Thermally Decomposed Binary Fe–Cr Alloys: Toward a Quantitative Relationship Between Strength and Structure

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1. Introduction

Binary Fe–Cr alloys are model alloys for ferritic steels proposed as structural materials for future fusion reactors. They are used to investigate the fundamental mechanisms of their degradation induced by heat and irradiation. Fe–Cr presents a miscibility gap, which induces Cr-rich (α’) regions in an Fe-rich (α) matrix. As this causes embrittlement, it is crucial to understand this phase decomposition and its role, starting with the heat impact. Fe–Cr alloys with 5–40 wt% Cr were annealed at 500 °C for up to 1008 h. The microstructure was probed by chemical mapping using scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (EDS) and atom probe tomography, and hardness was assessed by Vickers testing. Increasing Cr content increases hardness, and beyond 15 wt% Cr it further increases upon annealing. At 20 wt% Cr, nanoscale globular α’ precipitates appear, while at 40 wt% Cr an α’-percolating structure develops. In both cases, the α’ core composition reaches slightly more than 80 at% Cr, and hardness doubles. A unified relationship is found between the alloy strength and the α’ structure and it is shown that this type of hardening is a general mechanism for mature systems, independent of the nominal alloy composition.

Binary Fe–Cr alloys are model alloys for ferritic/martensitic steels, which have been considered for structural applications in future thermonuclear fusion reactors since the late 1970s,[1] due to their excellent thermal properties, corrosion properties, and swelling resistance under irradiation compared with austenitic steels.[1–3] One of the main challenges in this context is that structural materials in such reactors are expected to be exposed to temperatures where Cr segregation or even decomposition in Fe-rich α regions and Cr-rich α’ regions can occur, inducing the known “475 °C embrittlement.”[4,5] This causes a hardening of over 100% and a drop in impact strength by orders of magnitude.[5,6] Extensive irradiation, with a lattice damage of over 100 displacements per atom (dpa) caused by fusion neutrons,[3] adds another factor that potentially contributes to α–α’ decomposition. The Cr content of the relevant steels is typically set at around 10 wt% to achieve suitable corrosion resistance and above, as in oxide dispersion strengthened steels,[7] to avoid the γ-loop in case of an accidental excursion to high temperature. However, this also places them in a situation where the α–α’ decomposition becomes an issue,[8] as observed in a neutron-irradiated 9 wt% Cr model alloy.[9] It is therefore essential to mitigate the decomposition, starting with the investigation of Fe–Cr model alloys to avoid the complexity of steels that hinders the identification of the underlying fundamental mechanisms. This can in turn help understand Cr segregation and its interplay with irradiation-induced lattice defects,[10] which can have similar deleterious effects on mechanical properties. That is critical to optimize ferritic/martensitic steels for fusion reactors.

475 °C embrittlement was identified in the 1950s[4] as a phenomenon that is unrelated to the formation of the intermetallic σ phase, and the idea of the miscibility gap was firmly established soon after.[5] At that point, the essential concepts surrounding this phenomenon were settled, which relate to the α–α’ separation, governed by chemical and magnetic energies.[5,11] Research continued in the following decades, often focusing on mechanical properties.[6,12–14] Mössbauer spectroscopy and neutron scattering were common tools for obtaining information on the nanoscale structure. However, methods for detailed direct imaging were not available until the early 1990s, when advancements in atom probe tomography (APT) enabled 3D atomic mapping of the decomposed structures.[15,16] APT has since then become the most prominent method in the field.

In recent times, APT has been used extensively to resolve the decomposed α–α’ structure, in, for example, the works of Novy et al.[17] Tissot et al.[18] and Reese et al.[19] The first two studies showed detailed APT analyses of 20 and 19 at% Fe–Cr alloys annealed at 500 °C for up to about 1000 h. They agree well with each other and with previous work[5] concerning the equilibrium compositions at 500 °C, which were found to be at

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14 at% Cr in the α phase and at around 85 at% Cr in the α′ phase. Novy et al.\textsuperscript{[17]} suggested a nonclassical nucleation mechanism for the process, because the interfaces were ill defined and the early precipitates’ composition was lower than the one of the presumed equilibrium α′ phase. Tissot et al.\textsuperscript{[18]} compared results obtained from APT and small-angle neutron scattering and noted that a good agreement was only achieved if the magnetic state of α′ was considered, which is composition dependent.

A major question that cannot be explored with APT alone is the effect of dislocations and other crystal defects on α′ precipitation. Here the most prominent and complementary alternative is transmission electron microscopy (TEM), which is widely used in this area\textsuperscript{[20–24]} but is not ideal for the chemistry analysis because Fe and Cr have a similar scattering factor and hence do not present a significant contrast difference. The diffraction contrast due to potential lattice deformation is also small because the Cr-rich α′ phase is fully coherent with the matrix and the lattice parameters are similar: 2.87 and 2.89 Å for pure Fe and Cr, respectively.\textsuperscript{[25,26]} A few studies nonetheless presented evidence for nanoscale α–α′ decomposition by TEM only.\textsuperscript{[21,22]} Scanning transmission electron microscopy (STEM) combined with EDS for elemental identification allows nowadays chemical mapping with subnanometer resolution, which can resolve such α–α′ structures more reliably. With the advent of recent large-collection-angle EDS detectors, which increase the yield of X-ray counts by orders of magnitude, the method seems well suited to the task. This has been shown in recent studies by Westraadt et al.\textsuperscript{[27]} and Xu et al.\textsuperscript{[28,29]} resolving length scales that agree well with those obtained by APT.

The composition of the α′ precipitates, however, remains difficult to grasp via EDS. The Cr contents reported were at least 10 at% lower than literature values obtained by other methods.\textsuperscript{[14,17,18,27–29]} Xu et al.\textsuperscript{[28]} noted that precise composition measurements using EDS would require the samples to be thinner than the length scale of the decomposition, inherently leading to a weak EDS signal and making it challenging to obtain data sets of high quality. Preparing samples with the required thickness, that is, ≃10 nm or less, is indeed challenging, and surface effects become a significant issue in the measurement.

In addition, the exact boundary of the Fe–Cr miscibility gap on the Fe-rich side is still unclear.\textsuperscript{[18]} All methods applied to find the equilibrium composition are affected by issues such as the ill-defined transition between α and α′, the small length scales, and/or the changing magnetic properties. Thus, no satisfying agreement between the different methods has been achieved to date.

In this study, we explore the Fe–Cr miscibility gap at 500 °C by considering a Cr content of 5–40 wt%, which encompasses the α–α′ boundary on the Fe-rich side. The microstructure was investigated by STEM–EDS and APT to identify the occurrence of α′ precipitation as a function of Cr content and narrow down its debated composition via a critical analysis of the deployed methods.

Another important aspect of the α–α′ decomposition treated here is the impact of the associated structural change on mechanical properties, which is critical for the application of this alloy system. The difficulty of modeling the mechanical properties of decomposed Fe–Cr alloys, from both computational and empirical perspectives, lies in the ill-defined nature of the phase separation, especially in the early stage of decomposition, and the numerous factors involved in the process. Most recent fundamental studies on the topic focused solely on the composition and structure,\textsuperscript{[17,18,27,28,30]} while studies considering the mechanical aspects usually kept the discussion qualitative.\textsuperscript{[21,22,24,29,31,32]} Older publications often present an abundance of mechanical data\textsuperscript{[5,6,13]} but lack analyses of the microstructure and its relation to properties. In this study we evaluated the mechanical properties of Fe–Cr alloys by Vickers hardness upon annealing at 500 °C at different times, taking into account the crystal orientation and microstructure. By considering the α′-structure dimensions and its Cr content derived by STEM–EDS and APT after a critical scrutiny of the results, we evaluated quantitatively the relationship between the alloy’s microstructure and strength as a function of Cr content and annealing time.

### 2. Experimental Section

Binary Fe–Cr alloys with a nominal Cr content C\textsubscript{n} of 5, 10, 15, 20, and 40 wt% (respectively 5.35, 10.66, 15.93, 21.27, and 41.73 at%) were prepared with iron from Alfa Aesar GmbH and chromium from Materials Research S.A. Fe with a purity of 99.97 % contained 113 O, 62 Ni, 38 Co, 15 N, 14 C, 13 P, and 6 Si (main impurities, in ppm) and Cr with a purity of 99.96% contained in total less than 40 ppm of impurities. Alloys were produced by arc melting in 99.999 % Ar atmosphere. The as-solidified alloys were solutionized at 820 °C for 5 h, except for the 40 wt% Cr-containing alloy that was solutionized at 850 °C for 5 h. Pieces of the solutionized alloys were then annealed at 500 °C in sealed quartz-glass tubes filled with 99.999 % argon for 50, 150, 250, 480, and 1008 h. The tubes were placed in a preheated oven and later removed from the oven to be cooled in ambient conditions. The procedure resulted in a grain size of hundreds of micrometers in all alloys. Microsections were prepared from all solutionized and 500 °C-annealed alloy samples.

