Experimental investigation of the ordering pathway in a Ni-33at%Cr alloy

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Abstract

The present study involves a detailed experimental investigation of the concurrent compositional clustering and long-range ordering tendencies in a Ni-33at%Cr alloy, carried out by coupling synchrotron-based X-ray diffraction (XRD), transmission electron microscopy (TEM), and atom probe tomography (APT). Synchrotron-based XRD results clearly exhibited progressively increasing lattice contraction in the matrix with increasing isothermal aging time, at 475 °C, eventually leading to the development of long-range ordering (LRO) of the Pt₂Mo-type. Detailed TEM and APT investigations revealed that this LRO in the matrix is manifested in the form of nanometer-scale ordered domains, and the spatial distribution, size, morphology and compositional evolution of these domains have been carefully investigated. APT results also revealed the early stages of compositional clustering prior to the onset of long-range ordering in this alloy and such compositional clustering can potentially be correlated to the lattice contraction and previously proposed short-range ordering tendencies.

1. Introduction

Engineering alloys based on Ni-Cr-Fe have been utilized effectively throughout the entire modern history of materials development. While the Fe-rich alloys have been used to develop a variety of stainless steels, the Ni-rich alloys have been advanced to manufacture superalloys. Combinations of higher corrosion resistance, superior creep resistance, and better tensile properties at high temperature have made Ni-rich alloys most appropriate for industrial applications involving elevated temperatures.

Ni-15Cr-8Fe (all in at.%) such as INCONEL 600 (or alloy 600) has found extensive use in both the chemical industry and in nuclear reactors, for example, control rod drive mechanism (CRDM) nozzles, steam generator (SG) tubing, SG divider plates etc. that carry superheated steams in nuclear reactors [1]. Alloy 690 (INCONEL 690) with the nominal Ni-29Cr-9Fe composition has been selected to replace alloy 600 due to its increased stress corrosion cracking resistance under the operating conditions common in light water reactors (LWRs) [2]. This resistance has been attributed to the increased chromium content in comparison to alloy 600, and the ability to effectively passivate during oxidation without the resultant sensitization. Both Alloy 600 and Alloy 690 exist as an fcc solid solution at elevated temperatures. However, given the high chromium

content in Alloy 690, an ordered body centered orthorhombic phase, referred to as the Ni_2Cr or γ' phase can precipitate [2-4]. In general, it is believed that this ordered phase may embrittle the alloy, possibly due to the development of internal stresses associated with the secondary hardening precipitates [2-4]. This embrittling ordered phase has the potential to affect adversely the mechanical properties of the alloy in service [4-6]. As a result, the performance for components made from Alloy 690 could be greatly compromised.

The ordered Ni_2Cr or γ' phase, which has a Pt_2Mo -type crystal structure with Immm symmetry, has been reported to form in Ni-Cr alloys upon aging in the temperature range of 300-590°C for thousands of hours depending on the alloy composition [2, 4, 7, 8]. The body centered orthorhombic (BCO) structure of Ni_2Cr cell is shown schematically in Fig. 1 in relation to the parent fcc cell. The orientation relationship of this phase with the FCC matrix and the approximate cell parameters are given by:

$$\begin{aligned} \left[\begin{matrix} 001 \\ 110 \end{matrix} \right]_{fcc} \parallel \left[\begin{matrix} 001 \\ 100 \end{matrix} \right]_{g'} \quad a = \frac{3a_o}{\sqrt{2}}; b = \frac{a_o}{\sqrt{2}}; c = a_o \end{aligned}$$

In a commercial Alloy 690, Delabrouille et al. [9] reported long-range ordering after aging for 70,000 h at 420 °C. They reported dark-field TEM images that showed the formation of ordered Ni_2Cr domains in the alloy after this very long term annealing treatment. While there are only a few reports of γ' precipitation in Alloy 690, the nucleation and growth of this phase has not been investigated in great detail. It is obvious that one of the major drawbacks is the time required for ordering to occur. The binary stoichiometric Ni-33Cr alloy, on the other hand, has been reported to undergo an ordering reaction within the first few hundred hours of aging in the temperature range indicated [8, 10]. It is also known that, in the case of off-stoichiometric Ni-Cr alloys, the ordering kinetics are substantially slower than those of a stoichiometric alloy [10, 11]. The binary alloy with a ratio of two Ni atoms for one Cr atom, thus presents a more suitable option to study the early stages of this phase, and its subsequent evolution during aging.

