



# Synthesis and characterisation of high-entropy alloy thin films as candidates for coating nuclear fuel cladding alloys



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## ABSTRACT

Thin films of the quaternary system FeCrMnNi were synthesised by ion beam sputter-deposition. The films were deposited on a silicon substrate at approximately 350 K. A high-entropy alloy thin film (HEATF) and a non-equiatom thin film were obtained. Energy Dispersive X-ray Spectroscopy (EDX) and Transmission Electron Microscopy (TEM) were used to determine thin film composition and the atomic structure. The non-equiatom thin film exhibited a polycrystalline structure with nanometre-sized grains. Microstructural analysis of the HEATF, which had close to equimolar composition, showed large crystals and planar defects. The microstructural differences between the HEATF and the non-equiatom thin film are discussed in terms of current high-entropy alloy theory, previous work on thin films and nucleation theory.

## 1. Introduction

Thin film technology is a successful branch of materials science and metallurgy having numerous applications in surface treatments aimed at enhancing a wide variety of material properties such as mechanical strength, heat, wear, frictional and scratch resistance as well as reducing corrosion and oxidation in many metals [1]. The diversity and enormous potential of this technology have supported the progress of many scientific areas by means of coating functional materials used in applications that include optics [2,3], steel tools [4,5], space technology [6], computer chips and microelectronics [7,8], medicine [9] and the nuclear industry [10–14].

In the loss-of-coolant accident at the Fukushima-Daiichi complex in 2011, fuel rods made of a zirconium alloy were subjected to high-temperatures and underwent catastrophic oxidation producing H gas that leading to the core meltdown [15]. As a result, the nuclear community has recently initiated efforts to investigate new accident tolerant fuel (ATF) systems aiming at preventing and mitigating possible deleterious effects in structural nuclear materials under severe conditions [15,16]. One particular approach has been to coat zirconium alloys with hard thin films such as nitrides [17,18] and carbides [11,19]. Such ceramics are well known for their excellent corrosion resistance [20], chemical inertness [21,22] and reduced H pickup [23], however, their applicability is diminished in some cases where low ductility, reduced heat transfer rate and crack resistance are regarded as essential.

Parallel to the progress of the ATF program, recent scientific

investigations in the field of high-entropy alloys (HEA) have led to the possibility of designing new metallic alloys with superior metallurgical stability at room and high temperatures, improved radiation resistance and better corrosion behaviour when compared to conventional cladding alloys such as Zircalloys and stainless steels [24–29]. HEAs are a new class of alloy with four or more elements in equiatom composition [24,30]. This condition results in minimisation of the Gibbs free energy as the configurational entropy is maximised. This results in a material with superior phase stability, which enables HEAs to withstand significant doses of irradiation without accumulation of damage and degradation of their properties. To assess the radiation hardness, ion irradiation has been applied to several different HEAs and the most recent results have demonstrated evidence of self-healing effects in some of these systems [31–33]. The multicomponent nature makes it difficult to model such materials and predict their behaviour. Both modelling and experimental data are needed to shape our understanding of these alloys. The first papers on thin film HEA deposition used HEAs as target materials in reactive sputtering under a N atmosphere [34,35]. Pure metallic coatings were deposited later [36,37]. The possibility to adjust the elemental content and to alter material properties provides the possibility of tailoring properties to applications [38,39].

In this work, we report the synthesis of multicomponent materials based on the quaternary system FeCrMnNi, which at close to equiatom (e.g. equimolar) composition can be regarded as a HEATF. The technique of ion beam sputter-deposition was employed in order to produce the thin films. Transmission Electron Microscopy (TEM)

