PHASE SEPARATION IN PM 2000 FE-BASE ODS ALLOY: EXPERIMENTAL STUDY AT THE ATOMIC LEVEL

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Abstract

The coarsening of the three – dimensional microstructure resulting from phase separation during ageing at 748 K of a Fe-based PM 2000 oxide dispersion strengthened (ODS) steel has been investigated by atom probe tomography and hardness measurements. Phase separation resulted in the formation of isolated particles of the chromium-enriched α' phase. The aluminum and titanium were found to preferential partition to the iron-rich α phase. The partitioning of aluminum is consistent with theoretical calculations. The change in the scale of the chromium-enriched α' phase was found to fit a power law with a time exponent of 0.32 in accordance with that predicted by the classical Lifshitz, Slyozov and Wagner (LSW) theory. The solute concentrations of the coexisting α and α' phases were estimated from concentration frequency

distributions with the Langer, Bar-on and Miller (LBM) method and proximity histograms. The hardness was linearly related to the chromium content of the α' phase.

Keywords:

Phase separation; oxide dispersion strengthened steel; PM 2000; solute partitioning; atom probe tomography

Introduction

PM 2000™ is an mechanically alloyed, ODS Fe-20 wt % Cr-5%Al alloy that offers good combinations of creep and oxidation resistance. This alloy can be used for tubing in a combined cycle gas turbine heat exchanger in a biomass power plant [1, 2]. Recently, the alloy has been investigated as potential biomaterial for surgical implants [3]. For this application, a fine, dense and tightly adherent α -alumina layer is formed on the surface by thermal oxidation at high temperature (pre-oxidation temperature of 1100 °C). This in-situ coating process combines the inherent mechanical properties of the PM 2000 alloy substrate with the superior biocompatibility of bulk alumina.

Experiments performed with pre – oxidized PM 2000 revealed that the hardness increases when the alloy is annealed at 748 K (475 °C). This hardness increase is consistent with the so – called “475 °C embrittlement” that is characteristic of high chromium ferritic alloys. This phenomenon has been attributed to the phase separation into Fe-rich (α) and Cr-rich (α') phases which form within the miscibility gap in the Fe-Cr system [4-6]. Depending on the ageing temperature and the composition of the steel, phase separation can proceed either by spinodal decomposition or by a nucleation and growth mechanism.

Several different techniques have been used to characterize the phase separation in these types of ferritic alloys. Mössbauer spectroscopy (MS) can detect the α and α' domains at the early stages of their development.. However, no indication of the characteristic distances can be obtained as the information is only compositional. Small angle neutron scattering (SANS) can also be used but no information can be obtained concerning the detailed morphology of phases [7, 8]. Because of the nanometer scale at which the microstructural evolution takes place, transmission electron microscopy

(TEM) is often applied to this type of study. Unfortunately, in the Fe-Cr system, the combination of the similarity of the X-ray scattering factors of these elements, the presence of surface oxide films, and the coherency and morphology of the α and α' phases has limited its use for the characterization of the early stages of phase separation.

The atom probe has been shown to be an effective technique to study this ultrafine scale phase separation because it provides both atomic scale microstructure and microchemical analysis of the observed phases. The spatial resolution of the instrument is smaller than the extent of the emerging phases at the earliest stages of phase separation, and the mass resolution of this time-of-flight technique is more than sufficient to distinguish the solutes present. In this study, a wide field of view, local-electrode atom probe (LEAP[®]) has been used to quantify the scale and composition parameters of the α and α' phase separation, which is responsible for the hardening of a PM 2000 ODS alloy.

Material and experimental procedure

PM 2000 is yttria dispersion strengthened, mechanically alloyed, ferritic alloy containing ~20 wt % chromium and 5% aluminum for oxidation and corrosion resistance. 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 bars. The chemical composition of the commercial purity PM 2000 used in this study as determined by X-ray Fluorescence is given in Table 1. To reveal more in detail the microstructure of the steel, scanning electron microscopy was carried out on a Jeol JSM-6500F Field Emission Scanning Electron Microscope (FEG-SEM) operating at 7 kV in the back-scattered mode.

