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High-dose ion irradiation damage in $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ characterised by TEM and depth-sensing nanoindentation

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Abstract

One of the key challenges for the development of high-performance fusion materials is to design materials capable of maintaining mechanical and structural integrity under the extreme levels of displacement damage, high temperature and transmutation rates. High-entropy alloys (HEAs) and other concentrated alloys have attracted attention with regards to their performance under fusion conditions. In recent years, a number of investigations of the irradiation responses of HEAs have peaked the community's interest in them, such as the work of Kumar et al. [1], who examined $Fe_{27}Ni_{28}Mn_{27}Cr_{18}$ at doses as high as 10 dpa. In this work, we study $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloy with irradiation doses as high as 20 dpa. We find the presence of Cr rich bcc precipitates in both the un-irradiated and in the irradiated condition, and the presence of dislocation loops only in the irradiated state. We correlate the features found with irradiation hardening by the continuous stiffness method (CSM) depth-sensing nanoindentation technique and see that the change in the bulk hardness increases significantly at 20 dpa

for temperatures 450 °C. These results indicate that the alloy is neither stable as a single phase after annealing at 900 °C, nor particularly resistant to irradiation damage, as have been previously claimed.

Keywords: CrFeMnNi, self-ion irradiation, STEM-EDX, XRD, depth-sensing nanoindentation

1. Introduction

Alloys containing five or more elements in nearly equal atomic concentration or with more than 5 % concentration crystallising have been referred as high entropy alloys after Yeh at al. [2, 3] or as multi-component alloys (MCPs) after Cantor [4]. The high number of different combinations of elements in concentrated multicomponent alloys can make possible the discovery of materials properties that can not be achieved in conventional alloys, which typically contain one principal element. The interest of concentrated multicomponent alloys as high-temperature structural materials for nuclear industries has been motivated by some reports of attractive mechanical properties at elevated temperatures including hardness, strength, ductility, wear, and radiation and corrosion resistance [5].

The structural materials for fusion reactors plants will experience very demanding environments in terms of high temperatures (300-800 °C) and intense 14 MeV neutron irradiation fluxes [6] posing potential challenges to mechanical strength, fracture toughness and ductility and dimensional changes due to void swelling and creep [7]. The development of high-performance materials that are radiation resistant is critical for advanced nuclear reactor systems. Due to their chemical complexity, different atomic sizes and charge transfer among the elements in the random solid solution of concentrated multicomponent alloys, atomic-level stresses have been rationalised as the cause for reduced number densities of vacancy or interstitial defect clusters due to enhanced vacancy-interstitial recombination of defect clusters in the cascade following the thermal spike after irradiation by high energy particles [8, 9, 10].

Recently, attention has been drawn to concentrated multicomponent alloys, in particular, containing light transition metal elements Co, Cr, Fe, Ni, and Mn that form predominantly a single phase with secondary phase precipitates after prolonged heat treatments [4, 11]. For some of the alloys belonging to the family of CrMnFeCoNi but without Co, mechanical tensile

tests have indicated that these alloys can become brittle due to the presence of the hard and brittle σ phase [11, 12]. The embrittlement studies motivated the study of particular alloy compositions, specifically Cr content controlled to narrow down selection to composition $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ [13]. The composition of $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ is also favoured for nuclear applications due to the removal of Co. If Co is exposed to intense high energy neutron fluxes, it can transmute into ^{60}Co long-lived radioactive isotope [14].

In previous work [1], the microstructure and hardness of 5.8 MeV Ni irradiated $Fe_{27}Ni_{28}Mn_{27}Cr_{18}$ concentrated multicomponent alloy was studied up to doses of 10 dpa and temperatures of 700 °C by TEM and by depth-sensing nanoindentation. In the study, the concentrated multicomponent alloy was reported to be a single-phase solid solution and remain stable during irradiation. The essential radiation-induced features were high density dislocation loops, reduced grain boundary Cr and Fe and increased Ni segregation compared to FeCrNi austenitic stainless steels irradiated to similar doses, and lack of void formation. The authors rationalised the small size, and high number density of dislocation loops in comparison to equivalent irradiated FeCrNi austenitic stainless steels as being due to a reduced point defect recombination in this concentrated multicomponent alloy.

Heavy-ion irradiations have been used as simulation experiments for neutron damage in structural materials since they are amenable to flexible environmental conditions, including control of temperature and displacement per atom rate [15]. These parameters are not so easily controlled during in-reactor irradiation experiments. Furthermore, the high rates of displacement per atom from heavy ion irradiations, which are several orders of magnitude higher than for neutron irradiation, speed up the accumulation of radiation damage [15]. The drawbacks of heavy ion irradiation are mainly the few µm ranges of implanted damage depth that makes difficult sample preparation for microscopy.

This current work aimed to assess the irradiation behaviour of the $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ alloy in detail at high doses to further confirm the apparent irradiation resistance of the alloy. The structure of this paper is as follows: In section 2 the experimental methods for the thermomechanical processing of the sample preparation, teh self-ion irradiation, the depth-sensing nanoindentation and TEM sample preparation are described; In section 3 the microstructure of $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ is characterized in un-irradiated state by TEM, then the microstructure of the 5 MeV Ni irradiated $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ is characterized by TEM, and then hardening is studied from depth-sensing

nanoindentation measurements.

2. Experimental methods

2.1. Thermo-mechanical processing and sample preparation

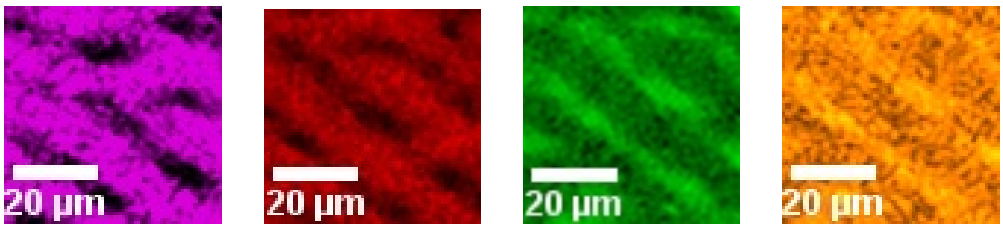
The $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloy specimens were prepared by arc melting in a Ti-gettered high-purity argon atmosphere by mixing high purity (99.9%) elemental Cr, Mn, Fe and Ni in the concentration of 18%-27%-27%-28% at. % respectively. The ingots were flipped and remelted several times during the arc melting process [1]. To cross-check the average chemical composition of the as-cast concentrated multicomponent alloys analysis with a FEI Quanta 650 SEM (Scanning Electron Microscope) Oxford instruments EDX (Energy Dispersive X-rays) was conducted over 10 regions of the approximate area of 100 µm by 100 µm. The resulting analysis is shown in Table 1, which agrees reasonably well with the expected composition values, thus indicating that no relative depletion of any alloy element in bulk occurred in the manufacturing process.