Micro-Vickers hardness measurements were obtained at room temperature in single grains by applying a load of 0.05–0.3 kg and a dwell time of 15 s. The resulting indent sizes were about 20–40 μm. Note that the load was varied to balance the limited space in single grains and the measurement reliability, which dropped severely for indent sizes below 25 μm. The procedure was optimized on the solutionized alloys, whereby first 3–5 indents per grain were made and 10–20 grains per alloy were tested. In these measurements, the crystal orientation with respect to the surface was considered. This was evaluated by electron backscatter diffraction (EBSD) performed on a scanning electron microscope (SEM) Hitachi SU70 at LMPT, ETH, operated at 20 kV. This SEM also allows EDS measurements, with an Oxford Instruments X-Max detector. Grains with an orientation close to the <100>, <110>, <111>, or <321> direction as identified by EBSD were chosen and indented at different angles. For that purpose, the Vickers indenter was rotated in steps of 22.5°. It appeared that the rotation of the indenter caused hardness deviations of up to ±10% with respect to the average grain hardness. The change in grain orientation caused deviations of up to about ±5% with respect to the average of all tested indenter-to-grain orientations. The averaging of two indenter orientations differing by 45°, however, proved to even out the impact of the indenter orientation to a large degree, as shown in Figure 1.

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**Figure 1**
With this information we established the following procedure to measure hardness: each grain was indented three times with two indenter orientations varying by 45° and averaged, and the average over ten grains was taken for the hardness of the alloy condition (see Figure 1). The standard deviation calculated from the latter average was taken as the uncertainty of the hardness values.

Interestingly, the surroundings of the indents, such as those shown in Figure 1, systematically exhibited groups of short line segments, which are approximately parallel to <011> directions. These may be the traces of dislocation glide planes [211], typical for the deformation of the body centered cubic iron structure.

TEM 3-mm disc samples were prepared according to Yao et al.,[33] and STEM-EDS measurements were performed for all conditions of the 20 and 40 wt% Cr-containing alloys and for the 15 wt% Cr-containing alloy in the initial state and in the state annealed for 1008 h at 500 °C. Samples in selected alloy conditions were also prepared as thin lamellae for TEM, using the focused-ion beam (FIB) technique with an FIB–SEM dual-beam FEI Helios 600i at ScopeM, ETH. TEM for imaging and STEM for chemical mapping were performed with a TEM FEI Talos F200X at ScopeM, ETH, operated at 200 kV. The instrument was equipped with a large-collection-angle Super-X EDS detector from Bruker. Chemical maps of 1024 × 1024 pixels were acquired with an electron beam current of about 1 nA for about 15 min each. The composition of α and α' was given by the local content in Cr, Cn, and Cα', in the corresponding areas in the chemical maps. It was quantified with the Cliff–Lorimer method using Bruker Esprit software.

The dimensions of the α' regions were characterized by measuring in the STEM–EDS chemical maps the outer diameter of the disk (for round shapes) or the width of the band (for elongated shapes) that encompassed the considered local α' feature. The quoted dimension, designated r, or equivalent radius, was taken as half of this size. It corresponds to the radius of the sphere or the cylinder that locally included the α' feature. The volume fraction of α' regions, f, was calculated using the nominal Cr content of the alloys, Cn, in at%, and the measured Cr concentrations in the core of the α and α' regions, that is, Cα and Cα', in at%:

\[
C_n = f C_{α'} + (1 - f) C_α \Rightarrow f = \frac{C_n - C_α}{C_{α'} - C_α}
\]  

Using the volume fraction of α', \( V_{α'} \), and the average radius of the α' regions, \( r_α \), the α' particle number density was estimated via

\[
n = \frac{f}{V_{α'}} \approx \frac{f}{3 π r_α^2}
\]  

Note the strong dependence on the values found for the concentrations and the size of the α' regions, which can be affected by experimental artefacts. The latter will be treated in detail later in the text. In case of the 15 wt% Cr-containing alloy, as these artefacts impeded the application of Equations (1) and (2), the number density was estimated directly by counting particles on larger-scale EDS maps, and the other parameters were derived from it.

The distance between particles from surface to surface, \( d_{p-p} \), follows directly from the particle number density, assuming a cubic primitive arrangement:

\[
d_{p-p} = n^{-\frac{1}{3}} - 2r_α
\]  

The uncertainty on \( f, n, \) and \( d_{p-p} \) was obtained by error propagation considering the errors of composition and size.

APT tip specimens were prepared by FIB milling with the FEI Helios 600i dual beam. Annular milling of the tips with low-energy showering to minimize Ga implantation resulted in APT-tip apex radii of about 50 nm. The tips were vacuum transferred from the FIB device directly into a local-electrode atom-probe tomograph, the CAMECA LEAP 4000X HR at ScopeM, ETH, with a vacuum environment remaining below 10^{-5} mbar at all times, to avoid oxidation.[14] The acquisition was performed at 65 K in laser-pulsed mode, applying a 200 kHz frequency of 150 pJ energy. 3D reconstruction and analysis were performed using the IVAS 3.6.14 and 3.8.4 software versions from Cameca.

Detailed APT results analysis was performed on subvolumes, avoiding known artefacts from crystallography-based trajectory effects. Clusters and precipitates were identified by applying three different methods.

The first one, hereafter named the proxigram, related to iso-concentration surfaces, where the composition of features was determined via the proximity-histogram (proxigram) method.[16]

![Figure 1. Procedure of hardness measurement, which considers the indenter-crystal orientation impact, illustrated for a grain close to <100> of solutionized Fe–40Cr. The Kikuchi line pattern (bottom right) is obtained from the same grain. The light micrographs (left) show indents labeled with corresponding indenter orientations and Vickers hardness numbers (VHN). The blue path leads to a hardness value averaged over different indenter orientations, while the green path indicates the optimized procedure, consisting of three indents per orientation and per grain, over 10 grains.](image-url)
applying here a bin size of 0.2 nm. For isoconcentration surface calculations, the voxel size was 0.80 nm and delocalization was 2.50 nm.

The second one was the cluster-search algorithm that relied on nearest-neighbor (NN) distributions and was based on the maximum separation method.[35] Parameters were defined according to the procedure suggested by Vaumousse et al.[36] and iterative refinement steps in IVAS. The critical parameters were \( d_{\text{max}} \), the maximum spacing between atoms defining a cluster; \( n \), the order parameter; \( N_{\text{min}} \), the minimum number of atoms defining a cluster; \( L \), the envelope distance; and \( d_{\text{erosion}} \), the erosion distance. The refined parameters were \( d_{\text{max}} = 0.34 \) nm, \( n = 1 \), \( N_{\text{min}} = 150 \), \( L = 0.34 \) nm, and \( d_{\text{erosion}} = 0.17 \) nm.

The third one was the 1D profiling across individual precipitates along the highest-resolution direction of the APT, which is the field-evaporation direction. For that purpose, cylinders 2 nm in diameter were placed manually in selected precipitates identified visually, and the 1D composition profile was taken along the cylinder axis with the atoms contained in the cylinder.

3. Results

3.1. Hardness Evolution

The hardness of the alloys in the initial condition (that is, directly after solutionizing at 820/850 °C) increased with increasing Cr content (Figure 2). From 5 wt%, and more so from 15 wt%, it exhibits a nearly linear dependence. When attempting a linear fit, it appears that pure Fe clearly deviates from it, as shown in Figure 2.

Upon annealing at 500 °C for times up to 1008 h, it appears that, while pure Fe and the alloys with 5–15 wt% Cr presented no significant change, the alloys with 20 and 40 wt% Cr exhibited a remarkable hardening with annealing time (Figure 3). The 20 wt% Cr-containing alloy showed a rapid initial increase from 133 to 176 VHN in the first 50 h, after which the hardening rate decreased, with a saturation at 245 VHN between 480 and 1008 h. The 40 wt% Cr alloy exhibited a similar behavior but higher hardening, with a rapid initial increase from 215 to 378 VHN within 50 h, after which the hardness increased more slowly and reached 448 VHN after 1008 h.

3.2. Microstructure Evolution

Figure 4 and 5 present the STEM–EDS chemical maps as a function of time of annealing at 500 °C for those alloys that exhibited a significant change in hardness, that is, the 20 and 40 wt% Cr-containing alloys, respectively.