Table 1. Chemical composition of PM 2000 as determined by XR Fluorescence

	Cr	Al	Ti	C	O	N	Y	Fe
wt.-%	18.60	5.20	0.54	0.04	0.09	0.006	0.391	balance
at.-%	18.50	10.10	0.58	0.17	0.28	0.022	0.228	balance

Cylindrical samples of 3 mm in diameter were cut with diameter parallel to hot rolling direction and mechanically thinned to thickness of $\sim 100\ \mu\text{m}$. From these discs, TEM samples were electropolished in a TECNUPOL device using 5 pct perchloric, 25 pct glycerol, and 70 pct ethanol as electrolyte, at 266 K with an applied voltage of 20 V. TEM examination was performed in a JEOL JEM-200 CX transmission electron microscope operating at 200 keV.

Atom probe tomography specimens were cut from bulk material and electropolished with the standard double layer and micropolishing methods [9]. For some specimens, a focused ion beam (FIB) technique was used in the final stage of specimen preparation. Atom probe analyses were performed in the ORNL local electrode atom probe (LEAP[®]) manufactured by Imago Scientific Instruments. The LEAP[®] was operated with a specimen temperature of 60K, a pulse repetition rate of 200 kHz, and a pulse fraction of 20%. 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 phase separation.

Results and discussion

General Microstructure of PM 2000

The microstructure in the as-extruded and hot rolled condition consists of fine ($\sim 0.5\ \mu\text{m}$) grains of ferrite (Figure 1). The grains were slightly elongated in the extrusion and

rolling direction and the microstructure exhibited no major rolling texture. This microstructure indicates that the rolling temperature is high enough for recrystallization to have occurred with possibly a little grain growth. Electron backscatter diffraction (EBSD) indicated that the high angle grain boundaries are well defined (Figure 2), which is also consistent with a recrystallized microstructure. Furthermore, texture analyses reveal a weak fiber texture, ~ 1.4 times random, with the $\langle 110 \rangle$ direction parallel to the rolling direction, i.e. the (110) plane is perpendicular to the bar axis. This texture is typical of body centered cubic materials deformed by either extrusion or rolling. No evidence of was found for Ti(C,N) precipitates as reported by Klimiankou and co-workers in a previous study of the as-extruded and hot rolled condition [10].

Annealing at temperatures of the order of 0.9 of the melting-point (1633 K for 3 h), and cooling in a switched off furnace yields a coarse grain structure with a grain size in the millimeter range. The grains are columnar and aligned along the extrusion direction (Figure 3). After this heat treatment, some aluminum-yttrium oxides were observed (Figure 4). The mean size of these particles was ~ 20 nm. The composition of the particles was estimated by energy-dispersive spectroscopy to be 43.4 at. % Al, 3.3% Y and 53.2% O which was not consistent with the original stoichiometry of the Y_2O_3 powder. This composition is also very different from that observed by Klimiankou et al, who observe a composition close to $YAlO_3$ [10]. The high aluminum content suggests that these oxides are not remnants of the original yttria powder and that the original yttria powder was dissolved into the solid solution during the mechanical alloying process and a new distribution of oxide particles formed during the extrusion or rolling processes. This high temperature annealing treatment was used prior to subsequent lower temperature ageing treatments to ensure a chemically homogeneous material. The

growth of grains is evidently anisotropic because of the strong alignment of the aluminum-yttrium oxide particles along the extrusion direction that hinder boundary motion more effectively in the transverse direction [11-13].

As the grain growth process can be influenced by solute segregation, the grain boundaries were investigated for evidence of solute segregation (particularly yttrium, since there is a remote possibility that fine yttria or yttrium containing oxide particles that are located at a grain boundary may partially or fully dissolve). Several randomly chosen boundaries were selected and orientated parallel to the incident electron beam; microanalysis scans at intervals of 2.5 nm were then conducted across the boundary plane over a distance of $\sim 0.16 \mu\text{m}$ on either side of the boundary, avoiding any particles. A concentration scan through a precipitate-free segment of the grain boundary (Figure 5(a)) revealed no evidence of solute enrichment at the grain boundary. For comparison, a scan across a segment of grain boundary with an aluminum-yttrium oxide particle is shown in Figure 5(b).

The experiments presented to this point have described the initial coarse grained microstructures. However, the main focus of this study was the phase separation that occurs during ageing at 748 K for times up to 3,600 h.