Table 1: Chemical composition of $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloys for this work, measured with SEM-EDX

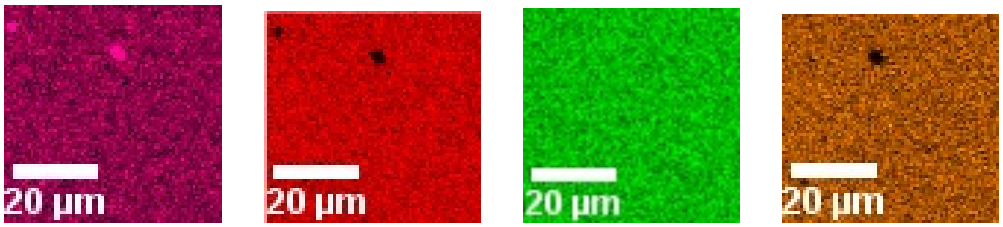
Element	wt.% ([1])	wt.% (this work)	at.% (this work)
Cr	18	16.7 ± 0.3	18.0 ± 0.1
Mn	27	25.6 ± 0.6	26.0 ± 0.6
Fe	27	28.1 ± 0.5	28.1 ± 0.3
Ni	28	29.3 ± 0.5	27.9 ± 0.3

More detailed analysis performed with EDX revealed micro-segregation at the µm scale with the presence of dendrite-like structures of approximately 20 µm separated see Figs. 1 (a)-(d). To homogenise and anneal possible sinks for irradiation defects in the microstructure we performed a homogenization heat treatment at 1200 °C for 48 hr and water quench, then deformed in an uniaxial compression to a thickness reduction of 40%. And finally a re-crystallisation heat treatment at 900 °C for 4 hr followed by furnace cooling. The results are shown in Figs. 1 (e)-(h) The heat treatment was performed to reproduce work by Kumar et al. [1].

[1]The samples were prepared at the University of Sheffield



(a) Cr as cast (b) Fe as cast (c) Mn as cast (d) Ni as cast



(e) Cr after HT (f) Fe after HT (g) Mn after HT (h) Ni after HT

Figure 1: Representative SEM EDX maps of Cr, Fe, Mn and Ni before a-d and after e-h homogenisation heat treatment in as cast $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloys at 1200 °C for 48 hrs. During the homogenization and recrystallization heat treatments MnCr oxide inclusions appeared, these are shown in the heat treated maps as black dots.

Thermomechanically processed specimens were electro-discharge machined into square blocks of approximate size 10 mm and thickness between 0.5 and 1 mm. Grinding and polishing were performed on an automatic spinner platen with abrasive SiC paper P800, P1200, P2400 and P4000, then followed by polishing with 1 μm polycrystalline diamond suspension in a cloth, and finally the specimens were OPS polished until grain boundaries appeared slightly etched in the optical microscope Zeiss Axio. The mean grain size in the recrystallised condition was found to be approximately $31 \pm 9 \mu$m by using a simple linear intercept method from the SEM micrograph in Fig. 2 a

The recrystallised condition was characterised by X-ray diffraction (XRD) to ascertain that the crystal structure is face-centred cubic (fcc) and to find the lattice spacing. The powder diffractometer used for this work was a Phillips XRD PANalytical X'Pert Pro using a combined characteristic radiation of CuKα_1 and CuKα_2 X-rays with a Ni foil to remove β X-ray radiation and a graphite monochromator to reduce fluorescence effects that can mask the diffraction peaks in samples containing transition metal elements (our sample has Fe, Cr, Mn and Ni). This diffractometer used the $\theta - 2\theta$ Bragg-

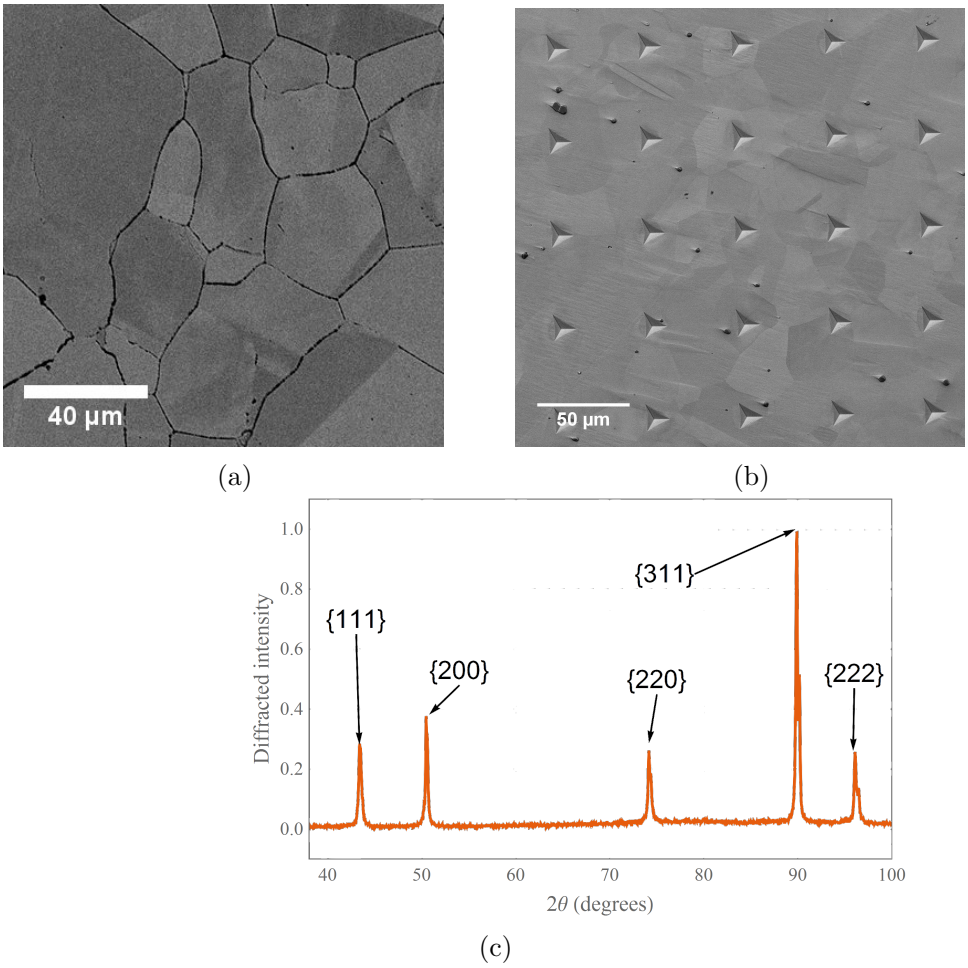


Figure 2: a) SEM Backscattered electron micrograph of the recrystallised microsctructure indicating the grain structure after etching with metallographic etchant of nitric acid and ethanol. b) Representative SEM image of array depth-sensing nanoindentation impressions after testing. The impressions are spaced approximately 50 μm apart and were performed on a sample irradiated at 300 °C and 20 dpa. c) XRD diffraction pattern as obtained from recrystallised $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloy. The secondary peaks to the right of the highest peaks are due to diffraction caused by longer wavelength of CuKα_2 radiation.