This study focuses on the ordering pathway involved in the development of LRO from a random solid solution in a Ni-33Cr alloy. Previous studies on ordering in Ni-Cr binary alloys report the formation of both short-range ordering (SRO) as well as LRO in these alloys [6, 8, 10, 12]. These studies focused on both Ni-25Cr (3Ni:1Cr) as well as Ni-33Cr (2Ni:1Cr) alloy compositions [12]. The SRO in these alloys has been described based on a dispersed order model [13] where highly ordered precipitates, on the order of a few nanometers, are uniformly dispersed within a disordered matrix. The experimental evidence presented in support of this SRO model was largely indirect in nature, i.e., presence of diffuse scattering and streaking of fundamental reflections in electron diffraction patterns, mottled contrast in bright-field TEM images, increases in resistivity and hardness, negative creep and lattice contraction. Marucco et al. [13] reported the formation of dispersed ordered zones, of the order of a few nanometers in dimension within a few hours of aging at temperatures below 500 °C. Taylor et al. [11] studied the

formation of localized order in the Ni₃Cr (or Ni-25Cr) alloy using resistivity and specific heat measurements during continuous slow heating and cooling experiments, and noted that LRO formation was sluggish in the same alloy [5]. It has been proposed that the coarsening of dispersed SRO nuclei does not easily take place due to their coherency in the matrix [5]. While these observations, which were captured by monitoring changes in cumulative physical properties such as resistivity, could be a result of the early stages of SRO in these alloys, there appears to be no definitive experimental evidence in support of the dispersed order model of SRO. In fact, Marucco [10] concluded that the TEM observations of SRO in these alloys require very careful interpretation. The experimental evidence for LRO, on long-term annealing of the same alloys, is much more conclusive. For example, the previously reported results clearly show the presence of superlattice reflections (e.g. at 1/3 and 2/3{022} positions) that are attributable to LRO [6, 12]. Additionally, dark-field TEM images recorded using these superlattice reflections also revealed the presence of coherent ordered domains [10] simultaneous with x-ray diffraction results that indicated substantial lattice contraction [13]. Typically, LRO initiates after 100 to 1,000 h annealing at ~500 °C in a Ni-33Cr alloy and is accompanied by sharp superlattice reflections in electron diffraction patterns and clearly defined domains in corresponding dark field images.

Past studies on ordering in these Ni-Cr alloys have largely employed X-ray diffraction (XRD), resistivity measurements, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) and were focused primarily on the development of LRO [14, 15]. However, rather limited information is available regarding the early stages of ordering in Ni-Cr alloys, especially with regards to the proposed dispersed order model, as well as the pathway leading from the disordered fcc solid solution to the development of ordered domains. Furthermore, the size and composition evolution of LRO ordered domains has not been investigated in detail. In the present paper, a systematic investigation was conducted of the formation and evolution of ordered domains with aging in a Ni-33Cr binary alloy, specifically focusing on the following aspects:

1. Synchrotron XRD experiments to identify the onset of long-range ordering (LRO) and evaluate the changes in lattice constant in the alloy with annealing. In addition, in-situ synchrotron heating and cooling experiments were used to capture the order-disorder transition in this system.
2. TEM to study the size, morphology and distribution of the LRO ordered domains after isothermal annealing.
3. Site-specific sample preparation along specific crystallographic directions, for atom probe tomography (APT) investigations, to directly visualize the size and morphology of the nanometer-scale LRO domains within the matrix and to determine the compositions of the LRO domains.
4. APT investigations of the early stages of compositional clustering prior to the onset of LRO.

2. Experimental Procedure

The binary Ni-33Cr alloy used in this investigation, was prepared by the Korean Atomic Energy Research Institute (KAERI). A Ni-33Cr plate was made by vacuum induction melting followed by hot rolling at 1200 °C, solution annealing at 1050 °C for 1 h and water quenching (WQ). This solution-annealed alloy was subjected to 3 different aging treatments at 475 °C (see Table 1).

Samples for synchrotron studies were prepared for the four conditions given in Table 1, with dimensions of 5 mm X 5 mm X 0.5 mm (thickness). The first set of experiments was performed on the 11-IDC beam-line (111 keV, $\lambda=0.11165\text{\AA}$) of the Advanced Photon Source (APS) at Argonne National laboratory (ANL). A CeO₂ standard (NIST diffraction intensity standard set: 674a) was used to calibrate the distance between sample and the 2D detector, the detector tilting angle, and position of the beam center. The scattered radiation was collected on a Perkin Elmer 2D detector system. The 2D diffraction data were integrated and converted to an intensity vs. two-theta (2θ) plot using the program Fit-2D [16]. Lattice constant values were obtained from the intensity vs. 2θ curves by Rietveld refinement. The Rietveld analysis was done using GSAS software with exp-gui interface by peak fitting with pure gamma-nickel fcc as the starting point. The first 5 peaks i.e. fcc – 111, 200, 220, 311, 222 were used for the refinement and determination of the lattice parameters [17]. Microhardness was performed using a Shimadzu Dynamic Ultra-micro Hardness Tester (ModelDUH-211) with a load of 1.96 N and a holding time of 10 sec. TEM lift-out samples for the 90 h, 240 h, and 8,000 h aged alloys were prepared using an FEI Nova 200 dual beam focused ion beam (FIB). TEM analysis was conducted using an FEI Tecnai F20 operated at 200 kV. Samples from the WQ, 90h, 240 h and 8,000 h aged alloys were also prepared for APT using the same FIB/SEM after identifying desired grain orientations using electron backscattered diffraction (EBSD) analysis. Standard lift-out techniques were used for APT sample preparation in the FIB before mounting the small sections of the samples on suitable holders for analysis. APT experiments were conducted on a CAMECA local electrode atom probe 3000X HR instrument. All experiments were performed in the temperature range of 20 K to 40 K with target evaporation of 0.5% and pulse fraction of 20 % of a steady-state applied DC voltage. APT data reconstruction and analysis were carried out using CAMECA IVAS® 3.6.8 software.