Thermodynamic analysis of PM 2000

The relationship between the composition of the PM 2000 alloy and the low temperature miscibility gap and the spinodal regions in the Fe-Cr system is shown in Figure 6. The free energy changes of the system (ΔG_M) were calculated from the Scientific Group Thermodata Europe (SGTE) solution databases and only considered the existence of body centered cubic phases. The position of the miscibility gap corresponds to the minima and the spinodal corresponds to inflexion points of ΔG_M

verses Cr-content curve. For comparison, the experimental Mössbauer spectroscopy and resistivity measurements data obtained by Kuwano [14, 15] on Fe-Cr alloys are superimposed on the theoretical calculations. The extension to the ternary Fe-Cr-Al system containing 11 at. % Al is also shown in Figure 7. This Al addition decreases the critical temperature T_{Cr} , from 898 K to 885 K and shifts the miscibility gap and spinodal region to lower chromium levels. The compositions of equilibrium α and α' phases at 748 K calculated for the ternary Fe-Cr-Al system are shown in Table 2. The yttria addition was ignored in these calculations although it is known that the formation of mixed Y-Al-Ti oxides will deplete the matrix of some solute additions. From the partitioning coefficient shown in Table 2, these calculations indicate that Al should partition strongly to the α phase. The addition of up to 11 at.% Al also suppresses the competing but extremely sluggish precipitation of the σ phase [16]

Table 2 Calculated equilibrium phase compositions in Fe-Cr-Al at 748 K

Solute	Fe-rich α (at. %)	Cr-rich α' (at. %)
Fe	78.2	7.0
Cr	8.6	92.1
Al	13.2	0.9
$c_{Al}^{\alpha} / c_{Al}^{\alpha'}$	14.7	

The vertical dashed line in Figure corresponds to chemical composition of the PM 2000 alloy. It is clear that PM 2000 falls inside the miscibility gap but outside the spinodal region at 748 K. 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. This calculation suggests that phase separation process should proceed by nucleation and growth rather than a spinodal mechanism.

Hardness measurements

The change in the hardness for recrystallized material during ageing at 748 K is shown in Figure 7. In contrast to a previous observation in a similar MA956 material by Spear and Polonis [17], which reported an initial rapid increase in hardness probably due to the formation of interstitial (C,N) precipitates [18], little hardening occurred during the first 10 h. Ageing for longer times resulted in an moderate increase in hardness. This hardness increase could result from the interaction of dislocations with the internal stresses and composition gradients [19] due to phase separation of the supersaturated substitutional solid solution into α and α' phases. The hardness values reach a plateau at ~ 1000 h. The time to reach maximum hardness was significantly shorter than that observed during the isothermal annealing of an Fe-30% Cr binary alloy at 743K (470 °C) [20].

Atom Probe Tomography

The fine scale microstructure for selected ageing times at 748K is shown in the atom maps in Figure 8. Clear indication of phase separation into Cr-enriched α' and Cr-depleted α regions is evident after ageing for 100 h. Phase separation is finer and less well developed after 10 h. Due to the relatively high number density of Cr-enriched regions and the field of view of the local electrode atom probe, it was necessary to limit

the thickness of these 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 therefore, they should not be used to estimate the size of these 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 present of a Ti- and Al-enriched phase. At this ageing temperature, this phase is present in a significantly lower number density compared to the Cr-enriched α' phase. 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 after the high temperature annealing treatment. In contrast to some other mechanically alloyed, oxide dispersed alloys such as MA957, 9 Cr, 12YWT and 14YWT [21, 22], 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 in Figure 9. At the longer ageing times, the roughly spherical α' particles 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 to the interconnected network structure observed in the higher chromium content (24-45%) binary alloys [23].

Scale

Although the size of the α' regions can be roughly estimated from the isoconcentration surfaces, a more robust statistical method, the autocorrelation function, was used [24]. The 3D radial autocorrelation function may be expressed as [25-27].

$$R_k = \frac{1}{\sigma^2} \sum_{r=0}^{r_{\max}-k} (C_r - C_o)(C_{r+k} - C_o) \quad (1)$$

where C_r is the concentration of a spherical shell at radius r from the chosen centre point, $r_{\max}$ is the maximal radius over which the analysis is taken, σ^2 is the variance of the compositions given by $\sum_0^{r_{\max}} (C_r - C_o)^2$, and C_o is mean concentration of the data (which may be slightly different from the mean concentration of the PM 2000 alloy).

