Phase Separation kinetics in Fe-Cr-Al alloy

C. Capdevila¹, M. K. Miller² and J. Chao¹

¹ MATERIALIA Group, Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio del Amo, 8, 28040 Madrid, Spain

² Materials Science and Technology Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6136, USA

Abstract

The α - α' phase separation kinetics in a commercial Fe-20 wt% Cr-6% Al oxide dispersion-strengthened PM 2000TM steel has been characterized with the complementary techniques of atom probe tomography and thermoelectric power measurements during isothermal ageing at 673, 708, and 748 K for times up to 3600 h. A progressive decrease in the Al content of the Cr-rich α' phase was observed at 708 and 748 K with increasing time, but no partitioning was observed at 673 K. The variation of the volume fraction of the α' phase well inside the coarsening regime, along with the Avrami exponent of 1.2 and activation energy of 264 kJ mol⁻¹, obtained after fitting the experimental results to an Austin – Rickett type equation, indicates that phase separation in PM 2000TM is a transient coarsening process with overlapping nucleation, growth, and coarsening stages.

Keywords: phase separation, ferrous alloy, mechanical alloying, tomography, thermoelectric power, spinodal decomposition

Introduction

The Fe-Cr-Al oxide dispersion strengthened (ODS) ferritic steels are manufactured by a complex powder metallurgy route. Due to their high creep rupture strength and excellent swelling resistance, many ODS ferritic steels are under developments for several types of nuclear reactors, such as sodium fast reactors (SFR) or super critical water reactors (SCWR) [1-2]. For such applications, these alloys face severe embrittlement problems because their service temperature lies in the range of 373-823 K. In this temperature range, the response of the material to extreme conditions (high temperature, irradiation as the origin of swelling and corrosion) is partly determined by the extent of the α - α' phase separation. Thus, in the last few years, the binary Fe-Cr model alloys have been the focus of significant basic research [3-8].

In the present study, atom probe tomography (APT) and thermoelectric power (TEP) measurements were used to monitor the kinetics of Cr diffusion during the α - α' phase separation process. APT is a unique technique that provides highly accurate quantitative data regarding the evolution of phase composition, size, morphology, and number density, in the nm-scale size range during the α - α' phase separation. TEP provides macroscopic volumetric information of the response of a material to ageing treatments and is also a powerful method to study the dissolution process of carbides in steels, as this technique is very sensitive to the amount of atoms in solid solution in iron [9-10]. Therefore, the combination of TEP and APT was used to determine not only the composition of the phases involved, but the kinetic parameters needed to characterize the α - α' phase separation during ageing (isothermal heat treatment) of PM 2000TM ODS alloy.

Isothermal reactions allow a detailed analysis of α' -phase precipitation kinetics from the direct fit of the data to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) [11-13] and Austin-Rickett (AR) [14] relations. From these analyses, kinetic parameters, such as the so-called Avrami exponent and the activation energy, can be calculated to provide significant understanding of the nucleation and growth process of α' precipitates.

Material and experimental procedure

PM 2000TM is a yttria dispersion strengthened, mechanically alloyed, ferritic alloy containing ~20 wt.% chromium and 5% aluminum for oxidation and corrosion resistance, respectively. The chemical composition

of the commercial purity PM 2000™ used in this study, as determined by X-ray fluorescence, is given in Table 1. After mechanical alloying, the alloyed powder is canned, hot-extruded, and hot rolled into bar. The PM 2000™ alloy used in this study was provided by PLANSEE GmbH in the form of as-rolled tubes. The microstructure of the as-extruded and hot rolled alloy condition consists of an elongated and fibrous structure, as reported elsewhere [15], with fine ($\sim 0.5\mu\text{m}$) grains of ferrite slightly elongated in the extrusion (and rolling) direction. The alloy exhibits a weak $\langle 110 \rangle$ texture. Furthermore, the microstructure contains a distribution of aluminum-yttrium oxides with an average size of 20 nm [16]. Heat treatments at 673, 708 and 748 K for times ranging from 10 to 3600 hours were performed to track the α - α' phase separation process.

