Effect of aluminium concentration on phase formation and radiation stability of $\text{Cr}_2\text{Al}_x\text{C}$ thin film

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Abstract

Near stoichiometric and under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.9$ and 0.75) amorphous compositions were deposited onto silicon substrate at 330 K in a layer-by-layer fashion using magnetron sputtering from elemental targets. The film thickness found to be $0.9\ \mu\text{m}$ and $1.2\ \mu\text{m}$ for the near and under stoichiometric compositions respectively. A transmission Electron Microscope (TEM) heating holder was used to heat thin sample lamellae prepared using focussed ion beam milling. Near stoichiometric Cr_2AlC thin films consisted of nano MAX phase after crystallisation at 873 K. Under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.75$) thin films contained MAX phase along with nanocrystalline chromium aluminides after crystallisation at 973 K. Ion irradiations with 320 keV xenon ions were performed at 623 K using a TEM with in-situ ion irradiation (MIAMI) facility. Near stoichiometric Cr_2AlC nanocrystalline films irradiated up to 83 displacements per atom (dpa) showed no observable changes. Also, irradiations of under stoichiometric nanocrystalline thin films up to 138 dpa did not show any observable amorphisation and recrystallization was observed. This radiation resistance of near and under stoichiometric thin films is attributed to the known self-healing property of $\text{Cr}_2\text{Al}_x\text{C}$ compositions further enhanced by nanocrystallinity.

Keywords: Amorphous thin films, Near stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ thin films, under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ thin films, MAX phase, chromium aluminides, ion irradiation, radiation hardness, self-healing, nanocrystallinity, recrystallisation.

1. Introduction

Cr_2AlC ternary carbide display exceptional properties due to the presence of metallic and ceramic components. These properties include; high thermal shock resistance, high damage tolerance, high hardness, high thermal and electrical conductivity[1–3]. The material has also shown high corrosion and oxidation resistance[4,5] which is due to the formation of dense and pore-free oxide layers. The formation of aluminium oxide surface layer is based on high aluminium mobility in the material. This high mobility has been observed in numerous experimental studies and is supported by the calculations from first-principles low migration energy[6]. Cr_2AlC has also shown to have self-healing properties from cracks, due to the high mobility of aluminium and formation of oxides in small cracks[7,8]. If the cracks are large [7] then there is also the formation of chromium carbides. Pure chromium carbides demonstrate lower corrosion resistance as compared to the alumina layer. Recently, good bonding between Cr_2AlC and Ni-based superalloy has been shown[9]. The bonding is also stable at elevated temperatures.

Synthesis of Cr_2AlC ternary compositions can be done in bulk form by hot pressing, spark plasma sintering, and pressureless sintering[10,11]. Cr_2AlC has also been produced as thin films[12–15] by magnetron sputtering from elemental or composite targets. In the case of bulk synthesis[5,16], the temperatures of at least 1323 – 1373 K were required to form crystalline high phase purity Cr_2AlC . The Cr_2AlC thin films produced by magnetron sputtering deposition have been reported to require deposition temperatures[12–15] of more than 723 K to crystallise. Crystalline films from amorphous Cr_2AlC thin films were produced by annealing at temperatures above 863 K.

During the synthesis of Cr_2AlC ternary carbides, both in bulk form and thin films, the formation of secondary phases [11,17–21] like Cr_2Al , Al_8Cr_5 , Cr_7C_3 , and γ - Cr_2AlC have been reported. In the case of the bulk Cr_2AlC [10,11,22–24], the crystallinity variations were attributed partially to synthesis parameters like temperature and homogeneity of raw powder mixtures. It is well known that the formation of various phases in Cr_2AlC is not too dissimilar to all MAX phase family of materials and it is well known. Probably the best and one of the most explicit examples is this accord is provided by S.Dubois et al [25]. With much attention to the growth parameters and materials it is possible to grow a large single phase crystals [26].