Brentano geometry, and the sample was spun along the normal to its planar surface. The working voltage of the diffractometer was 40 kV, and the operating current was 40 mA. The scanning region ranged from 35 ° to 110 °, in steps of 0.05°.

We use the CMPR software [16] to investigate the parameters of the structure by predicting the angular location for the diffracted intensities from basic crystallographic information and optimise the lattice constants to fit the experimental intensity peak positions.

2.2. Self-ion irradiation experiment

For the irradiation experiment, the recrystallised specimens were mounted on the sample end-stage at the 30 ° beamline from Dalton Cumbrian Facility [17]. The beam was focused and operated in rastering mode. The last beam slits were adjusted to trim the beam to irradiate an area uniformly of 7 by 7 mm^2 area for all of the samples reported in this study. The sample temperature was monitored continuously throughout the irradiation experiment by thermal imaging to measure the temperature increase due to the combined beam heating and external heaters (see Fig. 3 c). The real beam current on the sample was monitored through the continuous reading of charge deposited at the end-stage by a data acquisition system implemented with LabView National Instruments. Corrections were applied to measured current on the sample to compensate for the spurious secondary electron emission from the sample upon the impact of the heavy ions.

Table 2: Irradiations performed at Dalton Cumbrian Facility [17] with Nickel ions (excitation state +3) at 5 MeV under different conditions. The dose rate (dpa/s) was 2.4E-04 for all but the 2nd sample in the Table for which was 4.40E-04

Ion fluence (ion/cm^2)	Dose (dpa)	Temperature (°C)	Exposure (time)	
8.00E+14	2	300	2 h	19 min
8.00E+15	20	300	12 h	37 min
8.00E+15	20	450	23 h	9 min
8.00E+14	2	450	2 h	19 min
8.00E+13	0.2	450		14 min

The displacements per atom (dpa) were estimated from SRIM (2008 version) [18] code and at 80% depth of the Bragg peak for 5 MeV Ni ions with

+3 charge state. To make consistent our ion irradiation doses with potential future neutron irradiations we set up the SRIM simulation with lattice and surface binding energies of the Cr, Mn, Fe and Ni atoms equal to zero and we choose the Kinchin-Pease calculation mode following findings from [19]. For the displacement energies of the lattice atoms Cr, Fe, Mn and Ni the value 40 eV was used [19]. The peak dpa is estimated from SRIM dpa per fluence and the estimated fluence of the ion irradiation deposited charge corrected on each of our specimens (see Fig. 3 a).

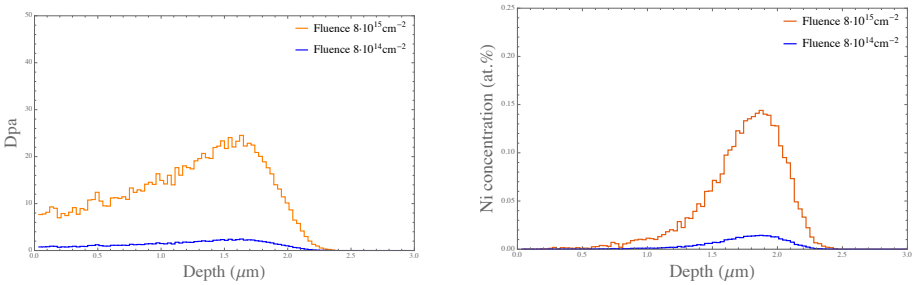
The peak dose achieved was approximately 20 dpa, and the peak Ni implantation was approximately 0.14 at.%, as indicated in Figs. 3 a, and b respectively. The values for the main parameters fluence, dose, irradiation temperature, exposure time and dose are detailed in Table 2.

2.3. Depth-sensing nanoindentation methods

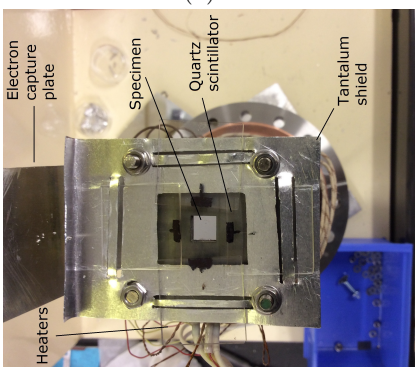
For carrying out depth-sensing nanoindentation, we used an MTS Nano Indenter XP equipped with a Berkvich geometry diamond indenter.. The maximum allowed drift rate was set to 0.15 nm/s and a surface approach velocity for the tip of 10 nm/s. The penetration depth examined in the irradiated specimens ranged from 0 to 2000 nm with a maximum load of 200 mN. The projected contact area of the tip was evaluated using a fused silica standard material with E_r=69.6 GPa and ν=0.17 over a contact depth range from approximately 5 to 1400nm. The average hardness values were determined from averaging 25 hardness values each being derived from a continuous load-displacement curve by using the continuous stiffness method (CSM) using the approach proposed by Oliver and Pharr [20]. The 25 (5x5) impressions were spread in an array of points separated by 50 μm to avoid interference effects due to localised plastic zones among the indents (see Fig. 2 b).

2.4. TEM sample preparation

TEM lamellae for characterising the 1 µm thin irradiated layer were prepared by the FIB lift-out method using Ga ions in an FEI Quanta 3D operated at 30 kV. Final cleaning-polishing was performed at 2 kV to minimise Ga ions induced damage on the microstructure until lamellae were electron transparent. The lamellae were mounted in a Cu TEM grid. The lamellae were observed in Tecnai F20, and an FEI Talos F200A with TEM and STEM-EDX modes both operated at the accelerating voltage of 200 kV. The scale bar for diffraction was calibrated by using the fitted lattice spacing for



(a) (b)



(c)

Figure 3: Displacement per atom (Dpa) (a) and Nickel (atomic %) implantation profile (b) in $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ for the two fluences considered in Table. 2 calculated with SRIM [18]. (c) Sample set up for irradiation experiment at beamline of Dalton Cumbrian Facility. An approximate area of 7 by 7 mm^2 delimited by scintillator quartz crystal is irradiated uniformly by the ion beam. The irradiation temperature is controlled by the heaters below the specimen and a chiller circulating continuously. The tantalum shield prevents the structural material of the stage from becoming activated by the incident radiation

fcc structure of the recrystallised condition in the powder diffraction measurements.

3. Results and discussion

3.1. Microstructural characterization in the un-irradiated condition

The XRD pattern from the recrystallised microstructure indicates that the fcc structure is the main phase within the detection limits of the signal-to-noise ratio (Fig. 2 c). The single-phase stability of $Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloys is in agreement with the chemical homogeneity colour maps of Cr, Mn, Fe and Ni in the SEM-EDX results after annealing (see Fig. 1). The lattice parameter was found to be 3.610 ± 0.005 Å in space group O_h^5, this corresponds to the stress free microstructure. A lattice parameter of 3.64 Å was found from the alloy of Cr, Mn, Fe and Ni with similar composition in the fcc phase [1]. The relative height of the diffracted intensities is different from that expected by the intrinsic lattice geometrical multiplicities of a randomly oriented aggregate of crystals as typically used in conventional powder diffraction. This is likely to be an indicator of some crystallographic texture resulting from the thermomechanical processing applied.