The principle of TEP is based on the Seebeck effect. If a metal sample is subjected to a temperature gradient ΔT , then a voltage difference ΔV is generated across the sample due to the Seebeck effect. For a low thermal gradient, the relationship $\Delta V = \Delta S \cdot \Delta T$ holds, where the Seebeck coefficient, ΔS , is the difference between the TEP of the sample (ΔS_1) and the TEP of the reference metal (ΔS_0). Schematic representations of the TEP measurement apparatus are given elsewhere [17-18]. The experimental procedure of the TEP measurement is the following: the sample is pressed between two blocks of a reference metal (in this case, pure copper). One of the blocks is held at 15 °C, whereas the other is held at 25 °C to obtain the ΔT . The ΔV generated is recorded instantaneously and precisely (to approximately $\pm 0.5\%$). The resolution is of the order of $0.001 \mu\text{V/K}$.

Atom probe tomography specimens were cut from the bulk material and electropolished with the standard double layer and micropolishing methods. For some specimens, a focused ion beam (FIB) technique was used in the final stage of specimen preparation. Atom probe analyses were performed in voltage mode in the ORNL local electrode atom probes (LEAP® 2017 and 4000X HR) manufactured by Cameca Instruments. The LEAP® was operated in voltage mode with a specimen temperature of 60K in order to mitigate the preferential field evaporation process of chromium atoms, a pulse repetition rate of 200 kHz, and a pulse fraction of 0.2. Only data sets with more than 2.5 million atoms were used to ensure that the reconstructed

volume of material is sufficient to characterize the α - α' phase separation. The treatment of the data is performed with standard APT analysis tools [19].

Thermodynamic model for phase separation

Calculations to determine the miscibility gap and spinodal region in Fe-Cr-Al-Ti system has been performed under Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) formulation with the commercial software MT-DATA thermodynamic database [20]. The total molar Gibbs free energy G^{tot} is given by:

$$G^{\text{tot}} = x_{\text{Cr}} G_{\text{Cr}} + x_{\text{Fe}} G_{\text{Fe}} + \Delta G_{\text{mix}} + G_{\text{mag}} \quad (1)$$

where the first two terms give the contribution from the mechanical mixture, the third term is the contribution from the free energy of mixing (ΔG_{mix}) for an ideal solution, and the last term accounts for the magnetic contribution to the free energy. A proper description of the magnetic term, G_{M} , has been reported by Hillert and Jarl [21] following the work of Inden [22]. In addition, in equation (1), x_{Cr} and x_{Fe} denotes the molar fraction of Cr and Fe, respectively, R denotes the gas constant and T is the absolute temperature. Likewise, ΔG_{mix} can be described by the following equation:

$$\Delta G_{\text{mix}} = T\Delta S_{\text{mix}} + G_{\text{xc}} = nRT(x_{\text{Cr}} \ln x_{\text{Cr}} + x_{\text{Fe}} \ln x_{\text{Fe}}) + G_{\text{xc}} \quad , \quad (2)$$

where ΔS_{mix} is the entropy of mixing and G_{xc} denotes the excess free energy, i.e., it describes the concentration dependent interactions of the free energy of mixing. The value of G_{ex} could be expressed as a Redlich-Kister polynomial,

$$G_{\text{xc}} = x_{\text{Fe}} x_{\text{Cr}} \sum_{p=0}^N L_p(T) (x_{\text{Cr}} - x_{\text{Fe}})^p \quad (3)$$

with N being the order of the composition dependent interaction (here $N = 2$) and $L_p(T)$ the p^{th} interaction parameter between Cr and Fe. The free energy of the pure elements, G_{Fe} and G_{Cr} , as well as the values of $L_p(T)$, are calculated with MT-DATA. The variation of ΔG_{mix} with Cr content could be evaluated for

temperatures ranging between 600 and 1000 K. The Fe-Cr miscibility gap calculated by applying the common-tangent construction to the mixing free energy (ΔG_{mix}) obtained as described above, is shown in Figure 1(a). Any homogeneous solution cooled into the miscibility gap will tend to decompose into Fe-rich and Cr-rich regions with a net reduction in the free energy. Note that if a homogeneous solution is cooled into the region between the chemical spinodal and the miscibility gap, then large composition fluctuations are needed before phase separation can occur, i.e., a nucleation and growth regime.

Recently, the reliability of the CALPHAD formulation has been questioned at temperatures below 800 K and for lean Cr contents, as it is based on experimental data above 700 K and for alloys with Cr contents >10%. However, it has been shown to appreciably underestimate the Cr solubility below this temperature [23-24]. The physical explanation for the higher solubility limit than that predicted by the standard phase diagram is the existence of a tendency for Cr atoms to produce short range order in Fe, which has been experimentally observed [25] and is also supported by density functional theory (DFT) calculations [26] that predict a negative heat of mixing below ~10% Cr. However, the standard CALPHAD parameterization does not consider this. Therefore, the Fe-Cr miscibility gap calculated in this work is compared in Figure 1(a) with the one predicted by Bonny et al. [27] following *ab-initio* studies and based on DFT theory. It is concluded that both miscibility gap predictions are similar in the temperature range of interest for this study.