The phase variations in Cr_2AlC thin films [18–21,27] are attributed to the substrate temperature and the type of magnetron targets used. In order to prevent the formation of these secondary phases and to improve material mechanical and oxidation properties, the ratio of Cr/Al has been varied, and solid solutions of Cr_2AlC ternary carbides investigated[18,21,27–31]. The mentioned work resulted in Cr-Al-C coatings with different stoichiometric ratios. The secondary phases were observed and positively improved the material hardness compared to stoichiometric Cr_2AlC thin films. Annealing of amorphous [21] Cr-Al-C coatings with 23.8 at % of aluminium at 1023 K resulted in the formation of Cr_2AlC , along with Al_8Cr_5 and Cr_7C_3 as secondary phases. The hardness and modulus recorded to be 19 GPa and 268 GPa, respectively. The values are higher compared to the stoichiometric thin films [3,32]. This was attributed to the presence of Al_8Cr_5 and Al segregation at grain boundaries, as confirmed by EDS mapping. Single-phase Cr_2AlC was obtained [18] with Cr/C ratios in the range of 1.72 – 1.93 and Cr/Al in the range of 1.42 – 2.03, respectively. However, when the ratios of Cr/Al and Cr/C increased, a formation of Cr_2Al and Cr_{23}C_6 secondary phases were noted along with Cr_2AlC .

In addition, Solid solutions of Cr_2AlC [30,31] by partial replacement of Cr with Titanium and Vanadium have shown the formation of crystalline phase at 573 K, and improvement in hardness observed. The formation of Cr_2AlC at this relatively low temperature was attributed to the presence of substitutional titanium atoms, secondary phases and high bias voltage used. The increment in hardness was attributed to the lattice strains due to the difference in atomic sizes. Also, solid solutions of Cr_2AlC [29] with Al replaced by Si showed some improvement in oxidation resistance.

The MAX phase containing materials are very complex chemically and structurally. XRD spectra with Rietveld Refinement modelling provides reasonably high level of certainty about phase composition. This has been shown by many publications and can be supplemented by the EDX mapping. But the modelling is complex and have been done in not so many instances. Discussions about specific MAX phase properties are only correct when authors can show that the property on the micro- or even nano-scale exactly related to chemically and structurally proven crystal. However, in many cases, we talk about a MAX phase containing material when different phases are presented. It might be not also surprising if crystallite sizes influence the measured properties.

During irradiation material atoms are knocked out from their initial lattice positions. The damage is then referred as dpa (displacements per atom). The displacement probability in broad terms is defined by the threshold displacement energy. The displacement energies can be in principle calculated but the amount of unknown and possible variables is overwhelming in many practical cases. It is generally accepted that setting universal energy of 40 eV for all atoms in the alloy produces reasonable agreement with the observed irradiation phenomena [33].

Ion irradiation studies of Cr_2AlC MAX phase are rather limited to date and the radiation effects have been predominantly studied at room temperature [32,34–37]. Cr_2AlC MAX phase synthesised [35] by spark plasma sintering and irradiated with 7 MeV Xe^{2+} and 500 keV He^{2+} at 300 K retained crystallinity in doses up to 1 displacements per atom (dpa), but significant changes in mechanical properties compared to pristine material were observed. Irradiation of magnetron-sputtered [37] Cr_2AlC thin films at room temperature, with fluences in the range of 10^{14} – 10^{15} Xe^{2+} ions·cm⁻² show partially amorphized material at 2.2 dpa. The proposed amorphisation proceeds possibly via transformation of Cr_2AlC MAX phase into γ -phase, and the complete amorphization, in this case, was observed at 6.2 dpa [37]. In our recent work [32], where the radiation response of magnetron-sputtered Cr_2AlC MAX phase as thin film studied at high temperature (650 K) up to a fluence of 2.1×10^{16} Xe^+ ions·cm⁻² (~90 dpa), outstanding resistance to amorphization observed for the first time.