The size and periodicity between α' regions and the rate of coarsening with ageing time may be estimated from the position of the first minima, $r_{\min}$, and the first maxima, r_1 , and their variation with ageing time [9]. The position at which the autocorrelation function crosses zero, r_0 , may also be used to estimate the size of the α' regions. In these data, little significance should be placed on the autocorrelation function beyond the first maximum. For the analysis of experimental data, a shell thickness of 0.1 nm and a $r_{\max}$ value of 100 nm were used. The results presented are the average of 10 autocorrelations centered at random positions within the volume of analysis.

The development of the autocorrelation function from 3D atom probe analyses of thermally aged PM 2000 is shown in Figure 10. The parameters obtained from the autocorrelation function for the different ageing conditions are summarized in Table 3. The increase in the parameters indicates the size of the α' regions increases with ageing time. After 10 h ageing at 748 K, the autocorrelation function does not show any

significant evidence of phase separation in PM 2000, whereas after 100 h significant deviation from random behavior is observed. As the ageing time increases, the first minimum becomes more pronounced. The experimental data were fitted to a power law, as shown in Figure 11, and the time exponent was estimated. A time exponent of 0.32 ($R^2=0.92$) was obtained from the measurements of the first minimum, and a corresponding value of 0.37 ($R^2=0.89$) for the measurements of the first maximum. The time dependent coarsening of particles can be compared to the LSW theory [28, 29]. In this theory, diametral rate of growth of particles slows as decomposition proceeds since the distance between the remaining particles gradually increases. The LSW theory predicts the power law growth of the mean precipitate size $R(t)$ varying as $\sim t^{1/3}$ which is similar to the value of 0.32 measures in this study. The growth exponent of $1/3$ is a limiting value since LSW theory only takes into account long range diffusion as method of growth. The results are also in general agreement with some SANS measurements for Fe-Cr alloys with 20, 35 and 50 at.% Cr [7].

Table 3. Size parameters estimated from the 3D radial autocorrelation function.

nm	10 h	100 h	500 h	1000 h	2040 h	3600 h
r_0		4	3.1	3.9	6	9
$r_{\min}$	1.5	4.3	4.8	6.7	7	14
r_1	2	9	9.7	10.1	14	34

Phase composition

The evolution of the compositions of the coexisting α and α' phases were estimated by several methods. Previous studies of phase separation in the Fe-Cr system have used

the statistical analysis of concentration frequency distributions [9, 28]. A frequency distribution is constructed by dividing the three-dimensional volume of atoms into equal sized blocks, estimating the composition of each block, and plotting the observed number of blocks at each composition. A random solid solution will conform to a binomial distribution. Upon phase separation, the frequency distribution will initially decrease in amplitude, broaden and eventually form two peaks corresponding to the concentrations of the coexisting phases. The experimentally observed and binomial distributions obtained for selected ageing times at 748 K are shown in Figure 12. In all cases, significant differences were observed between the experimental and binomial distributions indicating that phase separation had occurred at all ageing times.

The solute concentrations of coexisting phases were estimated with a maximum likelihood method [30, 31] based on the treatment of Langer – Bar-on – Miller (LBM) for solving the non linear Cahn – Hilliard – Cook diffusion equation which summarizes the kinetics of a spinodal decomposition process [32]. In the LBM method, the probability distribution function of the composition at an arbitrary position is represented by two Gaussian distributions of equal width, σ , centered at concentrations μ_1 and μ_2 . The composition amplitude, ΔC , of phase separation is given by $\mu_2 - \mu_1$. The LBM fits to the experimental distribution are also included in Figure 12 and the estimated values are summarized in Table 4. As ageing time increases, the amplitude of the distribution decreases and the width increases indicating phase separation. After ageing for 100 h, a broad high chromium tail became evident. However, the high χ^2 values for the longer ageing time indicate that the LBM model does not provide a good fit and therefore the μ_2 concentrations are underestimated. The underestimation of the chromium level in the α' regions was confirmed by constructing a narrow cross section

composition profile through the centre of one of the α' regions in the 500 h aged condition, as shown in Figure 13. The alternative Pa method [33, 34] which assumes a 50% volume fraction of the two phases was also found to be inappropriate due to the low volume fraction of the α' phase.