The extension to the quaternary Fe-Cr-Al-Ti system containing 11 at.% Al and 0.5 at.% Ti is also shown in Figure 1 (b). These Al and Ti additions decrease the critical temperature, T_{Cr} , from 898 K to 885 K and shift the miscibility gap and spinodal region to lower chromium levels. The compositions of the equilibrium α and α' phases at 673, 708, and 748 K calculated for the ternary Fe-Cr-Al system (indicated as full circles in Figure 1 (b)) are given in Table 2. The yttria addition was ignored in these calculations. It is known that the formation of mixed Y-Al-Ti oxides will deplete the matrix of yttrium and some solute additions [28]. From the partitioning coefficient ($k_{\text{Al}} = [\text{Al}]_{\alpha} / [\text{Al}]_{\alpha'}$) shown in Table 2, these calculations indicate that Al should partition strongly to the Fe-rich α phase. The addition of up to 11 at.% Al also suppresses the competing, but extremely sluggish, precipitation of the σ phase [29].

The vertical dashed line in Figure 1 (b) corresponds to the chemical composition of the PM 2000TM alloy. It is clear that PM 2000TM falls inside the miscibility gap, but outside the spinodal region, at 748 K for each of the thermodynamic calculations. As the chromium content of the alloy is close to the miscibility gap at this ageing temperature, a sufficiently low volume fraction of the chromium-enriched α' phase should form that will be below the percolation limit. Therefore, isolated particles of the α' phase should form rather than the interconnected network structure observed in higher chromium alloys [30]. This calculation suggests that the phase separation should proceed by nucleation and growth rather than a spinodal mechanism.

Atom probe tomography results

The as-received alloy was investigated by APT in order to check the randomness of the spatial distribution of Cr atoms and to measure the exact solute concentration before any ageing treatment. In the as-received material, a homogeneous distribution of Cr was observed in the atom maps. The measured chromium concentration, after correction for the overlapping $^{54}\text{Fe}/^{54}\text{Cr}$ isobars, in the overall analyzed volume was 18.5 ± 0.2 at. %. A value of $\chi^2 = 276.9$ with 24 degrees of freedom was found in the Cr distribution of the concentrations of 100 ion blocks¹.

The fine-scale microstructures that developed for selected ageing times at 708 K are shown by the Cr, Al, and Ti atom maps in Figure 2. Clear indications for phase separation into Cr-enriched α' and Cr-depleted α regions are evident after ageing for 100 h. The phase separation is of a finer scale and is less well developed at lower ageing temperatures. Due to the relatively high number density of Cr-enriched regions and the limited field of view of the LEAP, it was necessary to limit the thickness of the atom maps to clearly distinguish the different regions. Consequentially, the full extent of all the α' regions may not be contained within these 4-nm-thick atom maps and should not be used to estimate the size of the phase regions. The Cr-enriched α' regions were found to be depleted in Al in agreement with the thermodynamic predictions. The atom maps also reveal the presence of a Ti- and Al-enriched phase. At 748 K ageing temperature, this phase is present at a significantly lower number density compared to the Cr-enriched α' phase, but its

¹ The chi-square distribution (also chi-squared or χ^2 -distribution) with k degrees of freedom is the distribution of a sum of the squares of k independent standard normal random variables, according to Engineering Statistics Handbook of US National Institute of Standards (NIST - 2006).

number density increases at lower ageing temperatures (708 and 673 K). More details of this additional phase separation and its interaction with the α' phase will be reported separately. In spite of the processing route of this mechanical alloyed ODS material, which is likely to introduce some inhomogeneities in the microstructure, the α and α' phase separation was found to be uniform. In contrast to other mechanically alloyed ODS alloys such as MA957, 9 Cr, 12YWT, and 14YWT [31-32], no evidence of fine scale (2-4-nm diameter) Ti-, Y-, and O-enriched nanoclusters was found.