Single phase crystal growth is complex process and can be only a domain of high value applications. General bulk synthesis of MAX phases in many instances creates mixed phase materials. It is not entirely known how big variation in stoichiometry, e.g. variations in vacancies and interstitials, can be accommodated by the MAX phase. During bulk synthesis the amount of MAX phase is variable and as the whole material will be irradiated this raises a question of how MAX phase with under and over stoichiometry affects radiation stability. Currently, there are only a few publications on the crystallisation of under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ compositions, and there are no publications on their radiation stability at high temperatures. This work is therefore intended to partially fulfil the knowledge gap by studying processes of crystallisation of amorphous near stoichiometric ($x = 0.9$) and under stoichiometric ($x=0.75$) Cr_2AlC compositions at room temperature and following irradiation studies.

2. Materials and Experimental techniques

Magnetron sputtering deposition from elemental Cr, Al, and C targets used to synthesise the Cr_2AlC . The samples were deposited on Si (100) at 330 K. A full description of this deposition system has been reported in detail elsewhere [38]. After deposition time of 2 hours, the thin film thicknesses were about 0.9 and 1.2 μm for near and under stoichiometric Cr_2AlC compositions. The composition of samples shown in table 1 was determined by EDX in FESEM at 10 keV with a 5 % error in quantification.

The samples for crystallisation and in-situ TEM ion irradiation were prepared by conventional focused ion beam milling using 30 keV Ga ions. A platinum layer of 3 microns was deposited to avoid the surface damage from ion beam milling. Using the mean free path of 300 keV electrons in silicon [39] and the relative thickness of a TEM sample obtained using EELS spectra (~ 0.8 inelastic mean free path), the underlying Si lamellae thickness was found to be at around 150 nm. The $\text{Cr}_2\text{Al}_x\text{C}$ lamellae thickness correlated with silicon substrate by assuming that the substrate and the film had the same thickness.

Ion irradiations with 320 keV Xe^+ ions were performed at 623 K using the MIAMI-2 TEM with an in-situ ion irradiation facility located at the University of Huddersfield [40]. The specimens were irradiated up to a maximum fluence of 3.5×10^{16} ions/ cm^2 . The irradiation temperature was set to be at the functional value in Light Water Reactor (LWR) - 623 K. The ion damage was calculated using SRIM 2013 by setting thickness of 150 nm and with an average atomic density of 8.85×10^{22} and 8.3×10^{22} atoms/ cm^3 for $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.9$ and 0.75).

The amorphous $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.9$ and 0.75) thin films were crystallised by heating them in the TEM using a Gatan Model 636 heating holder. The heating rate was 373 K/min and the specimen was heated to a set of incremental temperatures and held for about 5 minutes at a given temperature. If no changes/crystallization observed within this time period, the specimen was heated to a higher temperature and the same procedure repeated until crystallization was observed. The heating was stopped only when the samples crystallised entirely, and the typical temperatures were found to be 873 and 973 K for near and under stoichiometric compositions respectfully.

The crystallised and ion irradiated $\text{Cr}_2\text{Al}_x\text{C}$ specimens were characterised using bright-field TEM (BF-TEM), selected-area diffraction pattern (SAED), dark field TEM (DF-TEM), energy filtered TEM (EF-TEM). Crystallographic indexing of the crystalline structure of the near and under stoichiometric compositions was performed using data reported previously in the scientific literature [3,13,20,32,37,41]. Normalised diffraction intensity for assessment of interplanar spacing (d) in Angstroms were generated by converting electron diffraction patterns using Image J software [42]. The plugin named “Radial profile angle” was utilised.

3. Results

Table.1 displays the material quantification results for as-deposited near stoichiometric and under stoichiometric films. In the case of near stoichiometric Cr_2AlC , the element concentrations are close to the stoichiometric composition and under stoichiometric material showed aluminium content of around 19 at. %, which was produced intentionally. The EDX spectrum only showed the peaks of elements present, indicating the deposited samples are sufficiently pure.

Elements	atomic %, Cr_2AlC , near stoichiometric	atomic %, $\text{Cr}_2\text{Al}_x\text{C}$ under stoichiometric
Cr	54	60
Al	22	19
C	23	21

Table.1: Chemical composition of near stoichiometric and under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ and their corresponding EDX spectra.