In the solutionized condition, SEM–EDS measurements confirmed the nominal composition of the alloys and indicated that they all present a uniform distribution of Cr in Fe down to the micrometer scale (not shown). STEM–EDS further revealed that this uniformity is preserved down to the nanometer scale as visible in the chemical maps such as those presented in Figure 4a and 5a. All other alloys yielded similar maps. Note that all materials, including pure Fe, contained small amounts of oxide inclusions of 0.5–1 μm in size, with distances of several micrometers between them, making a volume fraction of ≈0.1 vol%. The dislocation density, as determined in all materials by TEM, was 10^{12} m^{-2}, which means that there are several hundreds of nanometers between individual dislocations.

Upon annealing, STEM–EDS revealed in the 20 and 40 wt% Cr-containing alloys a significant \( \alpha \rightarrow \alpha' \) decomposition occurring at the nanometer scale. Figure 6 shows for comparison the distribution of Fe and Cr in the 15, 20, and 40 wt% Cr alloys imaged by STEM–EDS for the longest investigated annealing time of 1008 h at 500 °C. It appears that the alloy with 15 wt% Cr exhibits only a few widely scattered globular Cr-rich (\( \alpha' \)) precipitates, with a radius of about 3.6 nm, over an otherwise chemically uniform matrix (Figure 6a).

This reflects the initial uniformity of Cr distribution in this alloy and the lack of notable hardening upon annealing, because of the scarcity of potentially hardening \( \alpha' \) precipitates. In the
Figure 4. STEM--EDS maps of the Fe–Cr alloy with 20 wt% Cr in a) solutionized condition and b–f) after annealing at 500 °C for b) 50 h, c) 150 h, d) 240 h, e) 480 h, and f) 1008 h. The sample edge is at the top, with black representing no sample.

Figure 5. STEM--EDS maps of the Fe–Cr alloy with 40 wt% Cr in a) solutionized condition and b–f) after annealing at 500 °C for b) 50 h, c) 150 h, d) 240 h, e) 480 h, and f) 1008 h. The sample edge is at the top, with black representing no sample.
alloys with lower Cr content (that is, 5 and 10 wt%), there was no visible \(\alpha'\) precipitation. In contrast, the 20 wt% Cr-containing alloy presented globular \(\alpha'\) precipitates in a visibly much larger number density (Figure 6b). This morphology could indicate that precipitation resulted from a nucleation and growth mechanism. With 40 wt% Cr, the alloy exhibited a distinctly percolated \(\alpha'\) structure (Figure 6c), typical of a spinodal decomposition.

Table 1 shows the characteristic dimensions and Cr contents of the decomposed microstructures. The volume fraction, \(f\), the number density, \(n\), and the distance between \(\alpha'\) particles, \(d_{p-p}\), were deduced by respectively Equations (1), (2), and (3) when applicable.

With 20 wt% Cr (Figure 4), the alloy presents an \(\alpha'\) separation that is already visible after 50 h of annealing at 500 °C (Figure 4b), and that became increasingly well defined with increasing annealing time. In effect, after 50, 150, and 240 h, the \(\alpha'\) regions are loosely outlined (Figure 4b–d), while after 480 h and more so after 1008 h, they are clearly defined with image features that reflect precipitates of near-spherical shapes (Figure 4e–f). After 50 h, the radius of the \(\alpha'\) precipitates is about

![Figure 6. STEM–EDS maps of Fe–Cr alloys with a) 15 wt% Cr, b) 20 wt% Cr, and c) 40 wt% Cr after annealing for 1008 h at 500 °C. The images were acquired at the sample edge, with black representing no sample.](image)

Table 1. Phase decomposition structure of Fe–Cr alloys as a function of annealing time at 500 °C, characterized by STEM–EDS on electropolished samples unless stated otherwise.

| Alloy    | Ann. time [h] | \(\alpha'\) size [nm] | Cr content [at%] | \(\alpha'\) microstructure characteristics |
|----------|---------------|----------------------|------------------|------------------------------------------|
| Fe–15Cr  | 1008          | 3.6 ± 0.6            | 18 ± 1           | <0.001                                   |
| Fe–20Cr  | 50            | 2.0 ± 0.4            | 22 ± 3           | 0.13 ± 0.09                              |
|          | 1008          | 3.6 ± 0.6            | 15 ± 2           | 0.15 ± 0.06                              |
|          | 240           | 2.5 ± 0.4            | 17 ± 3           | 0.10 ± 0.06                              |
|          | 480           | 2.8 ± 0.4            | 17 ± 3           | 0.09 ± 0.06                              |
|          | "FIB"         | 2.9 ± 0.4            | 14 ± 1           | 0.3                                       |
|          | 1008          | 3.5 ± 0.6            | 17 ± 4           | 0.07 ± 0.06                              |
|          | "proxigram"   | 2.6 ± 0.4            | 14.6 ± 0.4       | 0.06                                     |
|          | "cl. search"  | 1.2 ± 0.8            | 15.6 ± 0.4       | 0.006                                    |
|          | "1D profile"  | 3.1 ± 0.8            | 16.4 ± 2.9       | 0.08 ± 0.04                              |
| Fe–40Cr  | Solutionized  | 52 ± 3               | 0.3              | 0.4 ± 0.5                                |
|          | 50            | 2.1 ± 0.4            | 33 ± 9           | 0.19 ± 0.16                              |
|          | 150           | 2.3 ± 0.4            | 35 ± 1.4         | 0.25 ± 0.10                              |
|          | 240           | 2.4 ± 0.4            | 37 ± 1.7         | 0.21 ± 0.07                              |
|          | 480           | 2.9 ± 0.4            | 43 ± 1.9         | 0.33 ± 0.04                              |
|          | 1008          | 3.2 ± 0.6            | 48 ± 2.6         | 0.32 ± 0.05                              |

\(a\)Proxigram, cluster search, 1D profile: APT; FIB: STEM–EDS on FIB samples. \(r\): radius of \(\alpha'\) regions (particles/veins), \(r_{act}\): size of \(\alpha'\) regions along randomly drawn lines, \(f\): \(\alpha'\) volume fraction, \(n\): \(\alpha'\) particles number density, \(d_{p-p}\): \(\alpha'\) interparticle distance. Uncertainty: standard deviation.
2 nm and after 1008 h it reached about 3.5 nm (Figure 4f). In the same time the volume fraction decreased from 0.13 to 0.07 while the number density decreased from 3.5 to $0.4 \times 10^{24} \text{m}^{-3}$. The EDS quantification, presented graphically in Figure 7a, reveals that the $\alpha'$-precipitate content in Cr increased with increasing annealing time and at a relatively fast rate at the beginning, reaching about 44 at% in average after 50 h. In the subsequent time steps, it further increased but more slowly, to reach about 80 at% in average after 1008 h. In the same time the $\alpha$ regions experienced an initial relatively fast drop in Cr content, after which it fluctuated at around 17 at%.

The evolution of the concentration of Cr in the $\alpha'$ regions, with an increase from 44 to 80 at% with increasing annealing time, explains with Equation (1) the $\alpha'$ volume fraction decrease by a factor of about 2. This, in turn, together with the change in radius from 2 to 3.5 nm, explains with Equation (2) the one-order of magnitude drop in number density.

The alloy with 40 wt% Cr (Figure 5) shows an interconnected network of Cr-rich regions, creating veins that are separated by Fe-rich regions that have a similar morphology and dimension. The $\alpha'$-vein radius (assuming locally a cylindrical shape) steadily increases with annealing time, reaching 3.2 nm after 1008 h. The EDS analyses of the 40 wt% Cr-containing alloy (Figure 7b) reveal that the mean Cr content in the $\alpha'$ regions was 78 at% after 50 h and afterward exhibited a slight increase, if any, toward a mean Cr content of around 80 at% ($82 \pm 3$ at% after 1008 h). The $\alpha$ phase overall was depleted in Cr content, dropping to around 20 at% ($23 \pm 4$ after 1008 h).

3.3. Atom Probe Tomography

The EDS measurements of the overall composition (obtained in SEM as well as in STEM) of the Fe–Cr alloys showed excellent agreement with the desired nominal compositions. However, doubt remained on the measurements made by high-resolution STEM with respect to the nanoscale decomposed regions, because of the spatial extension of the electron-beam profile, the specimen drift during the acquisition, and the overlap of $\alpha'$ regions with themselves and with the matrix in the measured volume that bias the composition assessment. That is also critical for the sizing of the $\alpha'$ regions, as chemical mapping is the only method in TEM to reveal them. As mentioned in the Introduction, APT is widely used in this realm. We thus applied the APT method as a benchmark to evaluate the STEM–EDS results, taking as exemplary case the 20 wt% Cr-containing alloy annealed at 500 °C for 1008 h (Figure 8). The APT results were themselves critically evaluated with respect to the available methods, as detailed in the following paragraphs.