3. Results and Discussion

Synchrotron x-ray diffraction

The high energy of the synchrotron beam permitted carrying out the XRD experiments in the transmission mode through relatively thick samples, leading to averaging over substantial sample volumes. “The samples were rocked from $\pm 5^\circ$. The beam was a square beam of $500 \times 500 \mu\text{m}^2$ and the thickness of the sample was about 1000 μm . With the average grain size of $\sim 25 \mu\text{m}$; $\{(500 \times 500 \times 1000) / (25)^3\} \sim 15000$ grains were included in the study”. XRD results from the WQ, 90 h, 240 h, and 8,000 h aged samples are shown in Fig. 2 where the normalized intensity of all four samples have been plotted against 2θ . The WQ and 90 h aged alloys only show the fundamental fcc peaks and these have been marked in Fig. 2(a) and (b). However, in contrast, the longer-term aged samples show

extra superlattice peaks in addition to the fundamental fcc peaks. These additional superlattice peaks can be attributed to the BCO structure and have been marked in Fig. 2(c) for the 240 h aged sample and in Fig. 2 (d) for the 8,000 h aged sample. These superlattice peaks with d-spacings of 3.76 Å, 3.24 Å, and 2.38 Å were indexed as the (020), (011), and (110) peaks respectively of the BCO structure, indicating Pt₂Mo-type ordering in these two samples. Based on these superlattice peaks, the lattice parameters of this ordered BCO structure were calculated to be a= 7.52 Å, b= 2.50 Å and c= 3.55 Å, and these were consistent with the previously reported values by Chan et al. [18] from first principle calculations.

The experimentally measured lattice constant from the major fcc diffraction peaks in this case correspond to an average effect of the ordered domains and the surrounding disordered matrix. The average lattice constant in Ni-Cr alloys has been studied in great detail by Maruccio et al. using XRD [19] who reported that it decreased due to the formation of ordered domains. In the present study, the matrix lattice constant for all the samples were accurately determined using Rietveld refinement of the synchrotron XRD patterns shown in Fig. 2 and are plotted against aging time in Fig. 3. This plot reveals that the fcc lattice contracted significantly during isothermal aging at 475 °C. The largest lattice constant was observed in the case of the WQ alloy and it progressively decreased upon aging to 8,000 h. The amount of lattice contraction was relatively low between the WQ and 90 h samples and was highest between the 90 h and 240 h aged samples. Therefore, the greatest lattice contraction can be attributed to the development of LRO in this alloy which occurs between the aging periods of 90 and 240 h, based on the appearance of distinct superlattice diffraction peaks in the XRD patterns (Fig. 2). Referring to Fig. 3, it should be noted that there is a small degree of lattice contraction in the 90 h aged alloy as compared to the WQ alloy. This contraction indicates that there is some atomic rearrangement taking place in the random fcc solid solution at these early stages of annealing, that is not large enough to be comparable to the development of fully ordered domains. This early stage lattice contraction has often been attributed to short-range ordering (SRO) in the literature [12].

To gain further insight into the order-disorder transformation, an in-situ heating experiment was conducted in the synchrotron. A sample from the 8,000 h aged alloy, which clearly showed extra superlattice peaks corresponding to the Ni₂Cr (or Pt₂Mo type) ordering as shown in Fig. 2(d), was heated up to 800 °C, held for 5 min and then cooled to ambient temperature. This experiment resulted in disordering of the ordered alloy and this disordered random solid solution is retained on cooling to ambient temperature. The rate of heating and cooling was 0.5 °C/s. X-ray data were collected during this whole experiment at 18 s or 9 °C intervals. Lattice constants were determined from selected data points along the heating and cooling cycles, and these have been plotted against temperature in Fig. 4(a). At the early stages of the heating cycle, the lattice was expanding at a linear rate, due to coefficient of thermal expansion. But above 620 °C, the rate of expansion increased substantially until nearly 750 °C. The change in the slope or the change in the rate of expansion might be attributed to the order-disorder transition in this alloy. This is further evidenced by the fact that during the cooling cycle, the slope remained the same as the heating cycle and the re-ordering did not occur resulting in

retention of the disordered solid solution at ambient temperature. XRD patterns, corresponding to three (3) regions, marked by circles are shown in Fig. 4 (b), (c), and (d) and establish the fact that the initial alloy containing ordered domains completely disordered. A significant difference in lattice parameter between the initial partially-ordered alloy and the subsequent disordered alloy is observed and clearly demonstrates that lattice contraction takes place due to ordering phenomena or conversely, disordering results in lattice expansion. The order-disorder transition temperature for this alloy is observed to be 620 ± 5 °C by the synchrotron experiment which was previously estimated to be 590 °C by DSC experiments [8].