Fig.1(a–d) shows BF-TEM and the corresponding SAED patterns of near stoichiometric Cr_2AlC thin films taken at different annealing temperatures. Fig 1a displays as-deposited amorphous Cr_2AlC composition and Fig 1b after heating to 673 K. In Fig. 1(c) the BF-TEM and diffraction patterns show signs of initial crystallisation at 823 K, as indicated by the change in contrast of the BF image (the circles indicate potential crystallites). Figure 1(d) taken at 873 K displays complete crystallisation with the formation of the Cr_2AlC MAX phase (discussed further below). The indexed planes in the electron diffraction pattern shown in fig.1d corresponds to Cr_2AlC MAX phase. The crystallised samples found to be homogenous in EFTEM images, which are not shown here.

Fig 1: *In-situ* crystallisation of the near stoichiometric Cr_2AlC thin film deposited at 300 K. The scale in fig 1(a) corresponds to 1(b-d).

Fig. 2: *In situ* TEM images showing the microstructural evolution of near stoichiometric Cr_2AlC thin film irradiated with 320 keV Xe^+ at 623 K and different doses. Uniform magnification and scale on all images

Fig. 2(a–d) shows BF-TEM images and SAED patterns of the crystallised near stoichiometric Cr_2AlC before and after irradiation up to 83 dpa at 623 K. The BF-TEM and SAED images in Figs. 2(b) and (c) show the sample being stable at 1 and 15 dpa, respectively, without any changes in the crystal structure. At the highest dose of 83 dpa shown in fig. 2(d), there is still no observable change in the sample as compared to the image before irradiation in fig. 2(a). The irradiation stopped at this dose for post-irradiation analysis. Higher magnification images showing the crystalline lattice and typical crystal sizes are shown in Fig. 3. The crystal size of the samples measured to be mostly nanocrystalline sizes varying from 20 to 90 nm. Atomic radial distribution functions (pair distribution function) calculated from electron diffraction patterns compared with published data on Cr_2AlC MAX phase are shown in fig. 4.

Fig 3: Post irradiation analysis of the near stoichiometric Cr_2AlC thin film. BFTEM and the high resolution (HRTEM) image in fig 3a-b. Fig. 3d is the dark field (DF) image from the selected spot in fig 3(c) of SAED, showing a crystal of about 250 nm.

Fig 4. Atomic radial distribution functions (pair distribution function) of pristine and after irradiation up to 83 dpa of near stoichiometric Cr_2AlC thin film compared with standard Cr_2AlC MAX phase, and Cr_5Al_8 [15,41,43].

The plots in the irradiated specimen displayed in fig.4 were generated from different areas to demonstrate the diffraction pattern dependence on crystallographic orientations. Fig.4a is radial plots with x-axis as interplanar spacing (d) in angstroms and fig.4b, with x-axis as 2-theta in degrees. As expected, the intensity of various peaks in the electron diffraction pattern depends on the orientation of the crystal. The standard patterns of Cr_2AlC MAX phase labelled with down triangle, chromium aluminides labelled with diamond boxes were taken from the published work [15,41,43]. The phases present were found to be Cr_2AlC MAX phase for most of the peaks. The intense peak at about $2.15 \text{ \AA}^0$ is typical to both MAX phase and Cr_5Al_8 phases, but other distinct peaks such as 1.23 , 1.47 , 1.61 , and $2.47 \text{ \AA}^0$ were found showing the presence of the Cr_2AlC MAX phase. Besides, the patterns were compared with other potential secondary phases like chromium carbides (Cr_3C_2 , Cr_7C_3 , and Cr_{23}C_6), and chromium aluminides Cr_2Al (which are not shown here) none of them found to match.

Fig. 5. *In situ* TEM images of the crystallisation process of the under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.75$) thin film deposited at 300 K. The scales in fig 5(a) apply to 5(b-d).