The three analytical methods deployed here to analyze as reliably as possible the APT results are 1) the proxigram, 2) a radial profiling of the results using the cluster-search method, and 3) a 1D composition profiling of individual precipitates along the direction of the APT yielding the highest spatial resolution (i.e., the field-evaporation direction). Figure 8a shows typical isoconcentration surfaces obtained for a threshold of 40 at% Cr (in green), which delineate the $\alpha'$ regions. The cylinders displayed in the figure (in blue) are those that were used to extract 1D composition profiles across the $\alpha'$ precipitates; they are 20 nm long and 2 nm in diameter.

Based on this APT measurement, the volume fraction and number density of the precipitates were calculated and reported in Table 1. For that purpose, all interfaces (as those shown in Figure 8a), including the unbound ones, were considered. The unbound interfaces are those which are cut by the boundary of the analyzed region of interest (ROI). This resulted in a number density of $7.0 \times 10^{23} \text{m}^{-3}$ and a volume fraction of 6.15%, which match reasonably well the values deduced from EDS of, respectively, $4.0 \times 10^{23} \text{m}^{-3}$ and 7% when considering the error bars (see Table 1).

The proxigram (Figure 8b), which is essentially the average composition profile across all $\alpha'$ precipitate–matrix interfaces, was calculated from the bound interfaces, which are fully contained within the ROI. The core of the precipitates has a Cr content of $83.0 \pm 1.5$ at%, as calculated from the average of bins between 1.7 and 3.1 nm from the interface (where a plateau in
composition is observed). The second method used to obtain this information is the cluster-search approach (Figure 8c). It yielded an average composition profile of the α’ precipitates with a core composition of 78.7 ± 2.1 at% Cr, obtained by averaging the results of three areas. The points in the range of 0–0.6 nm were considered for the core composition, as this region again showed a composition plateau. The particle size obtained from the cluster-search method, called the radius of gyration, was found to be 1.2 nm.

As a third method, the cylinders such as those shown in Figure 8a were used to extract 1D composition profiles across the α’ precipitates. Here, 30 such profiles were extracted. The region in each cylinder between the first and last data points revealing above 50 at% Cr was defined as the α’ core region; the remaining data points were considered to be part of α. To exclude the boundary region, all data points from the α–α’ transition inward were not considered as α’ core until the Cr composition decreased to the next data point for the first time. Likewise, from the α–α’ transition outward, the data points were not considered as α core until the Cr composition increased for the first time. The Cr contents of the α and α’ cores were then averaged to obtain the respective core compositions, amounting to 16.4 at% Cr for α and 77.4 at% Cr for α’, with an α’ radius of 3.1 nm, as defined by the composition threshold of 50 at% Cr.

It appears that for the measurement of Cr concentration in the core of α’ particles, the proxigram method based on isoconcentration surfaces is the most precise: it requires the usage of voxel and delocalization definitions, but due to the highest counting statistics, this method provides the highest confidence in concentration measurements compared with the other two methods. The cluster-search method in comparison is based on individual atom positions, hence giving a more precise position of the α’-particle cores, but it can be suboptimal for particles with diffuse interfaces to the matrix, such as in the Fe–Cr system. The 1D composition profiles along the analysis direction (field-evaporation direction) minimize the effects of artefacts coming from a possible trajectory overlap during simultaneous phase evaporation, even though this should be minimal for similar evaporation fields as is the case for Fe and Cr. However, the limited counting statistics due to the cylinders of 2 nm diameter generate the largest error bars compared with the other methods.

4. Discussion

4.1. Hardness

The evolution of hardness with increasing Cr content for the alloys in the solutionized state, with a nearly linear relationship from about 5 at% Cr (Figure 2), agrees reasonably well with previous studies.[31,32,37] Note that the initial lower hardness increase from 0 to about 5 at% Cr (as also shown in Figure 2) relates to the known Fe–Cr alloy softening at room temperature for Cr concentrations lower than 1 at%,[37] which implies that such an alloy is actually softer than pure Fe. Beyond that content, the hardening picks up and eventually reaches a linear dependence on the Cr content at large values. Upon annealing, the hardness evolution (Figure 3) agrees well with results by Miller et al.,[32] considering the slightly differing Cr content of the alloys. In the following paragraphs, we focus on the methods deployed and the results on microstructural information obtained in the present work, followed by the conclusions we draw on the evolution of the Fe–Cr microstructure upon annealing for the 20 and 40 wt% Cr-containing alloys. We then establish and discuss the relationship between these data and the measured hardness values as a function of Cr content and annealing time at 500 °C.

4.2. Impact of the STEM–EDS Specimen Preparation Method

In the quantification of the data from STEM–EDS, substantial differences arise depending on the specimen preparation route. The main issue affecting this analysis in measuring the composition of α and α’ is that where the electron beam is located only a single value is obtained, resulting from the integration of the signal through the whole sample thickness. A prerequisite for a proper measurement would thus be the finding of locations in the TEM sample that consist of either pure α or pure α’. This selection cannot be made with complete certainty, because Fe and Cr are each present in both phases, and the interfaces are diffuse. In addition, in areas where α or α’ are stacked on top of each other or α–α’ interfaces are present, the Cr content will be overestimated in α and underestimated in α’. Note that the gradual α–α’ interface makes up a significant portion of the sample...
volume. All these aspects are more problematic in finer and less clearly defined decomposition structures, which occur in the early stages of the decomposition. This is notable when comparing the compositions obtained in this study for the 20 wt% Cr-containing alloys with the results reported for similar alloys by Novy et al.\cite{17} and Tissot et al.\cite{18} as a better agreement is reached for the longer annealing times. Novy et al. and Tissot et al. applied APT, which in principle separates α from α’ regions more easily than TEM.

TEM samples prepared by FIB must have a thickness comparable with the size of the α’ regions to enable composition measurements of pure α’, which is difficult to achieve in practice. This caused the comparatively low Cr contents in α’ for the TEM samples prepared by FIB, as presented in Figure 7 and Table 1. For the measurement of α, a larger sample thickness is acceptable, as it is the dominant phase. In addition, it should be more precise than in electropolished samples, because with FIB no preferential etching was observed. The α compositions obtained from FIB samples are indeed in good agreement with APT results from the literature: annealing of the 20 wt% Cr-containing alloy for 480 h at 500 °C resulted in a Cr content of 14 ± 1 at%, while Novy et al.\cite{17} and Tissot et al.\cite{18} reported a Cr content of about 15 and 15.5 at%, respectively, for similar conditions. Note that our 40 wt% Cr-containing alloy annealed for 1008 h at 500 °C and prepared by FIB yielded an α Cr content of 17 ± 3 at%.

In electropolished TEM samples, the selective etching of α massively increased the availability of α’ regions that are well suited for composition measurements by EDS. However, selective etching also leached out Fe from the surface of the α’ regions. This effect can be observed clearly for α regions in specimens in the initial condition; even for the material of uniform composition (undecomposed), the EDS yielded consistently larger Cr concentrations in thin areas, as presented in Table 1, whereas the composition measured in successively thicker areas approached and eventually reached the nominal composition. The effect can also be observed for α’, which can lead to an adverse effect: in the thinnest sample-edge areas, Cr concentrations exceeding 90 at% in some α’ regions were measured, which is higher than the values reported in APT and Mössbauer studies at 500 °C.\cite{14,17,18} This may be due to dealloying of α’ (i.e., loss of Fe) coupled to poor statistics because these areas are extremely thin (below 10 nm), leading to a weak EDS signal. Thus, the quantification of the α and α’ compositions in electropolished samples seems to be more affected by artefacts than in samples prepared by FIB, noting also that in the latter preparation method EDS reliably yields the nominal composition, independent of thickness and annealing. Selective etching is especially pronounced for the 40 wt% Cr alloy, as it yields self-supported α’ features.

Nonetheless, it should be stressed again that selective etching enables a more accurate composition measurement of pure α’ regions by the removal of the surrounding α, making them stick out from the sample edges of the electropolished TEM samples (Figure 4–6). This leads to a bumpy surface, with larger thicknesses in α’-rich regions. It is probably this thickness variation that made possible the identification of α’ by TEM\cite{38} and high resolution TEM.\cite{21,22}

4.3. Structure Determined by STEM—EDS

In the 15 wt% Cr alloy (15.93 at% Cr), an α’ volume fraction of 2–3 vol% would be expected in a mature state, considering equilibrium Cr contents of 14 at% Cr for α and just over 80 at% Cr for α’. The observed volume fraction, however, is estimated to be 0.1 vol% at most, which implies that the α-matrix composition in the sample barely changed even after 1008 h of annealing. Note that in the studies of Novy et al.\cite{17} and Tissot et al.\cite{18} the Cr content of α decreased upon demixing from 20 and 19 at% to 14.2 and 14.8 at%, respectively. It thus appears that the decrease in Cr content due to demixing upon annealing is reduced for decreasing nominal Cr content, revealing less demixing close to the boundary of the miscibility gap. The few α’ particles observed for the 15 wt% Cr alloy are comparatively small and appear to be as well defined as those observed in the 20 wt% Cr alloy (Figure 4a,b), which indicates that they may have nucleated at an early stage of annealing, presumably heterogeneously at lattice defects. This hints at α’ nucleation as the limiting factor for α–α’ separation. The increased measured Cr content in α in the annealed state, as compared with the initial state, may indicate a structuring of Fe and Cr on a scale too small to be detected by EDS, as selective etching will increase the overall measured Cr content for all kinds of ordering. However, thickness differences of the considered areas may also explain the difference.