Microhardness testing

The microhardness of Ni-33Cr as a function of aging time at 475 °C is shown in Fig. 5. The hardness increased gradually with aging time from the WQ condition to the 475 °C, 8,000 h aged condition and the trend is similar to previous reports [2, 20]. A large increase in hardness was observed in the 240 h aged alloy and is attributed to the formation of LRO precipitates in the FCC matrix [11]. The further increase thereafter is minimal and is a contribution of either an increase in Ni₂Cr precipitates size with time or an increase in number density of Ni₂Cr precipitates.

Transmission Electron Microscopy

The Pt₂Mo type ordering has previously been identified and studied in detail in Ni-Mo and Ni-Mo-Cr systems [7, 21-23]. Selected area electron diffraction (SAED) patterns from the 90 h aged alloy are shown in Fig. 6(a) and (b), corresponding to the [001] and [011] zone axes (ZA), respectively. The lack of superlattice spots in either of these diffraction patterns confirms the absence of LRO in this sample and is consistent with the synchrotron results. For the samples aged for 240 h and 8,000 h, extra reflections were indeed observed in the [001] diffraction patterns shown in Figs. 6(c) and (e), respectively. These superlattice diffraction spots are located at the $1/3\{220\}$ in the [001] diffraction pattern. Centered dark field (CDF) images recorded using $1/3\{220\}$ reflections (Figs. 6(d) and 6(f)) reveal the size and distribution of the LRO domains in these samples. The diameter of the LRO domains is about 3 to 5 nm after aging for 240 h, and they increase to about 5 to 8 nm after 8,000 h of aging at 475 °C. The intensity profile along the black arrows in the Fig. 6(a), Fig. 6(c), and Fig. 6(e) are shown in Fig. 7(a), (b), and (c), respectively. These profiles show the position of the reflections arising from the ordered Ni₂Cr precipitates or LRO domains after the longer time aging treatments.

Atom Probe Tomography of Long-range Ordered Domains

Typically in APT analysis, clear distinction of a second phase precipitate from the matrix is possible when there is at least a certain degree of compositional difference. In cases where the ordered second phase and the disordered matrix have similar compositions as well as contain high solute concentrations, it is rather difficult to distinguish the two and, consequently, innovative approaches are needed to identify these ordered precipitates in

APT reconstructions. Recently, APT coupled with Orientation Imaging Microscopy (OIM) is becoming increasingly important in order to prepare site and orientation specific APT samples [24]. Such a priori knowledge of the crystallographic orientation of the APT reconstruction is immensely helpful for identifying, for example, ordered lattice planes within second phase precipitates.

The application of this technique of a priori identification of the grain orientation using EBSD and site-specific APT sample preparation is shown in Fig. 8. Greater details of this technique can be found in [24]. As described in Fig. 1, the {100} of the orthorhombic structure of the Ni_2Cr phase is parallel to the {110} axis of the fcc matrix. So a {110} oriented grain was chosen for the preparation of the lift-out specimen for APT analysis. Fig. 8(a) shows an SEM image during the major side milling of a {110} grain. After the actual lift-out, EBSD was again performed to confirm the correct grain was targeted, as shown in Fig. 8(b).

After preparing the needle-shaped APT specimen from the {110} oriented grain from the 240 h annealed alloy, it was field-evaporated under high vacuum. The pole figure of the {110} oriented grain is shown in Fig. 9(a), and the corresponding desorption map from the APT experiment is shown in Fig. 9(b). The desorption map is essentially a two-dimensional stacked view of the detector and only represents a limited region of surface of the needle. The map depends on the crystallographic direction during evaporation, and it is well known that poles, zone lines, etc. influence the map by introducing artifacts that appear as low-density hits or detection regions. Several poles could be observed in Fig. 9(b) that appear as darker and circular regions, and the strong pole near the center corresponds to the {110} fcc pole. The desorption map can also be regarded as a section of the pole figure shown in Fig. 9(a), but containing only a limited angular range from the center of the pole figure. A 5 nm slice of the APT reconstruction is shown in Fig. 9(c) where the {110} fcc pole appears as a low-density region throughout the reconstruction volume. Manual rotation, tilting, and sampling sections of the reconstruction distinctly identified atomic planes of the ordered cells. A magnified region embedding an ordered cell from the same reconstruction is shown in Fig. 9(d). They were distinctly different from the disordered fcc matrix because the disordered matrix will only reveal planes near the pole region whereas the ordered regions can maintain the planarity of atoms away from a pole. One possible reason is that the chemical bonding of atoms in the ordered regions is different from that of the disordered matrix, and thus the atoms field evaporate at different rates and also appear differently in the APT reconstruction.