The size and morphology of the Cr-enriched α' regions is more clearly shown in the isoconcentration surfaces for the microstructures formed after ageing for 500 and 3600 h at temperatures of 673, 708, and 748 K, as shown in Figure 3. At the longer ageing times, the spheroidal α' particles observed at 748 K are clearly isolated and do not form a percolated microstructure. The morphology of these α' particles is similar to that observed previously in Fe-19% Cr binary alloys and distinctly different from the interconnected network structures observed in higher chromium content (24-45%) binary alloys [27]. At the lower ageing temperatures of 673 and 708 K, the morphology of the Cr-enriched α' phase after 3600 h is of a finer scale and forms an interconnected network after much longer ageing times than that observed at 748 K, as shown in Figure 3.

The phase compositions were evaluated with the use of the proximity histogram [33], as implemented in the Imago Visualization and Analysis Software (IVAS). In this method, a chromium isoconcentration surface is constructed at a chromium level that defines the α and α' regions. A 30% Cr isoconcentration surface was selected in this work. A histogram of the concentrations of all the solute atoms at specific distances from this surface are then calculated. The process may be performed on individual particles or averaged over several or all of the particles. The resulting proximity histograms for Cr and Al for alloys aged at 673, 708, and 748 K for 100, 1000, and 3600 h, are shown in Figure 4. The resulting compositions of the α and α' phases obtained by the use of proximity histograms are summarized in Table 3.

It is clear from the atom maps (Figure 2) and proximity histograms (Figure 4) that the Al strongly partitions to the Fe-rich α phase in agreement with the thermodynamic predictions shown in Table 2. The Al partitioning factor (k_{Al}) increases since the early stages of phase separation at 748 K, whereas strong

partitioning in the α phase is only observed after 3600 h at 708 K and is negligible for 673 K, as shown in Figure 4 and Table 3. Moreover, the Al and Cr partitioning that governs the $\alpha - \alpha'$ phase separation process are coupled, as shown in Figure 5, where the evolution of k_{Al} with composition amplitude of Cr (ΔC_{Cr}) is represented. Even after ageing for 3600 h, the measured partitioning factor of 4.3 was significantly lower than the predicted equilibrium level of 14.7. This difference may arise because the alloy had not attained the equilibrium state with respect to Al within this time. The Ti was also found to partition to the Fe-rich α phase. The kinetics of the phase separation data, presented as the variation of ΔC_{Cr} with ageing time, is shown in Figure 5.

The chromium level in the center of α' regions progressively increases with ageing time, as shown in Figure 4. In addition, the chromium levels are significantly higher for the ageing temperature of 748 K than at 708 and 673 K. Therefore, the observation that the concentration of α' phase is not constant is a clear indication that phase separation cannot be described simply by either *classical* nucleation and growth nor spinodal decomposition processes. Moreover, as the chromium level in the α' regions does not appear to have attained a steady state value after the longest ageing time of 3600 h, the alloy can still be considered to be in the phase separation regime rather than the true coarsening regime. However, the kinetics of the phase separation data (Figure 5) can be fitted to a power-law with a time exponent varying according to $\sim t^{1/3}$, which agrees with the Lifshitz-Slyozov-Wagner (LSW) theory [34-35] for coarsening of precipitates. Therefore, the system appears to be in a transient coarsening regime, which is consistent with the results that the volume fraction increases with time even after the coarsening regime is achieved and the equilibrium Cr-concentration of the α phase is not yet attained (Table 3).

This transient coarsening regime during $\alpha - \alpha'$ phase separation was first pointed out by Novy et. al. [7] and is explained by an overlap between nucleation, growth, and coarsening processes, as proposed by Robson [36]. If the initial supersaturation is large enough, a significant nucleation rate is retained even when a substantial amount of the solute has been removed from the matrix, leading to an increase of the critical stable particle size. Consequently, all particles with a size under this critical value will dissolve. Then, whereas some α' precipitates are yet appearing, the coarsen of large particles and dissolution of small

particles lead to a reduction in number density. This is consistent with these experimental results since after 100 h the Cr-concentration in the α phase (matrix) is still close to the nominal value of 16.6 at.% (see Table 3) offering the possibility for nucleation to occur.

Thermo electrical power measurements

Physical background of the TEP measurement

The TEP measurement (ΔS) evolution with ageing times for 708, 723, and 748 K, are shown in Figure 6. The evolution of TEP with ageing time is governed by two effects [37]. The first effect is attributed to the gradual decrease of the solute content as precipitation proceeds. This is determined by the specific TEP of the solute atom in the matrix (chromium in iron for this alloy). This contribution is generally divided into two terms: a diffusion component and a phonon drag component, where the first term is usually taken as a linear function of temperature and includes the solute content and the second term depends on the electron and phonon scattering processes. Solute atoms can have a positive or negative influence on the TEP of the matrix. In particular, it is known that solutes decrease the TEP of iron [35]. The second effect is ascribed to the intrinsic effect of the precipitates formed during aging, which depends on the volume fraction, type, size, and morphology of the precipitates [38]. It has been reported that a low volume fraction (below 10%) of coarse, incoherent precipitates has a negligible influence on the TEP, whereas coherent and semi-coherent precipitates, such as the α' phase, may have a strong intrinsic effect on the TEP of the alloy. This result has been explained in terms of Bragg scattering of electrons by coherent particles [39].