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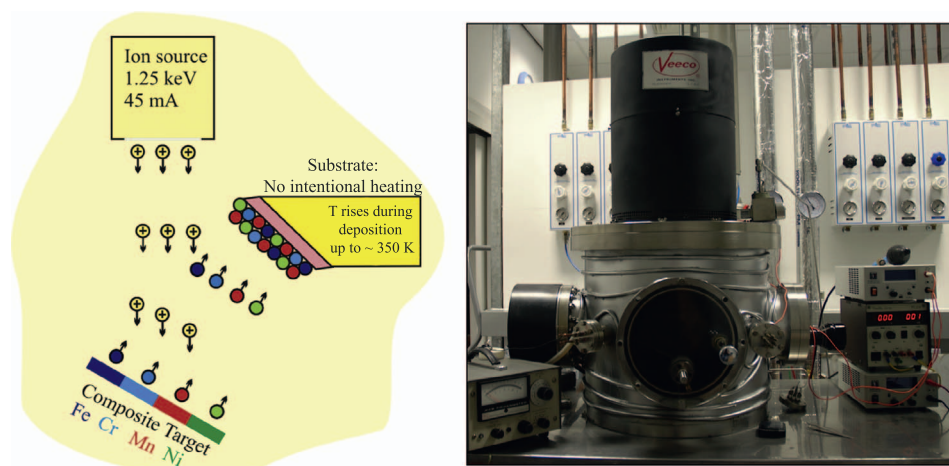


Fig. 1. The ion beam sputter-deposition system.

**Table 1**  
Elemental composition of the synthesised thin films.

Element	Composition [at.%]	
	Non-equiatomic thin film	HEATF
Fe	14.6 ± 0.7	23.7 ± 1.1
Cr	21.7 ± 1.1	22.9 ± 1.3
Mn	39.3 ± 2.0	25.8 ± 1.2
Ni	24.4 ± 1.2	27.6 ± 1.4

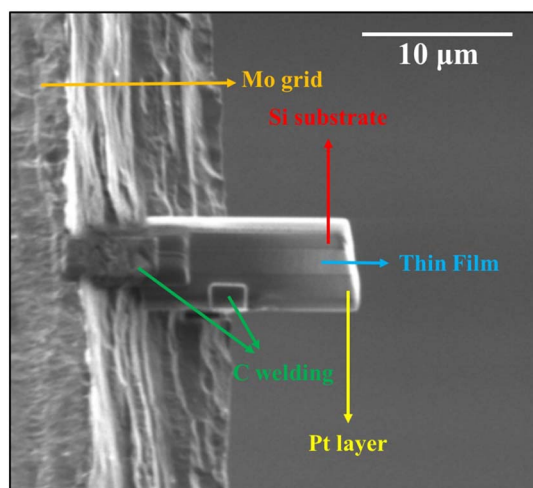
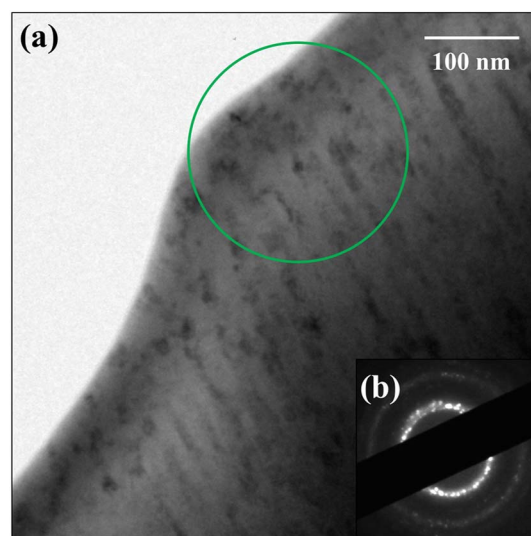


Fig. 2. SEM micrograph showing the HEATF TEM lamella attached to a TEM grid.

characterisation has revealed significant differences in the microstructure when the composition is far from equiatomic and when the film is in quasi-equiatomic composition. Given the metallic nature of the material, its potential high radiation hardness and oxidation resistance [39], the HEATF can be regarded as a metallic coating candidate within the scope of ATF research programs.