It should be noted that the field evaporation of atoms in APT is a sequential process and consequently when the evaporation axis is aligned near a crystallographic direction, the result is sequential evaporation of atomic planes. Since the resolution of these atomic planes is rather difficult to ascertain in the raw atomic view of the APT reconstruction, as shown in Fig. 9(d), the use of spatial distribution maps (SDM) is a useful tool to visualize these atomic planes [25]. An SDM is a 2D map that shows the distance of atoms relative to a central atom. Thus, the planarity of the atomic planes are much easier to visualize in the Ni-to-Ni SDM shown in Fig. 9(e), corresponding to the ordered region within the matrix where the Ni lattice planes appear as alternating yellow planes (many atoms

present) with blue regions in between where few atoms are present. The interplanar spacing was measured to be 0.37 nm, and the angle between the fcc {110} pole and the planes of the domain is measured to be around 55°. Given the fact that the angles between fcc {110} family of planes is either 60° or 90°, it is highly probable that the ordered planes that are observed are the {200} planes of the Ni₂Cr structure, lying parallel to a set of {110} fcc planes, whose plane normal is at an angle of 60° to the axis of the atom probe sample. Since the a set of {100} directions in the Ni₂Cr structure consist of an alternating sequence of pure Ni and pure Cr planes, as shown in schematic in Fig 9 (e) aligning this direction closer to the evaporation axis in atom probe can result in planar resolution. The bond energy of Cr-Cr bond is 152 kJ/mol and Ni-Ni is 204 kJ/mol [26], therefore it is easier to evaporate Cr-Cr planes thus the merging of 3 planes (2 Ni-Ni and 1 Cr-Cr) in atom probe reconstruction is observed. The neighboring Ni-Ni planes are 0.125 nm apart which are possibly evaporating together. As the voltage ramps up to evaporate a Ni plane the adjacent Cr plane is evaporated preferentially along with this plane. As a result these 3 planes, which are 0.125 nm apart each, appear as a single plane in the reconstruction. As a consequence, the adjacent planes in the reconstruction appear to be separated by a spacing of 0.37 nm which is about half of the spacing between [100] planes as shown in the figure. It is worth mentioning here that the SDM of Cr ions did not reveal any clear signature of planarity possibly due to field evaporation with the Ni ions. The presence of these distinct lattice planes permitted the identification of LRO domains within the disordered matrix. Multiple such LRO domains were identified based on the presence of lattice planes within the ordered regions in another APT reconstruction of the 240 h aged alloy, shown in Fig. 10(a). The Ni-to-Ni SDM analysis was also applied to one of these domains (Fig. 10(b)). A normalized intensity plot along the white dashed line is shown in Fig. 10(c) to show the periodicity of the lattice planes.

Due to the stronger directional chemical bonding between atoms in the ordered domains, the spatial density of atoms would be expected to be higher. This probably contributes to the lattice contraction as shown in Fig. 3. Bernard et al. [27] also mentions that the molar volume of the ordered region is lower as compared to the disordered matrix. APT reconstruction of the raw atoms offers the unique advantage that the density could be readily measured and visualized. Fig. 11(a) shows a truncated portion of a reconstruction, and the atomic density (per volume) was plotted as a 2D map. The red color indicates the highest density within the rectangle, next is yellow, then cyan, and blue represents the lowest density. Fig. 11(b) shows the entire reconstruction where multiple domains could be identified based on the superimposed 2D density map.

The APT datasets from the 8,000 h aged alloy were put through the similar rigorous analysis and are described in Fig. 12 and Fig. 13. Fig. 12(a) shows the EBSD pole figure from the {110} oriented fcc grain used for the site-specific lift-out. Fig. 12(b) shows the APT desorption map, Fig. 12(c), the APT reconstruction containing the [011] pole, the magnified view of the LRO domains (marked by red polygons) are shown in Fig. 12(d). Fig. 12(e) shows the Ni-Ni SDM showing the planes within one of the ordered domains. In this case the fcc {110} plane and the Ni₂Cr planes are almost parallel (less than 10° misorientation). As discussed earlier we observe a inter-planar spacing of about 0.38 nm which is possibly the {100} direction of the Ni₂Cr precipitate.

Fig. 13 shows the 2D density maps from the same alloy superimposed with the reconstruction.

The individual domains of ordered precipitates were extracted from the APT dataset and their compositions were analyzed individually, as shown in Fig. 14. Multiple such domains were analyzed and the compositions of these domains varied from at-22 % Cr to 37 % Cr in both 240 h and 8,000 h aged samples. This observation was consistent with the fact that the Ni_2Cr intermetallic phase is not a line compound on the binary Ni-Cr phase diagram [28], but rather can accommodate a large off stoichiometry within the range of 22% to 40% Cr.