Kinetic model

The analysis of reactions which proceed via nucleation and growth, such as $\alpha - \alpha'$ phase separation is commonly performed by means of JMAK and AR relations [40]. As these relationships are used in the present analysis, a brief description of these models is given here focusing on kinetic parameters. The JMAK model makes use of the so-called 'extended volume' concept where the individual nuclei grow without any

limitation of space. For diffusion-controlled precipitation, the volume V of the region transformed at time t , which nucleated at an earlier time t_0 , is defined as the volume of an imaginary fully depleted area around a precipitate needed to give a precipitate size equal to the real case with a diffusion zone. The volume V is written as:

$$V=A[G(t-t_0)]^m \quad (4)$$

where $G(t - t_0)$ is the growth rate, A and m are constants related to the initial dimensionality of the growth and the mode of transformation, respectively. From equation (4), the extended volume of the precipitates, which nucleated during the time interval $(\tau, \tau+dt)$ is written as:

$$dV_{\text{ext}}=AV_0I(\tau)[G(t-\tau)]^m, \quad (5)$$

where A is a constant, $I(\tau)$ is the nucleation rate, and V_0 is the initial volume. Integrating equation (5) over the time, introducing the expression $f_{\text{ext}} = V_{\text{ext}} / V_0$, and assuming that both the nucleation and growth processes are thermally activated (such that an Arrhenius-type relation for both nucleation $I(\tau)$ and growth rate $G(t-\tau)$ can be considered) yields

$$f_{\text{ext}}=\int_0^1 A I(\tau)[G(t-\tau)]^m d\tau=A_1[k(T)]^n, \quad (6)$$

where A_1 is a constant, n is a constant referred as Avrami exponent, and $k(T)$ is a temperature-dependent factor, which is usually taken as:

$$k(T)=k_0\exp\left(-\frac{Q}{RT}\right), \quad (7)$$

where R is the gas constant, k_0 is a constant, and Q is the activation energy associated to growth process in J mol^{-1} . However, only those parts of the change in extended volume that lie in untransformed regions of the parent phase can contribute to the change in the real volume. If nucleation occurs randomly in the parent material, then the probability that any change in the extended volume lies in untransformed parent

phase is proportional to the fraction of untransformed material at that instant. It follows that the real change in volume in the time interval $(\tau, \tau+dt)$

$$dV = \left(1 - \frac{V}{V_0}\right) dV_{\text{ext}} \quad (8)$$

which assumes that $f = V / V_0$ is equivalent to $(df/df_{\text{ext}}) = (1-f)$, and after integration results in

$$f(t) = 1 - \exp(-k(T)t^n). \quad (9)$$

The Avrami exponent n can be expressed as $n = a \times b + c$ [41-42] where the parameters a , b and c are related to the nucleation and growth processes as follows. The parameter a is the dimensionality of the growth (1, 2 or 3). The parameter b is related to the type of growth, which takes the value of one for interface-controlled growth and 1/2 for diffusion controlled growth. The parameter c is related to the type of nucleation rate. In isothermal paths, it takes a value of zero for site saturation (nuclei are present before the start of the transformation), a value of one for continuous nucleation (constant nucleation rate), a value between zero and one for decreasing nucleation rate, and greater than one for autocatalytic nucleation processes where the presence of nuclei enhances the formation of new nuclei.