Fig. 5 (a–d) displays BF-TEM and SAED images for $\text{Cr}_2\text{Al}_x\text{C}$ with reduced aluminium content ($x=0.75$) taken during the crystallisation process. There is no observable change in the sample after annealing to 673 K, as shown in fig. 5 (b). At 823 K, partial crystallisation and formation of secondary phases can be seen in BFTEM images and indicated with circles in SAED patterns. Figure 5 (d) taken after annealing at 973 K shows complete crystallisation of the sample with formation of Cr_2AlC MAX phase, and chromium aluminides as secondary phase, characterised by diffraction spots in the corresponding diffraction pattern and radial plots of electron diffraction in shown in fig. 9.

Fig. 6: *In situ* TEM microstructural evolution of crystallized Cr_2AlC ($x=0.75$) thin film with reduced aluminium irradiated with 320 keV Xe at 623 K and different doses. Uniform magnification and scale on all images.

Fig. 6(a–d) displays the images of reduced aluminium $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.75$) before and after irradiation to various doses up to a maximum fluence of 3.5×10^{16} ions/cm² at 623 K (~138 dpa). Fig 6(a) shows the BF-TEM image of the specimen and its diffraction pattern before irradiation. Fig 6(c) shows that the specimen remained crystalline after irradiation up to 39 dpa. Irradiations up to 138 dpa shown in fig. 6 (d) showed recrystallization of ultra-fine grains but no detectable transformation to the amorphous state.

Fig 7: Post irradiation analysis at 138 dpa, displaying nanocrystals as shown in (a–c), HRTEM, and its filtered image in (d–e). Note, the scale in fig.7a corresponds to fig. 7c as well.

Figure 7 (a–b) show the BF-TEM and SAED images of post irradiated sample with low aluminium content showing no observable amorphisation. Fig 7 (c) shows a DF image indicating the formation of nano-grains (nanocrystals at about 10–40 nanometres) seen with bright contrast. Fig 7 (d–e) is the HRTEM and corresponding inverse FFT of $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.75$) thin film, filtered to contain only the main diffraction spots, after irradiation to a fluence of 3.5×10^{16} ions/cm² (138 dpa) at 623 K. Fig 8 shows SAED patterns and DF images in other regions. These regions show the presence of oriented grains.

Fig 8: Post irradiation SAED and DF analysis for the sample irradiated to 138 dpa; 8 (a–b) Cr_5Al_8 SAED was taken from the crystal from BFTEM image and fig 8 (c–d) SAED and DF images of $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.75$) taken after irradiation to 138 dpa. See Fig.10-11 and associated text for more details.

Fig 9: Radial plots of pristine and after irradiation up to 138 dpa of $\text{Cr}_2\text{Al}_x\text{C}$ ($x=0.75$) compared with standard Cr_2AlC MAX phase and Cr_5Al_8 [15,41,43]

Fig. 9 displays the radial plots of the under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ extracted from the electron diffraction patterns after crystallisation (labelled as pristine) and post-irradiation taken in different areas of the sample (labelled as area 1 and area 2). Electron diffraction patterns from multiple areas were collected to confirm the presence of all the major diffracted beams to make sure that the phases indexed are present over the irradiated sample. Radial plots of Cr_2AlC MAX phase, and chromium aluminides (Chromium carbides (Cr_3C_2 , Cr_7C_3) not shown here) from references [15,41,43] shown for comparison.

Fig 10: a) Cr_2AlC MAX phase modelled pattern and fig b) Post irradiation SAED pattern

Figure. 10a shows a simulated diffraction pattern of Cr_2AlC and Cr_5Al_8 phase (Crystal Maker, Coll code). Fig. 10a shows reflections from two grains oriented along $[100]$ and $[001]$. Fig. 10b shows SAED pattern after irradiation to 83 dpa indexed with Cr_2AlC phase. The grains were rotated by about 4 degrees relative to each other to match some of the major reflections shown in fig:10 (b).

Fig 11: a) Cr_5Al_8 phase modelled pattern (ICSD CollCode 823) and fig b) Post irradiation SAED pattern.