Note that Figure 6a for the 15 wt% Cr-containing alloy only exhibits a single particle; we made the choice to display it this way to have micrographs with the same scale. As all the observed α’ particles lie tens of nanometers away from the sample edge, it is very likely that most of them are overlaid with α in the chemical maps, leading to the large spread of the α’ composition given in Table 1.

In the 20 and 40 wt% Cr alloys (21.27 and 41.73 at% Cr respectively), the decomposition structures obtained in this work are qualitatively in good agreement with the literature.\cite{17,18,27,28,12} For the 20 wt% Cr alloy the work of Novy et al.\cite{17} is a good comparison, where the main differences are that the alloy used by Novy et al. contained only about 19 wt% Cr and only APT was used for the analysis. The quantitative discrepancies with the larger α’ volume fractions and particle sizes observed in our study can be partially explained by the difference in Cr content. Another important factor may be that features with a diameter of less than about 2 nm can hardly be identified in EDS maps, effectively excluding the smallest α’ particles from our analysis by STEM—EDS. Another factor that significantly affects the particle size extracted from EDS maps is the definition of the particle itself: it requires an individual composition threshold for each interface, which takes into account the measured composition in the center of each particle. However, in the case of small α’ regions where the core Cr content is intrinsically low, which is the case for the shorter annealing times of for example the 20 wt% Cr alloy (Figure 4b,c), there is a large probability that the α’ regions overlap with the surrounding α matrix in the chemical map. This overlap leads to an apparent lower Cr concentration in the α’ core and is effectively indistinguishable from a map area that consists of the transition region. This is then often viewed as part of α’, which leads to apparent α’-area sizes.
that difference are larger than the real ones. This explains the decreasing difference in the measured α’ sizes between this work and Noy’s work,[17] with increasing annealing time.

In the 40 wt% Cr alloy, the separation into Cr-rich and Cr-depleted regions is already notable after 50 h of annealing (Figure 5b). However, the α regions still seem to contain substantial amounts of Cr, over 30 at%, even in their core areas. In the following heat-treatment steps, the Cr-rich regions grow moderately and the interface between α and α’ sharpens as the α phase continues to deplete in Cr (Figure 6b-f). In α’, the Cr content remains constant at around 80 at%, while the Cr in α decreases over time to 20–25 at% for the electropolished samples (Figure 7b), which is significantly higher than the presumed equilibrium composition of 14 at% deduced from APT,[17,18] and Mössbauer spectroscopy.[14] In contrast, the α composition obtained in samples prepared via FIB comes at 17 at% Cr, which is closer to this value. The discrepancy can be explained by the different erosion rates for α and α’ related to the preferential etching of Fe compared with Cr during electropolishing, in conjunction with the α–α’ decomposition structure, as mentioned earlier.

4.4. Structure Determined by APT

The APT results of the 20 wt% Cr-containing alloy annealed for 1008 h at 500 °C obtained in this study are in good agreement with the work of Noyv et al.[17] and Tissot et al.[18] More in detail, the match is particularly good with respect to the findings based on proxigrams, with a Cr content of 83 at% and a size of 2.6 nm for the α’ regions. STEM–EDS analysis yielded 80 at% and 3.5 nm, respectively. Taking APT results based on proxigrams as a benchmark, this indicates that STEM–EDS slightly underestimates the α’ Cr content, while the size is overestimated. The former stems from the averaging in a sample of variable thickness: in the thinnest regions, where α’ particles stick out (i.e., where they were uncovered by the matrix), the Cr content reaches 85 at%, a slightly higher value than can be explained by Cr enrichment, resulting from selective etching of Fe. In the slightly thicker regions considered for the measurements, the α’ Cr content was only about 70 at% due to the overlapping Fe-rich matrix. The underestimated size can be explained by beam broadening, specimen drift, and particle overlap. Let us look further into APT methods.

Looking further into the APT methods, we find the 1D profiles to yield data that show slight deviations to the proxigram results: the particle size is larger, at 3.1 nm instead of 2.6 nm, and thus closer to the STEM–EDS mapping results of this study (3.5 nm). The Cr composition in α is about 2 at% higher, at around 16.4 at%, and in α’ it is comparatively low at 77.4 at%, which is 5 at% less. This behavior is presumably caused by the chosen width of the cylinders: at 2 nm diameter, the sections around the α’ core incorporate parts of the boundary regions (poorer in Cr) for all but the largest particles, as judged from the proxigrams. Note that for the 1D profiles large particles were predominantly chosen, which artificially increases the average measured size. In STEM–EDS measurements, small particles were also overlooked, as they were often not identified as such, resulting in artificially larger average particle sizes. In addition, beam broadening, specimen drift during the acquisition, and particle overlap in STEM–EDS maps may also result in a slight overestimation of the particle size.

The cluster-search method yields an α’ core composition of 78.7 at% Cr, which is slightly lower than the values from literature and proxigrams in the present work and a bit higher than the one deduced from the 1D profiles. The radius of gyration, which essentially defines the core size of the α’ precipitates, was found to be significantly lower than the α’-region size obtained by the other APT analysis methods and by STEM–EDS. The cluster-search method shows smaller α’ particles, their core contains less Cr, and the interface width is about 3 nm (see Figure 8b,c). This partly explains why according to this method the interface is as diffuse as with the other two methods. The results further indicate that the α’-particle distribution includes finer precipitates than those deduced from APT proxigrams, 1D profiles, and EDS maps.

Summarizing the different APT analysis methods, one can conclude that the proxigram method yields the lowest uncertainty in the measured composition due to its combined high counting statistics and spatial localization, while 1D profiling along the field-evaporation direction yields the most precise method for the evaluation of the particle size and in particular interface width. The cluster-search method, on the other hand, allows the exploration of smallest clusters. APT thus provides a wealth of results, with each APT analysis method providing one aspect of the real microstructure. The most complete picture emerges when different data acquisition and processing methods are considered, correlated, and combined.

To sum up all methodologies deployed here, one should start with the sample preparation artefacts. For STEM–EDS, while electropolishing appears beneficial compared with FIB for isolating α’ regions from the matrix, one should keep in mind that the incurring preferential etching of Fe can lead to their dealloying, even if only slightly, which in turns leads to a slight overestimate of their Cr content. In contrast, FIB appears beneficial to probe the α matrix, because it does not suffer from preferential etching, but cannot isolate the α’ regions from the matrix without resorting to the challenge of preparing very thin samples. In contrast, APT is not affected by the sample preparation method as the analyzed volume is below the surface.

STEM–EDS appears as a suitable technique to complement APT, when the precipitation structures have a size range spanned by APT, due to the larger probed volume and the detection of crystallographic defects in TEM. The latter point may be a key to expand our understanding of the α–α’ decomposition, because, as remarked for the 15 wt% Cr-containing sample, the nucleation of the α’ phase may be promoted at such defects. This is critical for studying irradiated materials, when there is a relation between irradiation-induced dislocation loops and Cr segregation. Correlating APT and TEM (including STEM–EDS) is thus a fruitful approach for a more complete assessment of the Fe–Cr miscibility gap and, further, for studying irradiation effects in Fe–Cr.