SEM-EDX maps (shown in Fig. 1) and TEM selected area diffraction from the matrix (Fig. 4 c)) material confirmed the XRD predictions of fcc homogeneous solid solution phase except for oxide inclusions abundant in Mn and Cr associated to the spinel structure. Their presence could be related to the oxygen impurities in the raw materials or contamination in the manufacturing process in the arc melter. Similar inclusions have been found for Cantor alloy [21, 11].

TEM of the recystallised alloy revealed precipitates at the grain boundaries. The precipitates found are shown in Fig. 4 (e)-(i), where the structure of these precipitates is consistent with the bcc symmetry. We also found precipitates within the recrystallised grains in the samples. By calculating the distance between diffraction spots along with the (200) directions (Fig. 4 a), the lattice constant of the bcc phase (Fig. 4 b) is approximately 2.9 Å. The findings of a bcc phase with very close lattice constant to pure Cr has been reported in previous works for CrMnFeCoNi Cantor alloy [22]. The bcc precipitates are seen to be rich in Cr and depleted in Mn, Fe and Ni as shown in STEM-EDX maps in Fig. 4 e-h.

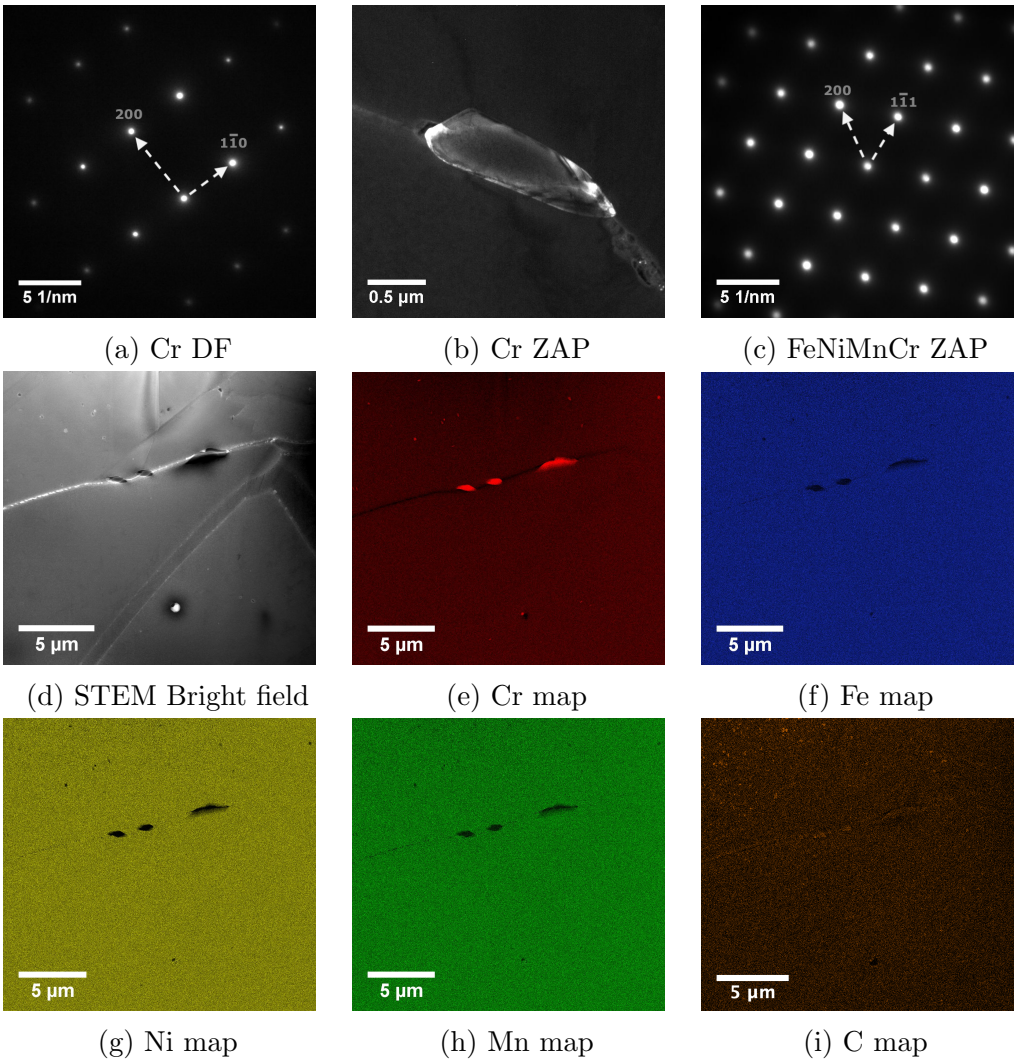
The presence of the bcc phase was not detected in previous studies performed with a CrMnFeNi concentrated multicomponent alloy with similar composition to the present work [1]. The phase stability of $Fe_{27}Ni_{28}Mn_{27}Cr_{18}$ concentrated multicomponent alloy has been investigated by first principles DFT cluster expansion and Monte Carlo simulations [23]. The simulations predicted that Cr tetrahedral clusters in the fcc lattice are not thermodynamically favoured and Cr segregation may precipitate into the bcc lattice, which is the ground state of pure Cr. The equimolar CrFeMnNi alloy has been predicted to be two phase (fcc+bcc) from solidification and stable in the temperature range T>1000 K and at lower temperatures two phase (fcc+σ). After annealing at 1273 K for 6 days, the equimolar CrFeMnNi was found to contain three phases: fcc, bcc, and σ. In particular, the concentration and lattice spacing of the bcc phase was predicted by CALPHAD calculation and measured by XRD and EDS-SEM to reveal a Cr concentration in the range 44.2-45.2 at. %, and a lattice spacing of 0.28 nm [24].

3.2. Microstructural characterization under irradiation

The Bragg peak corresponding to the Ni irradiation was found at the approximate depth of 1.6 μm from SRIM simulations, which according to our estimations from Fig. 3 a is separated from the Ni implantation peak which is at 1.9 μm (see Fig. 3 b).

The Cr-rich BCC particles were also observed in the irradiated specimens (see Fig. 5a)). These precipitates are most likely consistent with the BCC phase identified. An oxide phase, also rich in Cr and other elements such as Mn can also be distinguised from the same figure. It is likely that this phase is a spinel phase that was also observed in the un-irradiated specimens. The effect of irradiation in the volume fraction of the precipitates was not ascertained in this study, owing to the difficulties associated with making meaningful volume fraction measurements in the irradiated layer. The role that irradiation plays in these precipitates requires alternative techniques to the FIB used here to sample more irradiated volume and therefore get meaningful precipitate statistics. The findings of the Cr-rich BCC particles in the irradiated condition is in contrast to previously reported work in this alloy [1], which found no precipitates at all.