Analysis of Early Stages of Cluster Formation using Atom Probe Tomography

In addition to the analysis of the well-developed LRO domains in the 240 and 8,000 h sample, compositional clustering was investigated in the APT datasets for all the four samples, WQ, 90, 240, and 8,000 h. The primary motivation for such an analysis was to determine any compositional changes within the disordered fcc matrix of the Ni-33Cr alloy, prior to the onset of LRO in this alloy. The data-mining technique of cluster finding was employed, the details of this technique can be found in the literature [29], and the step-by-step procedure is described in the IVASTM 3.6.8 manual. Cluster analysis, in essence, identifies for a chosen atomic species, where the distance (d_{max}) between two atoms is smaller compared to the rest of the dataset. The values of d_{max} and N_{min} (minimum number of atoms in a cluster) were optimized to maximize the probability to detect any compositional clustering. With further data treatment the three-dimensional region with interatomic distances equal to or smaller than optimized valued of d_{max} and N_{min} (that yielded the biggest count of non-random clusters) were extracted from the data set. The results of this cluster analysis applied to the WQ, 90, 240, and 8,000 h samples of Ni-33Cr are summarized in Table 2.

While there were no detectable clusters of Ni in the WQ sample, the samples aged 90, 240, and 8,000 h clearly exhibited the formation of Ni-rich clusters within the fcc matrix. The average volume, diameter, and the aspect ratio (ratio of the longest-to-shortest dimension) of these clusters are listed in Table 2 and the corresponding visual depiction of these Ni-rich clusters is shown in Fig. 15. The results noticeably reveal that 90 h sample has the highest number density of the Ni-rich clusters, though this sample does not exhibit any LRO, as confirmed from the previously discussed synchrotron XRD as well as TEM results. Table 2 also shows that the average size of the Ni-rich clusters progressively increases with increasing isothermal annealing time from 90 to 8,000 h at 475 °C. These clusters have an average composition ranging from Ni-15Cr to Ni-19Cr, depending on the ageing time. The formation of these Ni-rich clusters could be a possible explanation for the effects attributed previously to short-range ordering (SRO) in this alloy. For example, Marucco et al [15] have discussed the possibility of Ni_3Cr type SRO phase which gradually enriches in Cr to give rise to the LRO domains of the orthorhombic body centered structure of Ni_2Cr type. While there are some interesting effects observed during the early stages of aging of binary Ni-Cr alloys, both Ni-33Cr as well as Ni-25Cr, such as lattice contraction, increases in resistivity, and changes in

specific heat, that have been attributed to SRO, conclusive evidence of such short-range ordering and the corresponding atomic scale structure is lacking, as discussed earlier. In addition to clustering of Ni ions, cluster analysis for Cr ions also located Cr-rich clusters in the 90 h, 240 h and 8,000 h aged samples. The number density of the Cr-rich clusters was lower than the Ni-rich clusters and their composition varied from 50-75 at% Cr in the clusters. The presence of Cr-rich clusters suggests the existence of a possible miscibility gap in Ni-Cr system, warranting a detailed investigation. Since Cr is a principal alloying element in many important super-alloys, establishing the details of Ni-Cr thermodynamic interactions, will be extremely helpful in predicting phase stability in multiple alloys after long term usage.

Suggested ordering pathway in Ni-33Cr

Since the average composition of the alloy is Ni-33at%Cr, starting from a disordered fcc solid solution, the simplest ordering pathway would be congruent ordering of the disordered solid solution to form the ordered Ni₂Cr structure. However, the experimental results presented in this paper clearly indicate that the ordering pathway adopted by this alloy during isothermal annealing at 475 °C is not simple congruent ordering. Thus, coupling the experimental results presented in this paper; synchrotron x-ray diffraction results, TEM, and APT, an unexpected and novel ordering pathway can be proposed for the disorder-order transformation in the Ni-33Cr alloy. Based on both the synchrotron x-ray diffraction as well as the electron diffraction results, it can be concluded that Pt₂Mo-type LRO in this alloy can be observed only after 240 h aging at 475 °C while the WQ and 90 h samples do not exhibit any LRO. However, detailed analysis of the APT data revealed that, while the WQ sample exhibited a nominally random distribution of both Ni and Cr atoms, the 90 h aged sample clearly exhibited a tendency for clustering of Ni atoms and consequently the formation of discrete Ni-rich clusters within the fcc matrix of the Ni-33Cr alloy. These clusters have been reconstructed in Fig. 15(a), while the quantitative analysis of these Ni-rich clusters is shown in Table 2. While the average diameter of these clusters is approximately 1.1 nm and their average composition is Ni-15Cr (at%) in case of the 90 h aged sample, the spread in their compositions is quite large, ranging from Ni-10Cr to Ni-25Cr. The presence of similar Ni-rich clusters was observed in APT investigations of Alloy 690 after isothermal annealing at temperatures less than 500 °C, the results of which are yet to be published. Such a tendency for Ni-clustering has also been reported previously in Ni-33Cr and Ni-Cr-Mo alloys by [30], based on atom probe results. It is tempting to associate the formation of these Ni-rich clusters to the ubiquitous short-range ordering (SRO) claimed in these alloys at the early stages of isothermal annealing at temperatures less than 500 °C. Since the existence of this SRO has largely been based upon its effect on lattice parameter, resistivity, and other physical properties, the exact structural and crystallographic details of the SRO structure are unknown. Furthermore, the diffraction data previously presented in support of this SRO [22, 31] clearly distinguishes this type of SRO from the $\langle 1\frac{1}{2}0 \rangle$ or $\frac{1}{3}\langle 420 \rangle$ type ordering found in case of Ni-Mo [31] and Ni-Mo-Cr [22] alloys. Therefore, it can be conjectured that the formation of Ni-rich clusters at the early stages of isothermal annealing at 475 °C could be related to the SRO that has been postulated to exist in these alloys.