The AR equation is a phenomenological equation that has been used successfully to predict the nitride precipitation process in an Fe-2 at. % Al system [41]. In the AR equation, the transformed fraction $f(t)$ as a function of time t is written as

$$\frac{f(t)}{1-f(t)} = k(T)t^n. \quad (10)$$

The fraction precipitated $f(t)$ could be related with the TEP values presented in Figure 6 by defining the ratio:

$$Y = \frac{\Delta S_t - \Delta S_i}{\Delta S_f - \Delta S_i}, \quad (11)$$

where ΔS_t is the relative power measurement obtained for a time t , ΔS_f and ΔS_i are the relative power measurement obtained at the stabilization level shown in Figure 6, and the initial stage, respectively. The $\ln[1/(1-Y)]$ and $\ln[Y/(1-Y)]$ versus ageing time, which results from combining equation (9) and (10) with equation (11), are shown in Figure 7. The initial value ($t = 0$ h) of ΔS was $-12.17 \mu V K^{-1}$. The data points are fitted by straight lines, which indicate the correlation factor R^2 . It is clear that the data are better fitted to the AR equation than to a JMAK-type equation. For this reason, it was decided to perform the analysis of $k(T)$ under AR equation results. The slope of these lines represents the coefficient n given in equation (10). The values of n and $\ln k(T)$ derived from Figure 7 are listed in Table 4.

These fits indicate an average value of $n = 1.2$, which is close to the ideal 1.5 value that in accordance with Starink [40], describes a three-dimensional, homogeneous nucleation with a very low nucleation rate. Therefore, the $\alpha - \alpha'$ phase separation process in PM 2000 could be described as particles growing in three dimensions starting from small sizes, with a growth rate controlled by volume diffusion (of Cr) and a decreasing nucleation rate. This conclusion is consistent with the APT results presented above, which indicate a transient coarsening mechanism, i.e., an overlap between nucleation, growth, and coarsening occurs because of the very low $\alpha' - \alpha$ interfacial energy and substantial supersaturation of Cr in the matrix.

The apparent activation energy (Q) deduced from TEP variations can be derived from the $\ln k(T)$ vs $1/T$ plot of values listed in Table 4, and are presented in Figure 8. It can be concluded from Figure 8 that the Q value for $\alpha - \alpha'$ phase separation in PM 2000 is 264 kJ mol^{-1} . This value is quite consistent with the activation energy for self-diffusion of Cr in α -Fe, which is 248 kJ mol^{-1} [43].

A comparison between the predicted volume fraction and the APT data for α' phase is shown in Figure 9. The experimental data for volume fraction of the α' phase were evaluated from the ratio of the experimental composition amplitude (ΔC_{Cr}) listed in Table 3 and the concentration amplitude indicated by the phase diagram (ΔC_{gap}) calculated in Figure 1(b), i.e., $\Delta C_{Cr} / \Delta C_{gap}$. The predicted volume fraction was derived from equation (10) and the parameters considered in calculations are $n=1.2$, $k_0 = \exp(27.20)$, and $Q=264 \text{ kJ mol}^{-1}$. It is clear there is good agreement between TEP measurements (Y) and the APT data ($\Delta C_{Cr}/\Delta C_{Gap}$).

Conclusions

1. The miscibility gap for Fe-Cr-Al system has been obtained by applying the common-tangent construction to the mixing free energy (ΔG_{mix}) calculated under CALPHAD approximation with the help of MTDATA thermodynamic database. The composition of the PM 2000TM ODS alloy is well inside the miscibility gap at the temperatures studied, suggesting that the α - α' phase separation process is governed by nucleation and growth processes.
2. The atom probe tomography results revealed that the concentration amplitude of the α' regions increases with ageing time, indicating the phase separation cannot be described simply by either *classical* nucleation and growth nor spinodal decomposition. After ageing for 100 h or longer, the spheroidal α' particles are isolated and do not form a percolated microstructure. From analysis of the APT data, the compositional amplitude (ΔC_{Cr}) was found to increase with a time exponent of 0.32, which is consistent with the LSW theory for coarsening of precipitates.
3. APT proximity histogram analysis revealed significant partitioning of the aluminum to the Fe-rich α phase during isothermal ageing at 708 and 748 K for times between 10 and 3600 h, but Al partitioning is negligible at 673 K. This experimental result is consistent with the expected trend from theoretical predictions. Although the Al depletion occurs more rapidly at 748 K than at 708 K, the calculated partitioning rate is far higher than that measured, even after 3600 h, which suggests that equilibrium levels have not been attained.
4. The combined results from APT and TEP measurements suggest that the α - α' phase separation corresponds to a transient coarsening process where nucleation of particles, growth, and coarsening are overlapping. This assumption is confirmed by the observation that the volume fraction increases with time even after the coarsening regime is achieved.
5. The fit of TEP measurements to an Austin – Rickett type equation determined an Avrami exponent of $n = 1.2$, which corresponds to particles growing in three dimensions starting from small sizes, with a growth rate controlled by Cr volume diffusion and with a decreasing nucleation rate. A value of

activation energy for $\alpha - \alpha'$ phase separation in PM 2000TM of 264 kJ mol⁻¹ was obtained, which is consistent with a value of 248 kJ mol⁻¹ for self-diffusion of Cr in α -Fe.