## 2. Materials and methods

Thin films were synthesised using the ion beam sputter-deposition technique from elemental targets of Fe, Cr, Mn and Ni. An ion source producing 1.25 keV Ar ions was used to sputter the elements onto a Si substrate (Fig. 1). The substrate is not intentionally heated in this work, but mainly due to radiation heating from the targets, the substrate temperature during the 2 h deposition rises to the region of 350–370 K. Base vacuum in the deposition chamber was  $1.5 \times 10^{-4}$  Pa and during



**Fig. 3.** The nanostructure of the non-equiatomic thin films. (a) is a BFTEM micrograph at focus. The SAED pattern from the area indicated by the circle in (a) is shown in (b).

deposition the pressure in the chamber was at around  $3 \times 10^{-2}$  Pa. The deposition time was the same for both thin films (120 min) discussed in this paper. A HEATF and a non-equiatomic thin film are presented in this work, produced under the same envelope of deposition conditions. Elemental targets under sputter ion beam were geometrically adjusted in order to achieve the non-equiatomic and equiatomic compositions. The elemental composition of the thin films is then directly related to the geometric configuration of the sputtering targets. The close to equiatomic composition was reached under a specific geometric configuration after several trial and error attempts.

The compositions were then determined using an Oxford EDX system in an FEI Quanta 3D FEG Scanning Electron Microscope (SEM). Atomic compositions of the HEATF and the non-equiatomic thin film are listed in Table 1. The standardless quantification method with ZAF correction [40] was used in order to estimate the composition from the X-ray analysis. Set of various electron energies (30, 20 and 15 keV) and measurements at different spots were also used to reduce uncertainties. Uncertainties for the composition were estimated to be approximately 4–5% of the measured values after extended acquisition time and standard optimisation and quantification algorithms provided by the manufacturer. Conventional Focused Ion-Beam (FIB) lift-out technique [41] was used to produce TEM samples that were further analysed in a JEOL 3010 TEM operating at 300 kV.

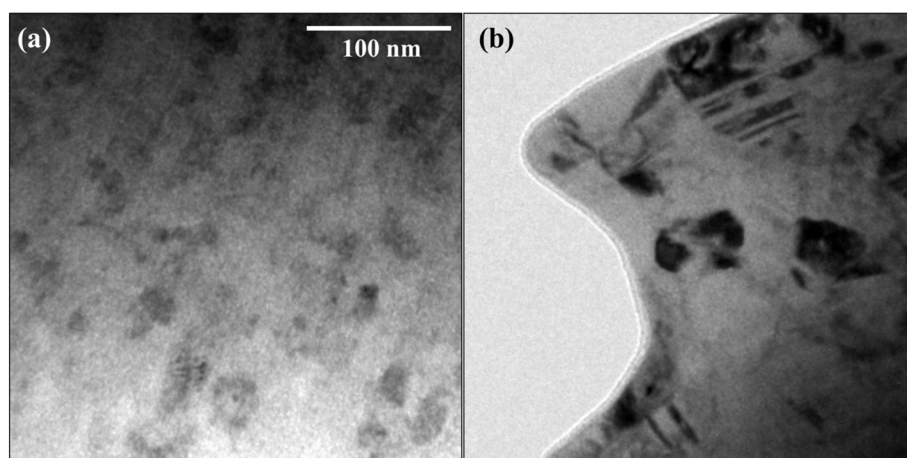


Fig. 4. BFTEM underfocused micrographs (a) of the non-equiatom thin film and (b) the HEATF showing surface roughening as evidenced by the speckled contrast. The defocus degree was of  $-0.95\ \mu\text{m}$  for both images. The scale marker in (a) also applies to (b).