Table 4. Parameters of the LBM fits to the composition frequency distributions

LBM	2h	10 h	100 h	500 h	1000 h	2040 h	3600 h
μ_1 (%)	18.7	17.1	16.6	15.8	15.8	15.4	16.4
μ_2 (%)	26.0	25.2	36.5	36.1	36.8	35.0	36.7
σ (%)	3.0	3.0	4.0	5.0	5.0	7.0	7.0
$f_{\alpha'}$ (%)	4.1	3.7	9.0	11.3	12.4	10.7	9.9
χ^2	25.6	76.4	2784	261080	85369	242112	2037381
d.f	32	37	52	54	54	56	60

Therefore, the phase compositions were evaluated with the use of the proximity histogram [35] as implemented in the Imago Visualization and Analysis Software (IVAS). In this method, a chromium isoconcentration surfaces is constructed at a chromium level that defines the α and α' regions. The concentrations of all the solute atoms that are within a specified small distance of this surface are then calculated. This process is repeated as a function of distance on both sides of the surface. The process may be performed on individual particles or averaged over several or all particles. A resulting profile for all the major solutes in the PM 2000 aged for 1000 h is shown in Figure 14. The strong partitioning of the aluminum to the Fe-rich α regions is observed.

A series of chromium profiles for the different ageing times is shown in Figure 15. The resulting compositions of the α and α' phases are summarized in Table 5. The chromium level in the center of α' regions progressively increases with ageing time, as shown in Figure 16. In addition, the chromium levels are significantly higher than that estimated by the LBM method in the longer ageing times indicating the poor LBM fit. However, the Cr level is slightly lower than the predicted equilibrium level possibly suggesting that equilibrium has not been achieved after ageing for 3600 h.

Table 5. Compositions of the α and α' phases for the different ageing times at 748K as estimated from the proximity histogram. The balance of the analyses is iron.

at. %	10 h	100 h	500 h	1000 h	2040 h	3600 h
Cr_α	17.1	16.6	15.7	16.0	15.6	17.0
Al_α	12.2	12.6	12.6	11.9	12.5	12.3
Ti_α	0.62	0.63	0.75	0.44	0.48	0.70
$\text{Cr}_{\alpha'}$	33.0	46.4	71.6	76.6	82.2	86.0
$\text{Al}_{\alpha'}$	13.7	10.0	5.78	4.62	3.45	2.86
$\text{Ti}_{\alpha'}$	0.44	0.39	0.27	0.16	0.12	0.32
$\Delta\text{C}_{\text{Cr}}$	15.9	29.8	55.9	60.7	66.6	69.0
$c_{\text{Al}}^\alpha / c_{\text{Al}}^{\alpha'}$	0.9	1.2	2.2	2.6	3.6	4.3

The experimental results revealed that both the scale and concentration amplitude of the α' regions increase with ageing time. Therefore, the phase separation cannot be

described simply by either *classical* nucleation and growth nor spinodal decomposition. 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.

Hardness

It is important to establish what principally determine the hardness increases of this PM 2000 alloy. Cahn [36] and Part et al. [37] related the increase in hardness with the internal stresses induced by the Fe – lattice distortions produced by Cr atoms, and the variations in elasticity modulus because of variations in Cr concentration. Analysis of experimental data indicated that as phase separation proceeds, both the size and chromium content of the α' domains increases. The relationship between these parameters and the alloy hardness is shown in Figure 17. Better linear fits were obtained for the concentration parameters (either the chromium content of the α' phase ($R=0.987$) or the difference in chromium between the α and α' phases ($R=0.990$)) compared to the size parameters $r_{\min}$ ($R=0.748$) and r_0 ($R=0.440$). This observation would lend support to the internal stress/modulus model due to the increasing chromium content in the α' domains.