Figure. 11a, shows a simulated diffraction pattern of the Cr_5Al_8 phase. Fig. 11a shows reflections from $[211]$ grains of the Cr_5Al_8 phase. Fig. 11b shows SAED pattern irradiated with 138 dpa indexed with the Cr_5Al_8 phase.

4. Discussion

Near stoichiometric Cr_2AlC consisted of nanocrystalline grains after crystallisation at 873 K. The presence of Cr_2AlC MAX phase was demonstrated by the electron diffraction patterns and their radial intensity plots (Fig.4) showing that all the peaks expected in the diffraction patterns [3,15,32] could be accounted for when analysing different regions of the specimen. The formation of Cr_2AlC MAX phase at 873 K in our case, which is the crystallisation temperature of amorphous Cr-Al-C compositions on heating, is in agreement with the previous studies [15,20]. The formation of disordered phase solid solution $(\text{CrAl})_2\text{C}_x$, which is but an intermediate phase is not present in our case. This can be attributed to even (atomic level random) distribution of atomic species during sputtering while in the previous work transformation of the grainy atomic species green body into a single phase is diffusion controlled. In other authors work, the presence of Cr_2AlC MAX phase was confirmed by the diffraction 002 peak (6.41 Å). The absence of 002 has been previously attributed to the presence of preferential orientation and synthesis parameters [44]. However, other peaks such as 101/100 peak (2.47 Å) [44] were used to confirm the presence of Cr_2AlC -MAX phase. We have adopted the same approach.

Furthermore, to confirm Cr_2AlC MAX phase it was compared with the simulated Cr_2AlC MAX phase, as shown in Fig 10a. The observed reflections such as (-100), (006) and (00-6), (100) in Fig.10b shown are an excellent agreement with the simulated reflections in Fig 10a. Other matching reflections are indicated on both the simulated as well as on the experimental diffraction pattern. It is worth mentioning that reflections such as (-100) and (1-10) are weaker and slightly shifted from their nominal position, indicating that the grain orientation may be slightly off the zone axes. Also, many other reflections are present due to smaller grain contribution to the observed diffraction pattern.

The ion irradiation at 623 K of near stoichiometric Cr_2AlC MAX phase demonstrated a high degree of resistance to amorphisation up to a maximum fluence of $1.9 \times 10^{16} \text{ Xe}^+ \text{ ions.cm}^{-2}$ (~83 dpa). This resistance to amorphisation at high temperature was also observed in our previous study [32] and also by other studies [45,46]. As deposited crystalline Cr_2AlC MAX phase [32], exposed to in situ ion irradiation up to 90 dpa with 320 keV Xe^+ at 623 K showed no observable changes in its crystal structure. This was attributed to the stability of MAX phase and the presence of nano crystallinity. The damaged crystallinity recovery on the first instance is based on the low migration energy of atomic species [17].

Presence of nano crystallinity in our case for both near and under stoichiometric Cr_2AlC thin films shown to enhance radiation hardness and protect the material from microstructural changes. This suggestion is an extension of previously discussed radiation hardness [47–49]. Bai et al.'s [47] showed that the simulation of nanomaterials which have large grain boundary area absorb interstitials and then later these interact with vacancies and coalescence within nanometre range for both at low and high temperatures. In addition, G. A. Vetterick et al. [50] showed that as-deposited nanocrystalline iron when irradiated had a higher resistance to radiation damage compared to annealed nanocrystalline iron. This was ascribed to the excess free volume present in non-equilibrium grain boundaries of as-deposited nanocrystalline materials. Thus, it is essentially the high surface area in such nano-grained materials that provides a very efficient defect sink.

We extend those ideas by suggesting that the defect traps on the nano grain boundaries are shallower as compared to the defect traps on grain boundaries of micron-sized grains. This allows more effective defect release back into the nanocrystals followed by the defect recombination and thus healing the crystalline structure.

