated systems were already observed in Ni-Al alloys [12, 13]. For Ni-Al, the decomposition could be described with a clusterdynamic decomposition model taking into account not only high initial supersaturations, but also small nucleation energies. It was suggested that the character of the decomposition reaction changed from classical nucleation and growth to a nucleation-free diffusion-controlled reaction with vanishing nucleation energy at increasing supersaturations.

In the literature, the formation of precipitates in Fe-Co-Mo alloys was sometimes described to proceed via spinodal decomposition [14]. From the present results it is concluded that, should spinodal decomposition play a role in the system studied here at 500 °C, it is most likely during the first 150 s where the strong increase of $R$ indicates strong compositional changes. After 150 s the precipitates should be close to their final composition and only smaller compositional changes seem to occur as indicated by the small changes in $R$. The substantiation of this conclusion will be subject of further work involving TEM and 3DAP investigations.

A comparison of integrated intensity $Q_m$ and hardness (HV10) of both materials also shows that there are significant differences in the two precipitation reactions (figure 6). While integrated intensity and hardness show similar behavior for each material, the shape of the corresponding curves for both materials is different. In both materials maximum hardness as well as maximum precipitate volume fraction was not reached within the observed period. The observed differences as well as precipitate volume fractions will be addressed in a forthcoming study.

Another difference in the decomposition reaction is observed in the mean precipitate size (figure 7). In the Fe-Co-Mo alloy $g_{\text{max}}^{-1}$ evolves with $t^{0.15}$ up to 2700 s, followed by a faster increase with $t^{0.21}$. In the Fe-Cu alloy $R_S$ grows with $t^{0.40}$ in the observed time interval, which is somewhere between the expected behaviour for particle growth ($t^{1/2}$) and coarsening ($t^{1/3}$). Since the maximum volume fraction was not reached in the observed time interval, both alloys were well before the coarsening regime. The very small growth exponent of the Fe-Co-Mo alloy and its increase could indicate quite early decomposition stages. Although similar exponents had also been observed in the context of spinodal decomposition [15, 16], they do not seem to be evidence for spinodal decomposition in this case for the reason discussed above. On the other hand, the much larger growth exponent close to 0.5 of the Fe-Cu alloy could indicate the growth phase of the classical nucleation and growth type of decomposition [17]. A full analysis of the data will become possible with numerical decomposition models.
5. Conclusions and Outlook
In the present study the early stages of decomposition in Fe-Co-Mo at 493 °C were investigated for the first time using in situ small-angle neutron scattering. From a comparison of nuclear and magnetic small-angle scattering intensity an initial stage in the formation of hardening precipitates was identified, which is completed after about 150 s. In this stage strong compositional changes occur, while further compositional changes afterwards are much smaller. From this result it was concluded that, if spinodal decomposition took place in the decomposition reaction, it is most likely in this initial stage. After the initial stage, growth exponents of 0.15 and 0.21 were observed for the inverse of the position of the maximum in the scattering curve.

Fe-1at% Cu was used as a reference system, in which the nucleation and growth of Cu precipitates at 495 °C after an incubation time of 800 s could be observed. A growth exponent of the mean precipitate radius of 0.40 was observed, indicating a strong growth of stable nuclei.

Additional in situ SANS experiments at different temperatures will help to understand the early decomposition stages in the investigated materials. Small-angle X-ray scattering experiments at a synchrotron source are also planned [18], which can give much better time resolution through the high intensity of the source. Moreover, 3DAP and TEM studies of both materials are currently being performed. The combination of these experimental techniques with suitable decomposition models is expected to lead to a comprehensive description of the precipitation reactions in the investigated materials. Especially the question if and when spinodal decomposition takes place in the system Fe-Co-Mo has to be addressed.

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