Note that besides the TEM sample preparation artefacts there are limits to TEM, such as beam broadening, sample drift, and precipitation overlap. However, with the advent of better optics for S/TEM (Cs correction) and developments in specimen preparation techniques (FIB at low energies and multi-ion species), STEM–EDS has great potential for improvement, in particular when combined with simulations of the EDS signal.
4.5. Precipitation Mechanism

Classical nucleation indicates that the formation of a nucleus has a constant composition (the one of the equilibrium precipitation phase) and presents a sharp interface to the matrix. Its volume Gibbs free energy and interface energy are then constant, which allow applying classical nucleation theory to for example deduce the critical radius beyond which the nucleus is stable. According to published phase diagrams of Fe–Cr that include in the miscibility gap the boundary or transition line to the spinodal decomposition,[139] one may expect a spinodal decomposition for the 40 wt% Cr alloy and classical nucleation and growth precipitation for the 20 wt% Cr alloy, as its content is larger than the published solubility limit of 14 at% at 500 °C. However, in our 20 wt% Cr alloy, classical precipitation may be questioned because the measured composition of the α′ phase regions varies widely and is below the published solubility limit of 85 at% at 500 °C, and the interfaces are ill defined. This was also reported earlier[17,18] for about the same alloy composition. Note that the transition line to the spinodal decomposition is not firmly established in the literature. The observed globular precipitates may then stem from spinodal decomposition, as in the 40 wt% Cr alloy. In fact, when comparing the 20 wt% and 40 wt% Cr-containing alloys, both globular and spinodal α′ structures reveal beyond 150 h of annealing about the same α′-core Cr content of around 80 at% (as determined by STEM–EDS in electropolished samples, thus slightly underestimated), which may support this idea. On the other hand, there is a different α′-core Cr content, of respectively about 14 and 17 at%, as determined by STEM–EDS in FIB-cut samples, which is slightly beyond the published solubility limit of Cr in Fe at 500 °C. Note, however, that the diffusion in Fe–Cr is slow, which means that the apparent spinodal decomposition may actually be the very early stages of classical nucleation at the nanoscale. Note that classical nucleation occurs when the solute content is close to the solubility limit, which in an Fe-rich matrix is about 14 wt% Cr at 500 °C according to published Fe–Cr phase diagrams. In the case of supersaturation, which would be the case for the 20 wt% Cr alloy, Cahn and Hilliard[40] illustrated that the precipitate–matrix interface becomes diffuse and the solute content in the nucleus decreases. The APT cluster-search method, which is best at identifying smaller particles, views some of the deformed (nonspherical) particles in Figure 8a as multiple entities, which may consist of merging particles and thus feature multiple local concentration maxima. Such an observation was evoked by Cahn and Hilliard,[40] when they remarked that in supersaturated solutions the precipitates’ nucleus is not homogeneous in composition, but may rather be described by a composition fluctuation. This indicates that such nonclassical nucleation would operate in the 20 wt% Cr alloy, which was invoked earlier.[17] In the Fe–Cr system, there is thus potentially a smooth transition from classical nucleation to spinodal decomposition with increasing Cr content (from the Fe side of the phase diagram), going through nonclassical precipitation, so that in the phase diagram there is no sharp transition line between them. Our results indicate that the boundary of the Fe–Cr miscibility gap at 500 °C is between 14 and 17 at% Cr on the Fe side and 80 and 83 at.% Cr on the Cr side. The former values are in average only slightly larger than published ones (14 at.%), while the latter values are lower than those found in the literature (85 at%).

4.6. Relationship Between Structure and Strength

The nanoscale α′ regions surrounded by α are crystallographically coherent with the matrix, as indicated by their invisibility in TEM and by the lack of additional diffraction spots, which make them potentially shearable by dislocations. This assumption is supported by molecular dynamics simulations of dislocation-precipitate interaction in Fe, which show that nanoscale spherical pure Cr precipitates in pure Fe are obstacles that are easily shearable by dislocations and, compared with other obstacle types, are rather weak.[41–43] When considering a constant α′ volume fraction, a potential transition upon further annealing from particles shearing to dislocations looping around them (leading to Orowan hardening) would be marked by a maximum in hardness at the respective time in the annealing process, because hardening due to dislocation looping would decrease as the α′ regions continue to coarsen, while particle shearing would have the opposite tendency. This behavior has generally not been observed, and most published studies on hardness related to α–α′ decomposition indicate a continuous hardness increase with annealing time in the same time range of 50–1000 h as considered in the present study.[5,11,13,31,32,38,44] There are, however, some isolated studies that revealed a hardness decline or plateau[6,11,21] Note that the possibility of dislocation looping has been considered in the past, by Marcinkowski et al.,[11] but it was dismissed because the hardness increase expected by looping around α′ would far exceed the observed one.

In the past, numerous and detailed efforts have been devoted to rationalize shearable-particle hardening and its various aspects,[11,45,46] with a distinct treatment of hardening due to spinodal decomposition.[45,47] The aim of the present work, however, is to compare the hardening of the two different types of decompositions we have observed, that is, globular versus spinodal decomposition. Such a comparison is achievable only when the same set of parameters can be applied to both mechanisms. In this view, we treated hardening via the same theoretical framework for both microstructures. This is justified by considering that the 3D interconnectivity of the secondary phase has no direct impact on the obstacle size experienced by a dislocation that moves in its glide plane. What matters is the obstacles’ footprint within the glide plane. We thus extracted an effective particle size from the spinodal structure. This parameter was obtained by measuring the extent of the α′ areas in the chemical maps along straight lines randomly placed. The resulting values can be found as σact in Table 1. Going forward, ract was used for the 40 wt% Cr alloy and rs was used for the 20 wt% Cr alloy as a substitute to r. It was consistently found that ract ≈ 1.5rs for all conditions of the 40 wt% Cr-containing alloy.

We then rationalized the induced hardening with the general expression by Deschamps and Bréchet developed for shearable obstacles.[48]

\[
\Delta \sigma_{cys} = \frac{3 \kappa MG}{4\pi \beta \sqrt{b}} \sqrt{r}
\]
Here, $\Delta \sigma_{\text{cps}}$ is the coherent particle strengthening, $\beta$ is a constant equal to about 0.5, $M$ is the Taylor factor, $G$ is the shear modulus of the matrix, $b$ is the modulus of the Burgers vector, $f$ is the particle volume fraction, and $r$ is the equivalent radius of the particles. The parameter $k$ represents the strength of the $\alpha'$ regions as obstacles to mobile dislocations. Because Equation (4) does not distinguish between the different aspects of coherent particle hardening, the chemical interface hardening, the lattice parameter mismatch, and the mismatch of the elastic constants between $\alpha$ and $\alpha'$ are all incorporated in the parameter $k$, which is thus specific to a given combination of matrix and particle material.

Rearranging Equation (4) to extract $k$, the obstacle strength, yields

$$
k = \left( \frac{4\pi \beta b}{3f r} \right)^{\frac{1}{2}} \left( \frac{\Delta \sigma_{\text{cps}}}{G} \right)^{\frac{1}{2}}
$$

(5)

For the system presented, $M$ was taken as 2.748$^{49}$ and the Burgers vector as 0.249 nm, because the dislocation analysis revealed dislocations to be of type $\frac{1}{2} a_0 < 111>$. Furthermore, $f$ was obtained from Equation (1) and $r$ was measured directly.

The shear modulus $G$ for binary Fe–Cr alloys is estimated by

$$
G [\text{GPa}] = 0.37C_{\text{Cr}} + 80.5
$$

(6)

where $C_{\text{Cr}}$ is the Cr content of the binary Fe–Cr alloy in at%. In the present case $C_{\text{Cr}}$ was used, that is, the Cr content in the core of $\alpha$, to estimate the shear modulus of the $\alpha$ matrix. This expression was derived from experimental data by Speich et al.$^{50}$

To extract the coherent particle strengthening by $\alpha'$, $\Delta \sigma_{\text{cps}}$, it is assumed that

$$
\Delta \sigma_{\text{cps}} = \sigma_{\text{tot}} - \sigma_{\text{ss}}
$$

(7)

where $\sigma_{\text{tot}}$ is the overall strength of the alloy and $\sigma_{\text{ss}}$ is the strength of the $\alpha$–Fe–Cr solid solution. This expression is obtained by considering that only the Fe–Cr solid solution and the shearable $\alpha'$ particles contribute significantly to the overall strength. This seems reasonable as work hardening and hardening by incoherent oxide particles are negligible due to respectively the low dislocation and oxide particle densities. Also, Hall–Petch strengthening does not need to be considered as indentation was made in single grains. Note further that a linear additivity of $\sigma_{\text{ss}}$ and $\Delta \sigma_{\text{cps}}$ is supported by simulations of Terentyev et al.$^{46}$ The overall strength $\sigma_{\text{tot}}$ in MPa may be obtained by multiplying the hardness values VHN by 3.2.$^{51}$ The solid-solution strength $\sigma_{\text{ss}}$ is estimated from the Cr content (in wt%) by a linear fit of the alloys’ hardness in the initial condition (presented in Figure 2)

$$
\sigma_{\text{ss}} \text{[MPa]} = 11.9C_{\text{Cr}} + 180
$$

(8)

Again, $C_{\alpha}$ was used for $C_{\text{Cr}}$ to represent the $\alpha$ areas. With this, all variables needed in Equation (5) to extract the obstacle strength of the $\alpha'$ regions, i.e. the parameter $k$, are known for the 40 and 20 wt% Cr-containing alloys for all annealing times. The resulting $k$ values are listed in Table 2. Note that $k$ reacts conservatively to changes in $\alpha'$-area size and volume fraction, leading to comparatively low uncertainty regarding $k$, even with significant uncertainty regarding the particle radius. For instance, the use of $r_0$ instead of $r_{\text{act}}$ for the 40 wt% Cr alloy would shift $k$ from 0.018 to 0.021.