We also observed a NiMn segregated region in the irradiated samples with STEM-EDX maps in the irradiated specimens, but it was not possible to confidently rule out that these formed earlier in the thermo-mechanical processing stage before irradiation. These are shown in Fig. 5c)-5d). The



(a) Cr DF (b) Cr ZAP (c) FeNiMnCr ZAP

(d) STEM Bright field (e) Cr map (f) Fe map

(g) Ni map (h) Mn map (i) C map

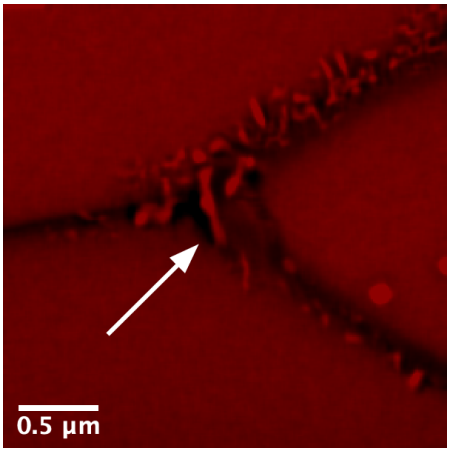
Figure 4: TEM selected area diffraction (the zone axis is [011] crystallographic direction for bcc phases (a), Dark Field Micrographs (b) and fcc phase (c).TEM selected area diffraction (the zone axis is [011] crystallographic direction for the fcc matrix). STEM Bright Field (d), and STEM energy dispersive X-ray maps of Cr (e), Fe (f), Mn (h), Ni (g), and C (i).

dimensions of these fine precipitates made it difficult to identify the structure and lattice spacing by selected area diffraction in the TEM. The presence of an $L1_0$ NiMn phase after ageing at intermediate temperatures has been reported before in similar alloys [22, 25].

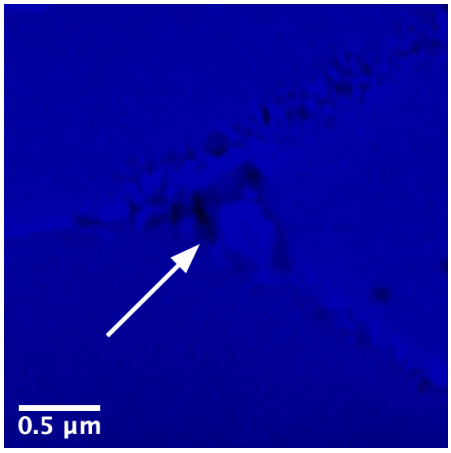
Recently, DFT(Density Functional Theory) based cluster expansion and Monte Carlo simulations published by the author have predicted the formation of $L1_0$ MnNi phase in $Fe_{27}Ni_{28}Mn_{27}Cr_{18}$ [23, 26] at temperatures T<1300 K. Furthermore, simulations for formation $L1_2$ $CrFe_3$ in the temperature range 500-1200 K were also predicted by the author simulations, however the experimental measurements in this work did not indicate the presence of $L1_2$ $CrFe_3$.

Voids and dislocation loops were found in pure Ni after self-ion irradiations at doses as high as 13 dpa and temperatures 300-725 °C [27]. Westmore et al reported significant difficulties in measuring the dislocation loop densities due to the their dense distribution. They estimated diameters ranging between 44 and 95 $\mathring{A}$, and number densities $3.0 \cdot 10^8 - 7.8 \cdot 10^{10}$ $\mathring{A}$. In this work, and in agreement with self-ion irradiated studies in a similar composition multicomponent alloy, we found dislocation loops and no voids. In Fig. 6 c)-d), we show dislocation loop contrast corresponding to Frank loops by using a two-beam condition ($\mathbf{g} = 220$). In fcc materials, the vacancies and interstitials are known to form dislocation loops of vacancy or interstitial types as well as voids. In situations where vacancy mobility is low due to an operating temperature less than approximately half of the melting temperature, vacancy dislocation loops are known [28] to be unstable due to the higher capture radius of dislocation for interstitial than vacancy point defects. Thus resulting in the annihilation of vacancy loops by diffusing interstitial point defects and leaving the only interstitial loops stable. Based on the dislocation bias argument we expect that the loops are of interstitial-type faulting.

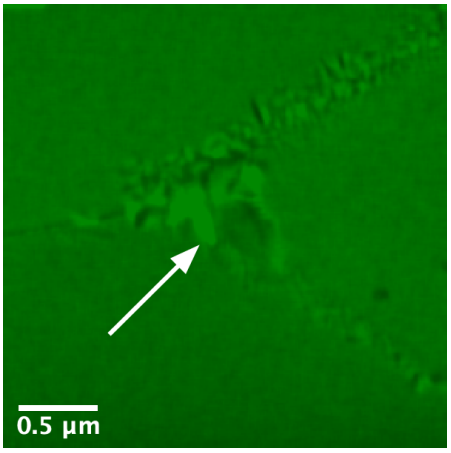
Preparation of TEM lamellae using Ga ions with the FIB technique can produce ripple-shaped contrast and black dot contrast [29]. A comparison of the un-irradiated and irradiated specimens shown in Figs. 6 a-b and Figs. 6 c-d demonstrates that the damage seen is not a result of FIB preparation; there is no damaged layer in the un-irradiated samples when compared to remaining irradiated samples Figs. 6 (c)-(f) . The Frank loops may therefore be attributed to the Ni 5 MeV irradiation field and not from the FIB preparation work. The depth of the observed damage layer in the irradiated sample in Fig. 6 d has a varying depth between 1.9 and 2.1 µm is consistent with SRIM 5 MeV Ni implantation and dpa simulations as shown in Figs. 3