Based on the experimental results presented in this paper, a transformation pathway for the development of LRO in the Ni-33Cr alloy can be proposed. This transformation pathway is schematically depicted in the three-dimensional free energy (G) versus composition and order parameter plot shown in Fig. 16. The random disordered fcc has been marked with a filled black sphere in Fig. 16. Since this random solid solution does not congruently order to form the Ni₂Cr phase, it can be speculated that there is a high-energy barrier for congruent ordering to take place in this system. Such energy barriers to congruent ordering have also been discussed by Soffa & Laughlin [32]. Such an energy barrier can be reflected as a substantial hump in the free energy surface along the order parameter axis, as schematically shown in Fig. 16. Since the experimental results clearly indicate a clustering or phase separating tendency in the disordered Ni-33Cr random solid solution, this is likely to be due to a miscibility gap in the free energy surface along the composition axis, resulting in a compositional instability/metastability. The lattice contraction observed in the 90 h aged alloy as compared to the WQ alloy, even in the absence of any LRO, is likely to be a manifestation of the atomic rearrangement due to this clustering process. This clustering leads to the formation of Ni-rich clusters of Ni-15Cr average composition, that are possibly the precursors to the Ni₂Cr LRO that eventually develops in this alloy after longer isothermal annealing time periods. These Ni-rich clusters lie on the free energy surface, shown in Fig. 16, at the location marked Ni-25Cr. Cluster size increases on aging from 90 to 8,000 h but number density reduces indicating the transformation of these clusters to LRO domains as the aging time is increased. Cluster size in 240 and 8,000 h are comparable, about 2-3 nm in both cases, which again establishes that the growth of these coherent clusters was prevented due to coherency strains [13]. Since the Ni-rich clusters are the precursors to the Ni₂Cr LRO domains, it can be conjectured that these clusters have a lower activation barrier for ordering, and this has been represented via a smaller hump in the free energy surface along the order parameter axis in Fig. 16, for the Ni-15Cr composition. This leads to the formation of off-stoichiometric Ni-rich LRO domains, as shown schematically in Fig. 16, and subsequently these domains increase in Cr content to reach their stoichiometric composition of Ni₂Cr. While this is one possible ordering pathway for the Ni-33Cr alloy, an alternative pathway could be one involving a concurrent increase in order parameter as well as Cr content within the Ni-rich clusters, if a lower activation barrier pathway is encountered by following such a path on the free energy surface. This has also been schematically represented in Fig. 16 using filled solid spheres. However, a more concrete and conclusive determination of the ordering pathway for these alloys will be possible only if the free energy versus composition and order parameter surface can be quantitatively determined using rigorous computational approaches.

4. Summary

Ordering in the Ni-Cr-Fe alloys still remains a stimulating problem. Ni-33Cr alloy is not only an interesting alloy in terms of practical usage, but is a good candidate for studying the congruent ordering in this system due to its relatively faster ordering kinetics. Ordering was studied previously via the indirect measurement of change of relative resistivity and relating that to the lattice contraction in Ni-33Cr. Utilizing synchrotron,

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4 this report is the first of its kind to directly measure the lattice parameters and
5 experimentally show by an in-situ setup that lattice contraction occurs due to ordering.
6 Also for the first time, the ordered domains were identified in atom probe tomography,
7 the ordered lattice planes within these domains visualized, and their size scale and
8 morphology were determined using data-mining algorithms. This study clearly shows
9 experimental evidence of Ni clustering at the early stages of isothermal annealing at
10 475°C in a random Ni-33Cr solid solution, where the compositions of these Ni-rich
11 clusters are of the type Ni_xCr ($x = 3$ to 9). These Ni-rich clusters could be potentially
12 associated with the previously claimed SRO in this system, which eventually transforms
13 to LRO domains of the Ni_2Cr type.
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30 **Figure Captions**