For the 20 wt% Cr alloy, the $k$ values increased with increasing annealing time and saturated after 240 h. Note that this happens at a time when coarsening starts to dominate compositional changes.$^{17,18}$ which is when the $\alpha'$ regions are seen to be well defined (Figure 4). It thus appears that $k$ remains constant once the compositions of $\alpha$ and $\alpha'$ are set, as expected. In the present case, the $\alpha'$ composition still evolves even in the presumed coarsening range, which might reflect the slight increase of $k$ to 0.019 after 1008 h of annealing.

The 40 wt% Cr-containing alloy showed large composition differences between $\alpha$ and $\alpha'$, already after 50 h of annealing: the Cr content in $\alpha'$ is nearly at the saturation value of about 80 at%, while $\alpha$ is further depleted in Cr in the subsequent annealing steps. The further increased differences between $\alpha$ and $\alpha'$ have, however, no notable effect on $k$, which remains close to 0.018 (Table 2). This indicates that the $\alpha'$ obstacle strength is constant.

When considering both the 20 and the 40 wt% Cr alloys, it appears that $k$, i.e. the strength of the $\alpha'$ regions as obstacles to the mobile dislocations, shows a dependence on the Cr content. This is clear in the 20 wt% Cr alloy: the Cr content as a function of annealing time presents the same behavior as $k$, with an increase at the beginning of the annealing and reaching a plateau for long annealing times (Figure 7a). In other words, the $\alpha'$ regions become harder with increasing annealing time. In the

**Table 2.** $\alpha'$ regions’ strength ($k$) of the Fe–Cr alloys as a function of annealing time at 500 °C in relation to the experimentally measured VHN.

| Alloy | Ann. time [h] | Hardness [VHN] | $k$ |
|-------|--------------|----------------|----|
| Fe–20Cr | initial       | 133 ± 5         | –  |
|        | 50           | 176 ± 5         | 0.010 ± 0.003 |
|        | 150          | 197 ± 5         | 0.013 ± 0.003 |
|        | 240          | 223 ± 3         | 0.016 ± 0.004 |
|        | 480          | 245 ± 3         | 0.018 ± 0.005 |
|        | 1008         | 247 ± 5         | 0.019 ± 0.006 |
|        | ‘’ proxigram |               | 0.022 |
|        | ‘’ cl. search|               | 0.061 |
|        | ‘’ 1D profile|               | 0.018 ± 0.005 |
| Fe–40Cr | initial       | 215 ± 5         | –  |
|        | 50           | 378 ± 6         | 0.018 ± 0.009 |
|        | 150          | 409 ± 3         | 0.018 ± 0.005 |
|        | 240          | 416 ± 8         | 0.018 ± 0.005 |
|        | 480          | 431 ± 4         | 0.018 ± 0.003 |
|        | 1008         | 448 ± 4         | 0.018 ± 0.004 |
|        | ‘’ FIB       |               | 0.017 ± 0.005 |

$^{4}$The value $k$, a measure of the strength of the $\alpha'$ regions as obstacles to mobile dislocations, is calculated with the VHN reported in this table and the characteristic dimensions of $\alpha'$ reported in Table 1, obtained by STEM–EDS on electropolished samples unless stated otherwise. Proxigram, cluster search, 1D profile: APT; FIB: STEM–EDS on FIB samples. The uncertainty is given by the standard deviation.
case of the 40 wt% Cr alloy, the Cr content in the α’ regions is nearly constant for all annealing times. With about 80 at% (Figure 7b), they have about the same obstacle strength as the ones in the 20 wt% Cr alloy when those also reach about 80 at % Cr after the longest annealing time. Indeed, at this point, $k$ is 0.019, which matches within the error margin the 0.018 of the 40 wt% Cr alloy. This indicates that the α’ regions present the same obstacle strength in both alloys for a given Cr content. Note that the variation in hardness of the 40 wt% Cr alloy with annealing time relates then to the variation in volume fraction and size of the α’ regions.

In the following, we further explore the sensitivity of the $k$ value to the method used to derive the needed microstructural information. The $k$ value deduced from results from the APT 1D profiles for the 20 wt% Cr alloy annealed at 500 °C for 1008 h (see Table 2) agrees well with the values deduced from the EDS measurements, which reflects the similarity in the measured Cr content and size of the α’-regions core between the two methods. The $k$ stemming from the proxigram is with 0.022 (see Table 2) somewhat higher than the EDS value of 0.019, but within the uncertainty limit of the latter. The uncertainty limit of the proxigram-derived values is not given because in this case the volume fraction is a directly measured result and not calculated via the α’ radius and composition, as is done for EDS and the 1D profiles. The difference in $k$ eventually relates to the smaller radius detected by the isoconcentration method in comparison with the EDS method, which, as explained earlier, does not resolve the smaller particles and slightly overestimates the size of the visible ones. In contrast, the $k$ value derived from the APT cluster-search method is with 0.061 about three times larger than the values deduced from EDS and the two other APT analysis methods. This relates to the fact that the APT cluster-search method resolves smaller and grouped particles better, whereas these are measured as single particles by the other methods, reducing the measured particle size in the cluster-search method. The latter is, however, less discerning with immature α’ regions, that is, with Cr contents of less than about 70 at%, which leads to a particle number density roughly identical to the other methods. This together with the smaller particle size generates a smaller volume fraction, which explains the much higher $k$ value. While the cluster-search method has the advantage of detecting smaller particles, its sensitivity may miss an important part of the microstructure characteristics and thus can cause misinterpretations. Thus, when deriving macroscopic properties, this method should be used with greater caution, while the APT-proxigram and 1D-profile methods appear to be more adequate for this purpose.

To sum up, in Fe–Cr, the strength of the α’ regions as obstacles to mobile dislocations, or $k$, consistently and remarkably reached the same value (of about 0.018–0.019 as deduced from STEM—EDS measurements) for two different nominal Cr contents, 20 and 40 wt%, and different α’ morphologies, that is, a globular one and a spinodal one. This indicates that this value applies for both types of morphology of the α’ regions in an α matrix, provided that they contain the same respective amount of Cr, that is, about 80 at% Cr in α’ and about 15 at% in α. We thus have provided a direct link between hardness and structure, defined specifically by the total α’-volume fraction and average α’-regions equivalent radius, in Fe-dominated Fe–Cr alloys.

5. Summary

We studied the decomposition of Fe–Cr alloys into Fe-rich α and Cr-rich α’ phases upon annealing at 500 °C and its impact on mechanical properties assessed by Vickers hardness. We focused in particular on the phase decomposition of Fe–Cr alloys with 20 and 40 wt% Cr at different stages of their decomposition for annealing times of up to 1008 h, as analyzed mainly by STEM—EDS, and APT, serving as a correlative benchmark. Our specific conclusions are as follows. 1) The 20 and 40 wt% Cr-containing alloys showed upon annealing a remarkable increase in hardness from 133 to 247 VHN and 215 to 448 VHN, respectively, whereas the alloys with lower Cr content showed a hardness plateau. 2) There is a significant α’–α decomposi- tion upon annealing in the 20 and 40 wt% Cr alloys, while the 5 and 10 wt% Cr alloys showed no phase separation. The 15 wt% Cr-containing alloy exhibited some decomposition, but very limited compared with the alloys with higher Cr contents, and no hardening. 3) The 20 wt% Cr alloy presents a dense dispersion of globular α’ precipitates, whose radius after 1008 h of annealing is 3.5 nm, as measured by STEM—EDS. It is similar or larger than the one found by APT, which ranges from 1.2 to 3.1 nm depending on the APT analysis method deployed, with the 1D profile presenting the best match to the STEM—EDS measurements. Upon annealing, the Cr content, as measured by STEM—EDS, reaches in α’ about 80 at%, while it falls to about 14 at% in α. The STEM—EDS data on the α’ Cr content, considering the slight underestimation, closely matched the APT proxigram method result of 83 at%. This demonstrates that a correlation between high-resolution techniques is increasingly needed to accurately decipher nanoscale features. 4) The 40 wt% Cr alloy exhibits a spinodal decomposition with vein-like α and α’ regions. Their equivalent radius at 1008 h of annealing, as determined by STEM—EDS, is 3 nm. Upon annealing, the Cr content in α’ rapidly reached about 80 at%, a value slightly underestimated, while in α it continually decreased in the imparted time of 1008 h, down to 17 at%. 5) The decomposed Fe–Cr alloy with 15 wt% Cr was found to feature less α’ than what would be expected by its nominal composition. It was below 0.1 vol%, which explains the lack of hardening. It is proposed that homogeneous nucleation may be hindered at such low supersaturation and that the observed α’ regions primarily nucleated at defects. 6) STEM—EDS was assessed with respect to the reliability of local compositional data acquired from EDS maps on Fe–Cr alloys. The results in terms of composition and α’-area size were found to be consistent with the APT results. Samples prepared by electropolishing seem well suited for analyzing the composition of α’ due to preferential etching of α. Samples prepared by FIB yielded more reliable values for α. 7) The contribution of the α’ regions to the strength of the decomposed Fe–Cr alloys was evaluated according to Deschamps and Bréchet’s equation,\[^{48}\] which is based on the assumption that the α’ regions are obstacles to mobile dislocations that are shearable. For the 20 wt% Cr alloy, the values for $k$, which is a measure of the strength of such an obstacle, show an initial increase with annealing time and stabilize at around 0.018 after a few 100 h at 500 °C. The Fe–Cr alloy with 40 wt% Cr yields similar $k$ values to those of the mature 20 wt% Cr alloy at about 0.018, for all studied annealing times. A $k$ value of around 0.018 classifies α’ regions as comparatively weak obstacles.
8) Overall, once the system reached a certain state of maturity, the \( k \) values were found to remain constant at around 0.018, remarkably independent of the nominal composition and the shape of the \( \alpha' \) regions. This maturity level is reached when the \( \alpha' \)-regions equivalent radii are more than 3 nm and the \( \alpha' \)-Cr contents are over 65 at\%, as measured by STEM–EDS. 9) These results present a quantitative description of the \( \alpha' \)-\( \alpha' \) decomposition and the resulting hardening in Fe–Cr alloys, which are model systems for ferritic steels that are proposed as structural materials of future fusion reactors. Advancing the understanding of this fundamental aspect with respect to the embrittlement mechanism of those ferritic steels will allow mitigating the risk of failure, making them more reliable, which is of great importance for future sustainable power systems.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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atom probe tomography, decomposition, Fe–Cr, hardening, phase separation, scanning transmission electron microscopy