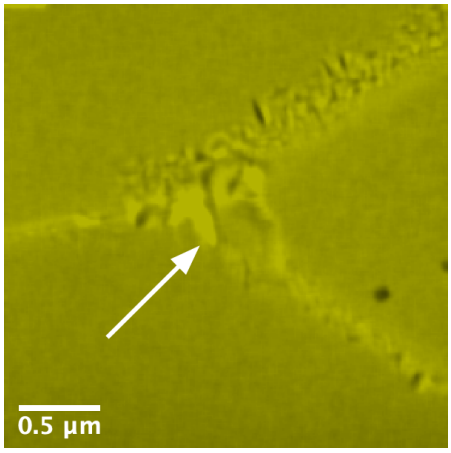
(a) Cr map



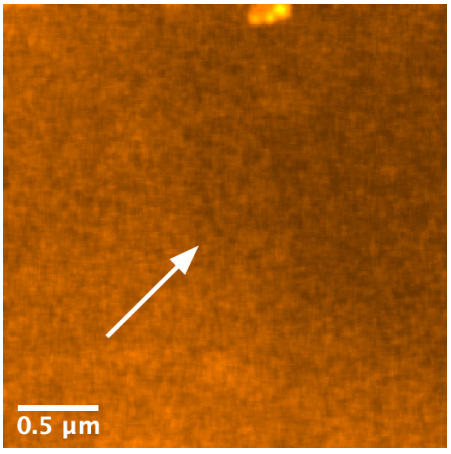
(b) Fe map



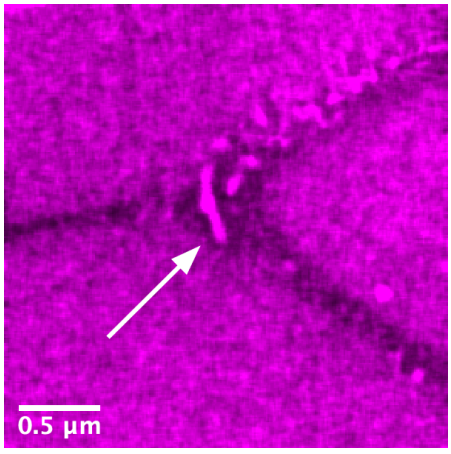
(c) Mn map



(d) Ni map

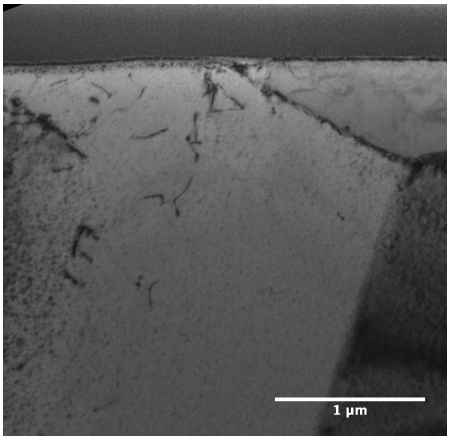


(e) C map

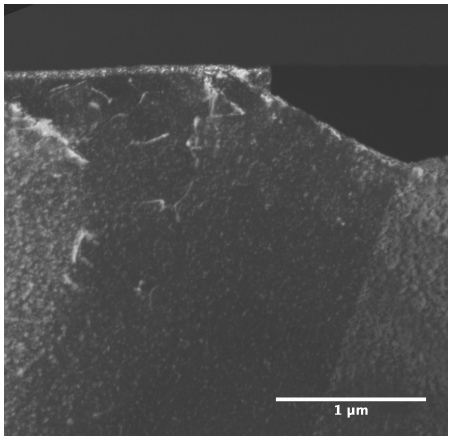


(f) O map

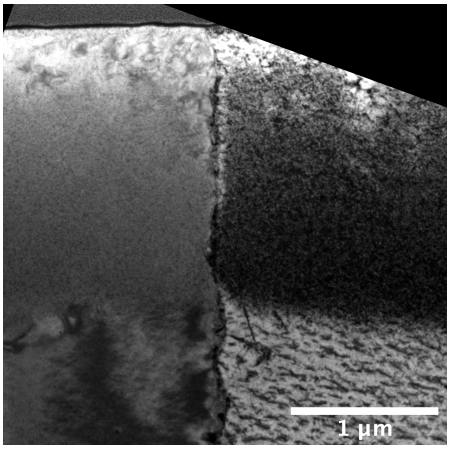
Figure 5: STEM EDX maps of Cr, Fe, Mn, Ni, C, and O at a triple junction. The arrow points to the NiMn phase.



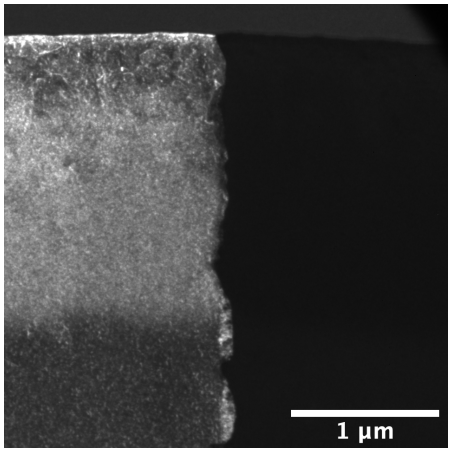
(a) Bright field un-irradiated



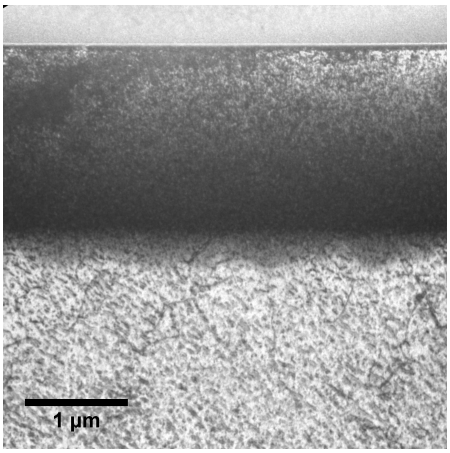
(b) Dark field un-irradiated



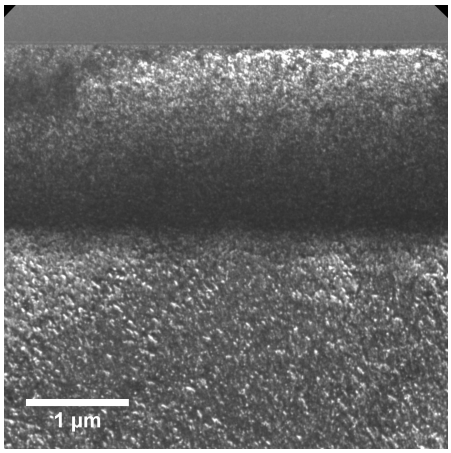
(c) Bright field 2 dpa 450 °C



(d) Dark field 2 dpa 450 °C



(e) Bright field 20 dpa 450 °C



(f) Dark field 20 dpa 450°C

Figure 6: Micrographs of un-irradiated a)-b) and irradiated concentrated multicomponent alloys lamela prepared by the FIB lift-out method c)-f). In the lamellae, the platinum layer of protection is found at the top of the images. The platinum location indicates the entry direction of the ion irradiation as it penetrated the bulk of the recrystallised specimen. In Fig. (c) the half grain in the top left corner is cut off due to the image rotation in the TEM.

a and (b)