Al and Ti partitioning

An interesting topic of phase separation in PM 2000 is the partitioning behavior of Al. It has been suggested that Al does not partition significantly to the Fe-rich phase, and even the phase separation in Fe-Cr-Al is possibly a paraequilibrium transformation with respect to Al [38, 39]. The behavior of Al was discussed in terms of competing

chemical and stress in the nanophase material and the influence of such a structure on its thermodynamic description [38]. It is clear from the atom maps (Figure 8), concentration profile (Figure 13) and proximity histogram (Figure 14) 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 between the α and α' phases was found to continuously increase with ageing time, as shown in Table 5. 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 of alloy had not attained the equilibrium state even after ageing for 3600 h. The Ti was also found to partition to the Fe-rich α phase.

Conclusions

Phase separation between α and α' phases is the predominant mechanism responsible for hardness increase detected in a PM 2000 ODS alloy during ageing at 748 K. The hardness increase was found to be linear dependent on the chromium content of the α' regions.

The atom probe tomography results revealed that both the scale and concentration amplitude of the α' regions increase with ageing time. Therefore, the phase separation cannot be described simply by either *classical* nucleation and growth nor spinodal decomposition. After ageing for 100 h or longer, the roughly spherical α' particles are isolated and do not form a percolated microstructure. From analysis of the atom probe data with the autocorrelation function, the size of the α' regions was found to increase with a time exponent of 0.32 which is consistent with the mean precipitate size $R(t)$ varying as $\sim t^{1/3}$ predicted by the LSW theory.

Atom probe composition profiles and proximity histogram analysis has revealed significant partitioning of the aluminum to the Fe-rich α phase, which is consistent with the theoretical calculations performed. The partitioning factor was found to increase with ageing time.

Some 20-nm-diameter aluminum-yttrium oxide particles were observed. The composition was estimated by energy-dispersive spectroscopy to be 43.4 at. % Al, 3.3% Y and 53.2% O. The high aluminum content suggests that these oxides are not remnants of the original Y_2O_3 powder and that the original yttria powder was dissolved into the solid solution during the mechanical alloying process and a new distribution of oxide particles formed during the extrusion or rolling processes.

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Figure Captions

Figure 1. Electron backscattered images of the as-rolled microstructure of PM 2000 (a) longitudinal direction, and (b) transverse direction. Arrow indicates extrusion and hot rolling direction

Figure 2. EBSD analysis of a transverse sample to rolling direction showing the grain morphology and texture.

Figure 3. (a) Longitudinal and (b) cross-section of recrystallized microstructure of the bar after annealing at 1633 K for 3 h

Figure 4. PM 2000 after isothermal heat treatment at 1633 K for 3 h: (a) Particle orientation, (b) distribution sizes, and (c) EDS spectra. SD stands for standard deviation

Figure 5. STEM - EDX microanalysis of the grain boundary. Linescan length of 320 nm. (After [12])

Figure 6. Influence of the addition of 11 at.% Al to the Fe-Cr system on (a) miscibility gap, and (b) spinodal region.

Figure 7. Hardness evolution of PM 2000 during ageing at 748 K. Horizontal dashed line represents the hardness value in the as-received condition ($HV1=270\pm8$).

Figure 8. Atoms map of PM 2000 after ageing between 2 and 3,600 h at 748 K. The development of the Cr-enriched and Al-depleted α' phase and a Ti- and Al-enriched phase are evident.

Figure 9. Chromium isoconcentration surfaces of PM 2000 after ageing between 10 and 3,600 h at 748 K. After 100 h, the morphology of the Cr-enriched α' phase is

approximately spherical and the size of the Cr-enriched α' phase increases on further ageing.

Figure 10. Development of autocorrelation function analysis of 3D atom probe data of PM 2000 aged at 748 K for 10 h, 100 h, and 2040 h

Figure 11. Evolution of the scale of the α' regions in PM 2000 during ageing at 748 K.

Figure 12. Experimental and binomial composition frequency distributions and the LBM fits after ageing PM 2000 at 748 K for between 2 and 500 h.

Figure 13. Composition profile across an α' region. Direction is indicated by the arrow

Figure 14. Proximity histogram of all α' regions in PM 2000 aged for 500 h at 748K.

The partitioning of Al to the Fe-rich α phase is shown.

Figure 15. The proximity histograms of all α' regions for the different ageing times at 748K. A progressive increase in the Cr content of the α' regions with ageing time is shown.

Figure 16. Evolution of the amplitude of phase separation with ageing time.

Figure 17. The linear relationship between hardness and the size and chromium content of the α' phase and composition amplitude, ΔC .

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