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[1] R. L. Klueh, A. T. Nelson, J. Nucl. Mater. 2007, 371, 37.
[2] E. A. Little, Mater. Sci. Technol. 2006, 22, 491.
[3] S. J. Zinkle, J. T. Busby, Mater. Today 2009, 12, 12.
[4] R. M. Fisher, E. J. Dulis, K. G. Carroll, Trans. AIME 1953, 197, 690.
[5] R. O. Williams, H. W. Paxton, J. Iron Steel Inst. 1957, 185, 358.
[6] P. Grobner, Metall. Trans. 1973, 4, 251.
[7] R. Lindau, A. Moslang, M. Rieth, M. Klimiukov, E. Materna-Morris, A. Alamol, A. A. F. Tavassoli, C. Cayron, A. M. Lancha, P. Fernandez, N. Baluc, R. E. Schäublin, E. Diegelo, G. Filacchioni, J. W. Rensman, B. van der Schaff, E. Lucon, W. Dietz, Fusion Eng. Des. 2005, 75–79, 989.
[8] L. Malerba, N. Anento, J. P. Balbuena, C. S. Bequest, N. Castin, M. J. Caturla, C. Domain, C. Guererroo, C. J. Ortiz, P. Cournier, S. Serra, Nucl. Mater. Energy 2021, 29, 101069.
[9] V. Kuksenko, C. Pareige, P. Pareige, J. Nucl. Mater. 2013, 432, 160.
[10] R. E. Schäublin, B. Decamps, A. Prokhodtseva, J. F. Löfler, Acta Mater. 2017, 133, 427.
[11] M. Marcinkowski, A. Szirmae, R. Fisher, Trans. Metall. Soc. AIME 1964, 230, 676.
[12] D. Chandra, L. Schwartz, Metall. Trans. 1971, 2, 511.
[13] S. Brenner, M. Miller, W. Sozza, Scr. Metall. 1982, 16, 831.
[14] S. M. Dubiel, G. Inden, Int. J. Mater. Res. 1987, 78, 544.
[15] M. Miller, M. Hetherington, Surf. Sci. 1991, 246, 442.
[16] O. C. Hellman, J. A. Vandenbroucke, J. Rüsing, D. Isheim, D. N. Seidman, Microsc. Microanal. 2000, 6, 437.
[17] S. Novy, P. Pareige, C. Pareige, J. Nucl. Mater. 2009, 384, 96.
[18] O. Tissot, C. Pareige, M.-H. Mathon, M. Rousset, E. Meslin, B. Décamps, J. Henry, Mater. Charact. 2019, 151, 332.
[19] E. R. Reese, M. Bachhav, P. Wells, T. Yamamoto, G. R. Odette, E. A. Marquis, J. Nucl. Mater. 2018, 500, 192.
[20] E. Wakai, A. Hishinuma, Y. Kato, H. Yano, S. Takaki, K. Abiko, J. Phys. IV 1995, 5, 277.
[21] O. Soriano-Vargas, E. O. Avila-Davila, V. M. Lopez-Hirata, N. Cayetano-Castro, J. L. Gonzalez-Velazquez, Mater. Sci. Eng., A 2010, 527, 2910.
[22] V. M. Lopez-Hirata, O. Soriano-Vargas, H. J. Rosales-Dorantes, M. L. S. Muñoz, Mater. Charact. 2011, 62, 789.
[23] Z. Jiao, V. Shankar, G. S. Was, J. Nucl. Mater. 2011, 419, 52.
[24] P. Hedström, S. Baghsheikhi, P. Liu, J. Odqvist, Mater. Sci. Eng., A 2012, 534, 552.
[25] M. Straumann, C. Weng, Acta Crystallogr. 1955, 8, 367.
[26] I. Seki, K. Nagata, ISIJ Int. 2005, 45, 1789.
[27] J. Westraadt, E. Olivier, J. Neethling, P. Hedström, J. Odqvist, X. Xu, A. Steuwer, Mater. Charact. 2015, 109, 216.
[28] X. Xu, J. Odqvist, M. H. Collander, M. Thuvander, A. Steuwer, J. E. Westraadt, S. King, P. Hedström, Metall. Mater. Trans. A 2016, 47, 5942.
[29] X. Xu, J. E. Westraadt, J. Odqvist, T. G. Youngs, S. M. King, P. Hedström, Acta Mater. 2018, 145, 347.
[30] X. Xu, J. Odqvist, M. H. Collander, S. King, M. Thuvander, A. Steuwer, P. Hedström, Acta Mater. 2017, 134, 221.
[31] M. Miller, J. Hyde, A. Cerezo, G. Smith, Appl. Surf. Sci. 1995, 87, 323.
[32] M. Miller, J. Hyde, M. Hetherington, A. Cerezo, G. Smith, C. Elliott, Acta Metall. Mater. 1995, 43, 3385.
[33] Z. Yao, S. Xu, M. Jenkins, M. Kirk, J. Electron Microsc. 2008, 57, 91.
[34] S. S. Gerstl, S. Tacke, Y. Chen, J. Wagner, R. Weipf, Microsc. Microanal. 2017, 23, 612.
[35] A. Cerezo, L. Davin, Surf. Interface Anal. 2007, 39, 184.
[36] D. Vaumousse, A. Cerezo, P. Warren, Ultramicroscopy 2003, 95, 215.
[37] J. R. Stephens, W. R. Witzke, J. Less Common Metals 1976, 48, 285.
[38] D. Chen, A. Kimura, W. Han, J. Nucl. Mater. 2014, 455, 436.
[39] W. Xiong, M. Selleby, Q. Chen, J. Odqvist, Y. Du, Crit. Rev. Solid State Mater. Sci. 2010, 35, 125.
[40] J. W. Cahn, J. E. Hilliard, J. Chem. Phys. 1959, 31, 688.
[41] S. H. Haghighat, D. Terenteyev, R. Schäublin, J. Nucl. Mater. 2011, 417, 1094.
[42] R. Schäublin, S. H. Haghighat, J. Nucl. Mater. 2013, 442, 643.
[43] S. H. Haghighat, R. E. Schäublin, D. Raabe, Acta Mater. 2014, 64, 24.
[44] R. E. Schäublin, J. Henry, Y. Dai, C. R. Phys. 2008, 9, 389.
[45] M. Kato, Acta Metall. 1981, 29, 79.
[46] D. Terenteyev, G. Bonny, L. Malerba, Acta Mater. 2008, 56, 3229.
[47] A. J. Ardel, Metall. Trans. A 1985, 16, 2131.
[48] A. Deschamps, Y. Brechet, Acta Mater. 1998, 47, 293.
[49] J. Rosen Berg, H. Piehler, Metall. Trans. 1971, 2, 257.
[50] G. Speich, A. Schwoebel, W. C. Leslie, Metall. Trans. 1972, 3, 2031.
[51] D. Tabor, in The Hardness Of Metals (Eds: W. Jackson, H. Fröhlich, N. F. Mott), Oxford University Press, Oxford 1951, 79.