3.3. Irradiation hardening from depth-sensing nanoindentation tests

Bulk equivalent hardness in irradiated specimens, H_0, is computed from fitting the contact depth-dependent hardness $P[h_c]/A_c[h_c]$. The hardness plots are shown in Fig. 7 a) and b). Several models for irradiation hardening have been reported in the literature [30], the simplest one being Kasada two parameter model[31]. The hardness- contact depth plots were fitted to Kasada's film/substrate model in terms of parameters h_0 and H_0 similar to the Nix-Gao indentation size effect (ISE) [32], $H[h_c] = H_0\sqrt{1 + h_0/h_c}$. The inflection point in the hardness envelope plots of the irradiated samples can be observed from Figs. 7 a) and b). The inflection points in (0.2, 20 dpa for 450C and 2, 20 dpa for 300C) are approximately located at 200 nm. This sets the upper end for fitting of the data to Kasada's model, $H[h_c] = H_0\sqrt{1 + h_0/h_c}$, which was approximately given by $3 < 1/h_c < 10$ (see Fig. 7 c)-d)). Note that this range for data fitting is approximately consistent with similar ion-irradiated specimens [31, 33], and that the hardness squared curve for the non-irradiated curve in the corresponding range fits to a straight line (see 7 e)) as in Nix-Gao model. The dashed lines in Figs. 7 c) and d) correspond to the fitting of the data to Kasada's film/substrate model. The intercept of this lines with the vertical axis determines H_0^{irr}. The curve for 2 dpa at 450 °C is not really showing the inflection point. This could be a material issue or an irradiation issue. Bulk equivalent irradiation hardening in the damaged layer of self-ion implantation is then estimated by subtracting the equivalent bulk hardness of the un-irradiated specimens from the each of the bulk-equivalent hardness in the irradiated samples i.e. $\Delta H_{irr} = H_0^{irr} - H_0^{nonirr}$. These irradiation hardening quantities are obtained from the fits in Fig. 7 c)-d) and the numerical values are indicated in Table 3 as a function of dose and irradiation temperature.

From the irradiation hardening $\Delta H_{irr} = H_0^{irr} - H_0^{nonirr}$ for each of the irradiated samples in table 3 we find that hardness increases with dose up to 4 GPa at all irradiation temperatures. Furthermore we find that irradiation temperature effects from 300 and 450 ^{o}C resulted in no significant change in the irradiation hardening. Kumar et al [1] reported room temperature and 500 °C depth-sensing nanoindentation results in ion-irradiated CrMnFeNi. We have compared their data to ours in Table 3. In this work, we explored high doses to 20 dpa, and find that the increase in hardness after irradiation at 450 °C is 4.4 GPa, which expands the knowledge of the irradiation behaviour

of this alloy after the hardness increase value of 0.47 GPa reported in [1] after 3 dpa of irradiation. The error bar magnitude difference for the low dose data at 300 °C of 0.9 is attributed to scatter and difficulty to fit the data. The remaining samples showed less scatter in the data, and the error bar could be reduced to less than 0.7 GPa.

Self-ion irradiation in Ni has primarily been focused in void swelling [27], and to the best of our knowledge there are no data with increase in hardening data from dislocation loops in pure nickel. Recently, Voyevodin et al. performed 1.4 MeV Ar ion irradiations in a multicomponent CrFeMnNi alloy (with composition 20, 40, 20, 20 $wt.\%$ respectively) to investigate the radiation behaviour by nanoindentation [33]. They have shown that the increasing in hardness measured from continuous stiffness depth-sensing nanoindentation followed by fitting to Kasada method [31] in the CrFeMnNi were 0.75, 1.0 ,and 1.25 GPa after 0.3, 1 and 5 dpa of Ar ion irradiations. They also showed that if the multicomponent alloy CrFeMnNi contained a dispersed oxide the increase in hardness could reach higher magnitudes that the precipitate free irradiated samples.

The effect of Cr-rich precipitates dispersed in the matrix of CrMnFeNi concentrated multicomponent alloy is expected to contribute to work hardening when compared precipitate free condition approximately as the square root of the precipitate volume fraction. The powder diffraction limiting resolution is estimated to 5% volume fraction. Our XRD analysis could not detect the presence of the Cr-rich precipitate particles in the concentrated multicomponent alloys (Fig. 2 c), and the TEM analysis could evaluate the presence of not more than 1 or 2 Cr-rich precipitates overall (Fig. 4 b). Therefore the expected contribution to work hardening in CrMnFeNi concentrated multicomponent alloy by the Cr-rich precipitates is estimated to be negligible and independent of irradiation. A more accurate evaluation of the role of irradiation in the precipitate volume fraction would require alternative techniques in between XRD, and TEM.

4. Conclusion

In the un-irradiated condition, we find Cr-rich bcc precipitates in the fcc-$Fe_{28}Ni_{28}Mn_{26}Cr_{18}$ concentrated multicomponent alloy matrix, in contrast to previously reported work in this alloy [1], which found no precipitates in any condition. In the irradiated state we find that dislocation loops of interstitial-type occur under irradiation, but in very high number densities

Table 3: Irradiation hardening (in GPa units) concerning non-irradiate condition as obtained from this work (first two rows), and previous work [1] (last two columns). The un-irradiated samples had a reference hardness of 2.6 ± 0.2 GPa

Irradiation temperature (° C)	Low dose (0.2 dpa)	Medium dose (2 dpa)	High dose (20 dpa)
300		2.5±0.9	3.7±0.4
450	0.5±0.5	0.3±0.2	4.4±0.7

	Low dose (0.3 dpa)	Medium dose (3 dpa)
25	2.31 ([1])	
500	0.33 ([1])	0.47 ([1])

making quantitative analysis difficult. The TEM experimental observation of a damaged layer with depth varying between 1.9 and 2.1 µm is consistent with SRIM 5 MeV Ni implantation and dpa simulations. To understand the implications of these radiation-induced defects in concentrated multicomponent alloys we use a hardening model based on previous work to convert measured depth-sensing nanoindentation hardness in the damaged layer of thickness 1400 nm to bulk equivalent hardness. Change in hardness is measured at 0.2, 2, and 20 dpa and at irradiation temperatures of 300 °C and 450 °C. The findings of this work suggest that irradiation hardening at 20 dpa is as high as 4 GPa. As a conclusion, it is found that at a very high dose, the effect of irradiation hardening is not significant in the CrFeMnNi multicomponent concentrated alloy, and the alloy is not stable to precipitation of secondary Cr-rich bcc phase.

5. Supplementary material

5.1. Deformation microstructure after recrystallization

We find significant dislocation pile-up and dislocation arrays in Figs. 8 a-b in the recrystallised microstructure before irradiation, indicating a build-up of stress at the phase boundaries between fcc grains or fcc-bcc boundaries. This is likely to occur from the sample preparation procedure of electropolishing.

5.2. depth-sensing nanoindentation

Excel files with depth-sensing nanoindentation data.
Nothing else here?