Acknowledgements

PM 2000TM is a trademark of Plansee GmbH. LEAP[®] is a registered trademark of Cameca Instruments. CC and JC acknowledge financial support to Spanish Ministerio de Ciencia e Innovación through in the form of a Coordinate Project in the Energy Area of Plan Nacional 2009 (ENE2009-13766-C04-01). Research (APT and MKM) supported by ORNL's Shared Research Equipment (ShaRE) User Facility, which is sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy.

References

- [1]. Klueh RL, Gelles DS, Jitsukawa S, Kimura A, Odette GR, van der Schaaf B, Victoria M. J. Nucl. Mater. 2002; 307–311:455.
- [2]. Lindau R, Möslang A, Schirra M, Schlossmacher P, Klimenkov M. J. Nucl. Mater. 2002; 307–311:769.
- [3]. Capdevila C, Miller MK, Russell K. J. Mater. Sci. 2008; 43:3889.
- [4]. Capdevila C, Miller MK, Toda I, Chao J. Mater. Sci. Eng. A 2010; 527:7931.
- [5]. Bley F. Acta Metall. Mater. 1992; 40:1505.
- [6]. Miller MK, Kenik EA, Russell KF, Heatherly L, Hoelzer DT, Maziasz PJ. Mater. Sci. Eng. A 2003; 353:140.
- [7]. Novy S, Pareige P, Pareige C. J. Nucl. Mater. 2009; 384:96.
- [8]. Odette GR, Alinger MJ, Wirth BD. Annu. Rev. Mater. Res. 2008; 38:471.
- [9]. Caballero FG, Capdevila C, Alvarez LF, de Andres CG. Scr. Mater. 2004; 50:1061.
- [10]. Caballero FG, Garcia-Junceda A, Capdevila C, de Andres CG. Scr. Mater. 2005; 52:501.
- [11]. Kolmogorov N. Izv Akad Nauk SSSR 1937; Ser Mat 3:355.
- [12]. Johnson WA, Mehl RF. Trans Am Inst Met Eng 1939; 135:416.

- [13]. Avrami M. J Chem Phys. 1940; 8:212.
- [14]. Austin JB, Rickett RL. Trans Am Inst Met Eng 1939; 135:396.
- [15]. Capdevila C, Miller MK, Russell KF, Chao J, González-Carrasco JL. Mater. Sci. Eng. A 2008; 490:277.
- [16]. Capdevila C. Metall. Mater. Trans. A 2005; 36A:1547.
- [17]. Caballero FG, Capdevila C, de Andres CG. Mater. Sci. Technol. 2001; 17:1114.
- [18]. Caballero FG, Alvarez LF, Capdevila C, de Andres CG. Scr. Mater. 2003; 49:315.
- [19]. Miller MK. Atom Probe Tomography: Analysis at the Atomic Level. New York: Kluwer Academic – Plenum Publishers; 2000.
- [20]. MTDATA. Phase diagram calculation software. Teddington: National Physical Laboratory; 2003.
- [21]. Hillert M, Jarl M. CALPHAD 1978; 2:227.
- [22]. Inden G. Physica B 1981; 103:82.
- [23]. Bergner F, Ulbricht A, Heintze C. Scr. Mater. 2009; 61:1060.
- [24]. Bonny G, Terentyev D, Malerba L. Scr. Mater. 2008; 59:1193.
- [25]. Filippova NP, Shabashov VA, Nikolaev AL. Phys. Met. Metall. 2000; 90:145.
- [26]. Olsson P, Abrikosov IA, Vitos L, Wallenius J. J. Nucl. Mater. 2003; 321:84.
- [27]. Bonny G, Terentyev D, Malerba L. J. Phase Equilib. 2010; 31:439.
- [28]. Klimiankou M, Lindau R, Möslang A, J. Crystal Growth 2003; 249:381.
- [29]. Dubiel SM, Inden G. Z. Metallkd. 1987; 78:544.
- [30]. Miller MK, Hyde JM, Hetherington MG, Cerezo A, Smith GDW, Elliott CM. Acta Metall. Mater. 1995; 43:3385.
- [31]. Miller MK, Russell KF. J. Nucl. Mater. 2007; 371:145.
- [32]. Pareige P, Miller MK, Stoller RE, Hoelzer DT, Cadel E, Radiguet B. J. Nucl. Mater. 2007; 360:136.
- [33]. Hellman OC, Vandenbroucke JA, Rüsing J, Isheim D, Seidman DN. Microsc. Microanal. 2000; 6:437.
- [34]. Lifshitz M, Slyozov VV. J. Phys. Chem. Solids 1961; 19:35.
- [35]. Wagner C. Z. Elektrochem. 1961; 65:581.
- [36]. Robson JD. Acta Mater. 2004; 52:4669.
- [37]. Pelletier JM, Borrelly R. Mater. Sci. Eng. 1982; 55:191.