The Crystallisation of under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ ($x= 0.75$) thin films showed initial crystallisation at 823 K (550 °C), believed to be chromium aluminides and Cr_2AlC MAX phase from the measured interplanar spacings. Further investigation is intended to be done in future to confirm these phases at this temperature. The complete crystallisation of under stoichiometric thin films was found at 973 K (700 °C) with final structure consisting of Cr_2AlC MAX phase and chromium aluminides as a secondary phase. Atomic radial distribution plots in fig. 9, confirms the presence of Cr_2AlC MAX phase and Chromium aluminides only. The plots of the under stoichiometric samples were compared with Chromium carbides. The high intensity peaks of Cr_3C_2 does not match with experimental patterns. The formation energies [51,52] for chromium aluminides synthesised through mechanical alloying and chromium carbides in bulk form were shown to be -15 and -73 kJ/mol. Furthermore, the SAED patterns of under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ ($x= 0.75$) after irradiation to 138 dpa were compared with standard Cr_5Al_8 phase (Fig. 11a), shown to be consistent with [211] grains.

The formation of secondary phases [18,21,27,53] in under and over stoichiometric Cr-Al-C and Ti-Si-C compositions was reported earlier. Crystallisation of amorphous Cr-Al-C compositions with reduced aluminium had resulted in formation of Cr_2AlC MAX phase along with chromium aluminides, and Cr_7C_3 confirmed by XRD and TEM [21]. The formation of Cr_2AlC MAX phase along with Cr_7C_3 was found when there is deviation in stoichiometry and temperature of deposition or annealing was above 1023 K (750 °C) [18,43]. However, in our case formation of only Cr_2AlC MAX phase and chromium aluminides are found. This can be attributed to difference in synthesis parameters and amount of carbon content present. In addition, the formation of pure Cr_2AlC MAX phase was also found when the amorphous samples deposited on to superalloy and annealed at 620 °C for 20 h [27]. Furthermore, synthesis of Ti_3SiC_2 [53] by pressureless reactive sintering, with varying silicon resulted in the formation of single phase. However, further addition of silicon resulted in the formation of titanium silicide solid solutions and silicon carbide as secondary phases [53].

Ion irradiations of under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ showed resistance to amorphisation up to a maximum employed fluence of about $3.5 \times 10^{16} \text{ Xe}^+ \text{ ions/cm}^2$ (~138 dpa). Extensive irradiation was observed to result in the partial recrystallization of nano-grains at high damage levels, as shown in Fig 7c. Recrystallisation during ion irradiation at high temperatures has been reported previously for various materials at high enough for the process temperature [54–56]. Sintered uranium titanates [55] irradiated at room temperature and 973 K with 800 keV Kr^{+2} displayed amorphisation up to 930 K and resistance to amorphisation and nano-recrystallisation at 933 and 973 K irradiation temperatures. High temperature recrystallisation are usually attributed to the generation of point defects due to ion irradiation, acting as nucleation sites.

5. Conclusions

Amorphous near and under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ ($x = 0.9$ and 0.75) thin films were crystallised by in-situ heating using a TEM holder at 873 K for near stoichiometric Cr_2AlC and at 973 K for under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$. The Crystallisation of near stoichiometric Cr_2AlC sample resulted in the formation of Cr_2AlC MAX phase. The ion irradiation of crystallised near stoichiometric thin film at 623 K to a maximum fluence of 1.87×10^{16} Xe ions/ cm^2 (~83 dpa) showed no observable changes in the crystal structure. In the case of under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$, crystallisation resulted in the formation of Cr_2AlC MAX phase and chromium aluminides as a secondary phase. Ion irradiation of under stoichiometric $\text{Cr}_2\text{Al}_x\text{C}$ to a fluence of about 3.5×10^{16} Xe ions/ cm^2 (~ 138 dpa) at 623 K, showed resistance to amorphisation and recrystallisation of some nano-grains at 138 dpa. The high radiation resistance in both cases is attributed to the MAX phase stability, nanocrystalline nature of the grains, and high defect mobility. Future work intended to address the mechanical and corrosion properties of amorphous and crystalline near and under stoichiometric Cr-Al-C thin films. In addition, to study the intermediate microstructure for both near and under stoichiometric Cr-Al-C thin films.

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