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32 1. Schematics of a Pt_2Mo structure (solid lines) with a fcc cell (broken line)
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34 2. Synchrotron X-ray peaks from Ni-33Cr alloy (a) WQ alloy (b) 90 h aged (c) 240 h
35 aged (d) 8,000 h aged. Initial portions of the respective curves are magnified and are
36 shown as insets. In addition to the fcc peaks that are present in all alloys, (c) and (d)
37 shows peaks (red colored) from Pt_2Mo -type domains. They are absent in (a) and (b)
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40 3. Lattice constants derived from synchrotron X-ray peaks of Ni-33Cr alloy. Note
41 the gradual contraction of lattice parameter from WQ alloy to 8,000 h aged alloy.
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44 4. In-situ experiment of order-disorder transition of Ni-33Cr alloy in synchrotron. (a)
45 Lattice constant during heating and cooling as a function of temperature. Lattice
46 constants were derived from synchrotron X-ray peak at each temperature. X-ray peaks
47 from three temperature positions are also shown in (b), (c), and (d)
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49
50 5. (a) SAED pattern of 90 h aged alloy along ZA [001] (b) SAED pattern of 90 h aged
51 alloy along ZA [011]. Both (a) and (b) reveal no super-lattice reflection. (c) SAED
52 pattern of 240 h aged alloy along ZA [001]. Super-lattice reflections from Pt_2Mo - type
53 domain could be seen at equivalent $1/3$ and $2/3$ positions. (d) DF image from $1/3220$
54 of (c) (e) SAED pattern of 8,000 h aged alloy along ZA [001] (f) DF image from $1/3220$ of
55 (e)
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6. Normalized intensity along the black lines in Fig. 4. a) 90 h aged alloy from Fig. 4(a) b) 240 h aged from Fig. 4(c) c) 8,000 h aged from Fig. 4(e). Arrows indicate the existence and position of the super-lattice reflections.

7. Site-specific sample preparation for atom probe by [110] oriented grain identification by EBSD. Example shown from 240 h aged alloy (a) SEM image of [110] grain lift-out step inside FIB/SEM (b) Grain maps of the alloy after the lift-out. White box demarks the area for lifted-out portion.

8. (a) Pole figure from EBSD of the lifted-out portion of 240 h aged alloy (b) Desorption map from atom probe showing [110] pole in red circle. (c) 5 nm slice of the reconstruction of the whole data-set. Red rectangle demarks the ordered domain (d) Magnified view of red rectangle to visualize the planes from the ordered domain. (e) SDM of Ni-to-Ni atoms of the ordered region in (d) clearly depicting the planes from the ordered domains.

9. (a) Selected regions of a 5 nm slice of a different atom probe reconstruction of 240 h aged alloy. Red lines demark the ordered domains (b) SDM of Ni-to-Ni atoms from a ordered domains from (a) clearly depicting the planes (c) 1D plot of SDM in (b).

10. (a) 2D density map of a 0.5 nm slice of a reconstruction from 240 h aged alloy. Note that the red area indicating higher density corresponds well with the Pt_2Mo cell atomic planes. (b) The whole reconstruction showing multiple Pt_2Mo cell represented by red areas.

11. (a) Pole figure from EBSD of the lifted-out portion of 8,000 h aged alloy (b) Desorption map from atom probe showing [110] pole in red circle. (c) 5 nm slice of the reconstruction of the whole data-set. (d) Magnified view of the reconstruction to visualize the planes from the ordered domain demarked by red polygons. (e) SDM of Ni-to-Ni atoms from a ordered domain in (d) clearly depicting the planes from the ordered domains. (f) 1D plot of SDM in (b).

12. (a) 2D density map of a 0.7 nm slice of a reconstruction from 8,000 h aged alloy. (b) The whole reconstruction showing multiple Pt_2Mo cell represented by red areas.

13. (a) Magnified view of the reconstruction of 8,000 h aged alloy, the ordered planes can be visualized. (b) (c) (d) and (e) show various ordered domains along with their Cr concentration.

14. Clusters identified and extracted by the cluster analysis algorithm in IVAS (a) 90 h aged (b) 240 h aged (c) 8,000 h aged alloy. Each color scheme represents an individual cluster in a data-

Table 1. List of Heat Treatment conditions

Alloy Notation	Heat treatment condition
WQ	SA + WQ
90 h aged	SA + WQ + Aged for 90 h at 475 °C
240 h aged	SA + WQ + Aged for 240 h at 475 °C
8,000 h aged	SA + WQ + Aged for 8000 h at 475 °C

Table 2. Summary of cluster analysis of Ni atoms

References

Alloy	$d_{\max}$ (nm)	# of Clusters	$N_{\min}$	Analyzed vol. (nm ³)	Average vol. of clusters (nm ³)	Average dia. (nm)	Volume Fraction of clusters	Average aspect ratio	Approx. Compositi on
WQ	0.25			Not Clustered					
90 h aged	0.25	1278	20	25x25x30	0.83	1.10	0.057	1.71	Ni-15Cr
240 h aged	0.25	66	72	25x25x30	10.20	2.44	0.036	1.56	Ni-15Cr
8000 h aged	0.25	73	80	20x25x40	11.37	2.50	0.033	1.64	Ni-19Cr

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