- [38]. Brahmi A, Borrelly R. *Acta Mater.* 1997; 45:1889.
- [39]. Raynaud GM, Guyot P. *Acta Metall.* 1988; 36:143.
- [40]. Christian JW. *The theory of transformations in metals and alloys. Part I: equilibrium and general kinetics theory, vol 1.* Oxford: Pergamon Press, 1981.
- [41]. Starink M. J. *Mater. Sci.* 1997; 32:4061.
- [42]. Gutiérrez-Urrutia I. J. *Mater. Sci.* 2011; 46:3144.
- [43]. Paxton HW, Kunitake T. *Trans. Metall. Soc. AIME* 1960; 218:1003.

Figures

Figure 1. Miscibility gap calculated for (a) Fe-Cr system and (b) Fe-Cr-Al system. A comparison with the phase diagram calculated according to Bonny et al. (after [25]) also shown.

Figure 2. 4-nm-thick atom maps for selected times during ageing at 708 K (volume of 4×20×40 nm³).

Figure 3. 30% Cr isoconcentration surfaces for 500 and 3600 h during ageing at 748, 708, and 673 K.

Figure 4. Proximity histogram of all α - α' regions in PM 2000TM aged at 748, 708, and 673 K for 3600, 1000, and 100 h. The partitioning of Cr to the Fe-rich α' phase and depletion of Al is shown.

Figure 5. The α - α' phase separation during ageing at 748, 708, and 673 K: (a) Al partitioning coefficient evolution and (b) α' precipitation kinetics in recrystallized samples.

Figure 6. TEP measurement evolution during isothermal ageing treatments in PM 2000TM at 673, 708, and 748 K.

Figure 7. (a) $\ln \ln[1/(1-Y)]$ as a function of ageing time (JMAK equation) and (b) $\ln [Y/(1-Y)]$ as a function of ageing time at temperatures of 708, 723, and 748 K. Correlation factor R^2 is shown.

Figure 8. $\ln K$ vs $1/T$ plot derived from AR equation for TEP data measured at 708, 723, and 748 K.

Figure 9. Comparison between 3DAP data and JMAK (equation (9)) and AR (equation (10)) models for material aged at (a) 748 K, (b) 708 K, and (c) 673 K.

(a)

(b)

Figure 1. Miscibility gap calculated for (a) Fe-Cr system and (b) Fe-Cr-Al system. A comparison with the phase diagram calculated according to Bonny et al. (after [25]) also shown.

Figure 2. 4-nm-thick atom maps for selected times during ageing at 708 K (volume of $4 \times 20 \times 40 \text{ nm}^3$).

500 h

3600 h

Figure 3. 30% Cr isoconcentration surfaces for 500 and 3600 h during ageing at 748, 708 and 673 K.

Figure 4. Proximity histogram of all α - α' regions in PM 2000 aged at 748, 708 and 673 K for 3600, 1000 and 100 h. The partitioning of Cr to the Fe-rich α' phase and depletion of Al is shown.

(a)

(b)

Figure 5. The α - α' phase separation during ageing at 748, 708 and 673 K: (a) Al partitioning coefficient evolution, and (b) α' precipitation kinetics in recrystallized samples.

Figure 6. TEP measurements evolution during isothermal ageing treatments in PM 2000 at 673, 708 and 748 K.

(a)

(b)

Figure 7. (a) $\text{LnLn}[1/(1-Y)]$ as a function of ageing time (JMAK equation) and (b) $\text{Ln}[Y/(1-Y)]$ as a function of ageing time at temperatures of 708, 723 and 748 K. Correlation factor R^2 is shown.

Figure 8. $\ln K$ vs $1/T$ plot derived from AR equation on TEP data measured at 708, 723 and 748 K.

(a)

(b)

(c)

Figure 9. Comparison between 3DAP data and JMAK (equation (9)) and AR (equation (10)) models for material aged at (a) 748 K, (b) 708 K, and (c) 673 K.