6. Acknowledgements

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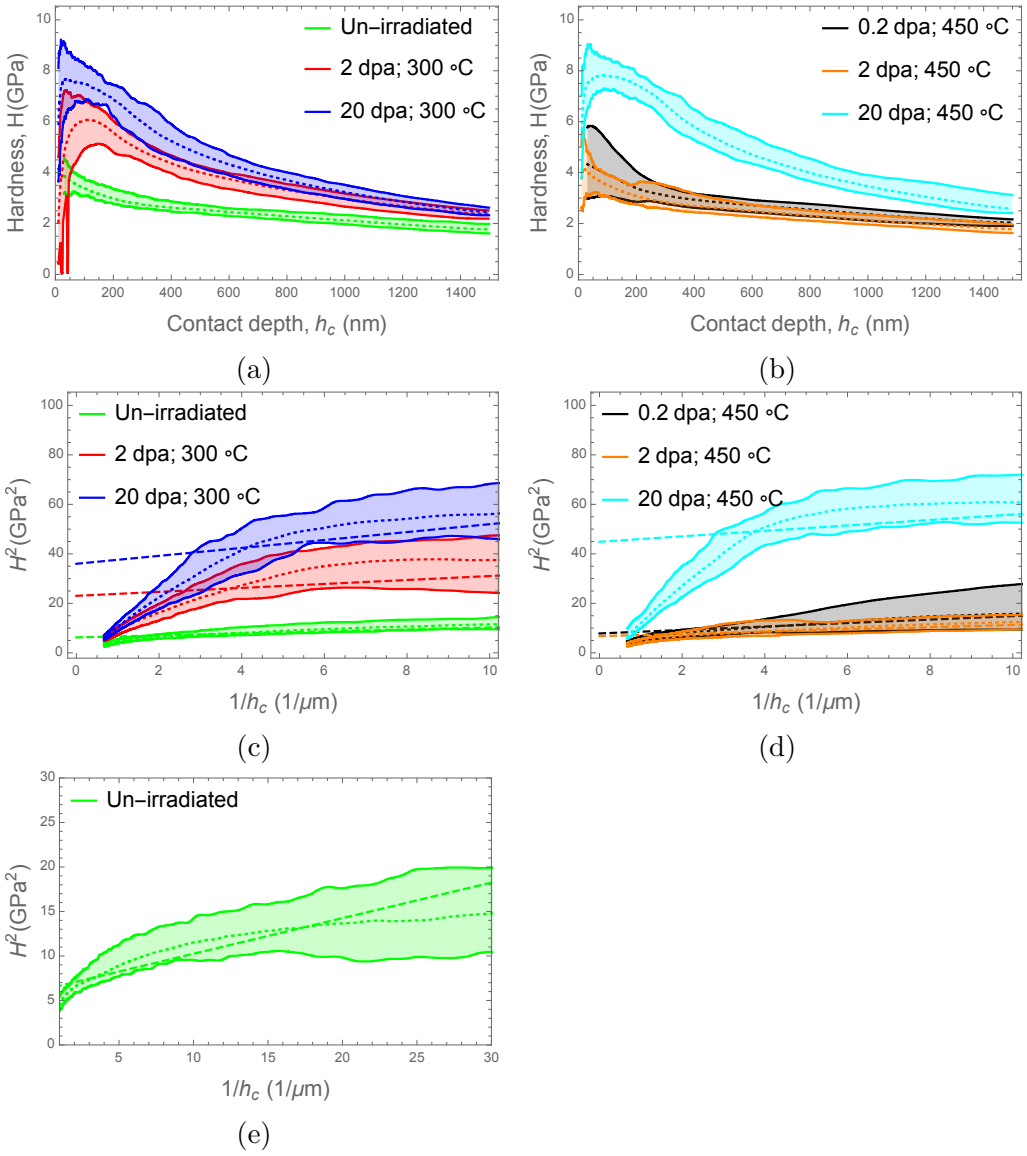
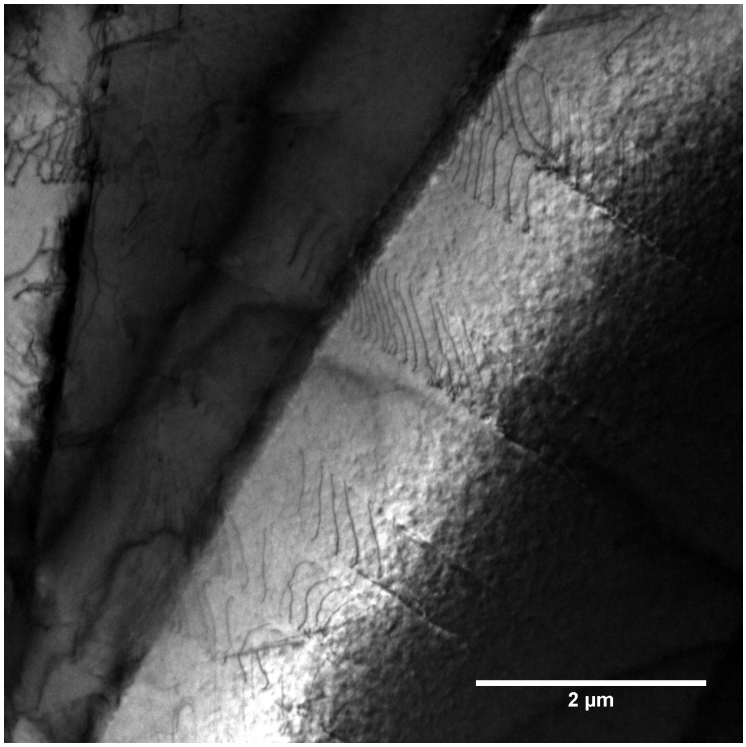
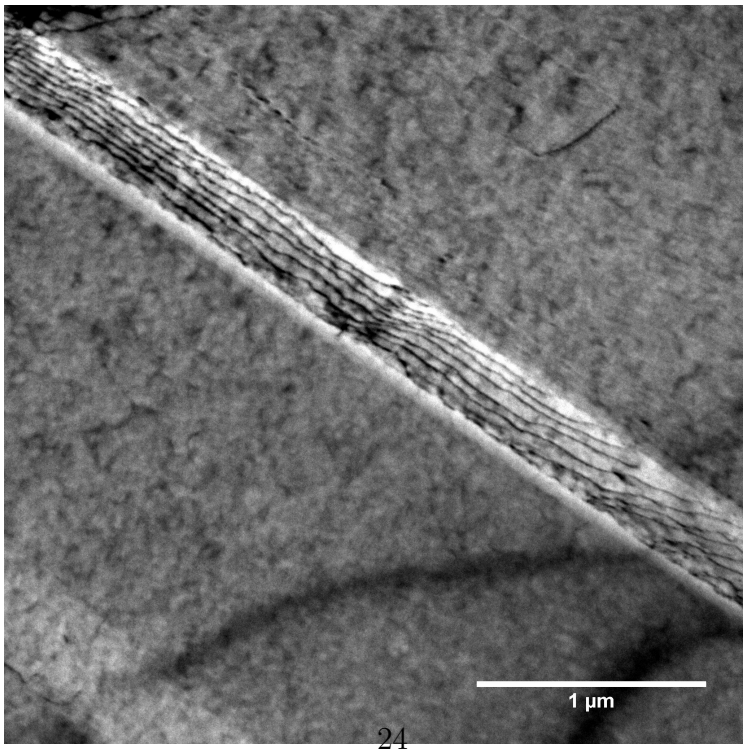


Figure 7: Hardness and hardness squared envelope plots, a)-b) and c)-d) respectively. The envelope is a consequence of the statistical spread from 25 indentations and CSM data per sample/condition.



(a)



(b)

Figure 8: TEM micrographs of the recrystallised condition. (a) for pile up of dislocations; (b) for slip band of dislocations