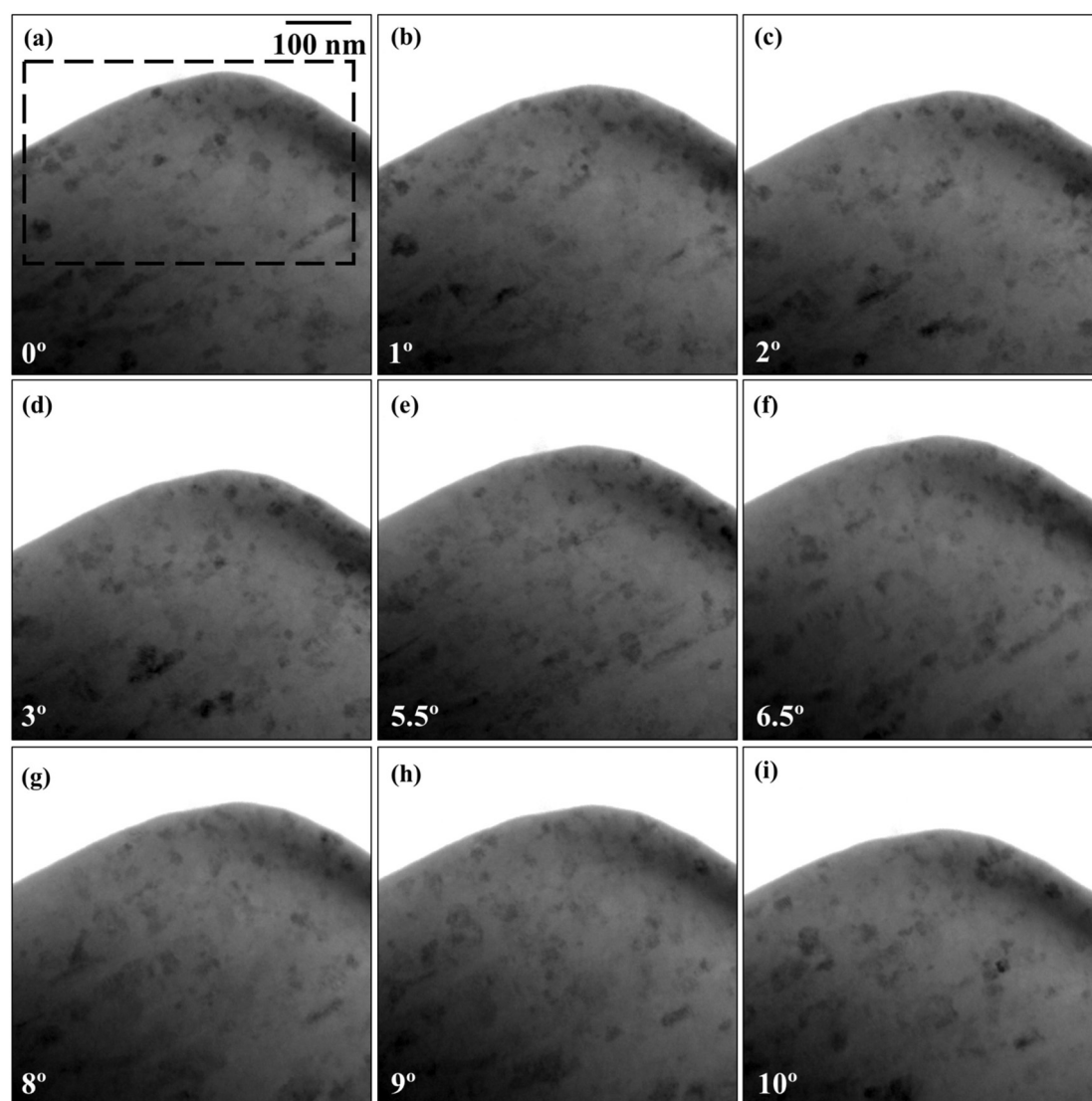


Fig. 5. BFTEM images of the non-equiatom thin film from  $0^\circ$  to  $10^\circ$  x-axis tilt. The dashed rectangle in (a) is the area analysed to compose Fig. 6a.

### 3. Results

Fig. 2(a) shows a TEM lamella attached to a Mo grid. The lamella has a top layer protection of Pt and it was welded onto a TEM grid with carbon deposition. After multiple measurements with cross-sectional

SEM micrographs, it was concluded that the non-equiatom thin film has  $1.51 \pm 0.06\ \mu\text{m}$  thickness, while the HEATF has thickness of  $1.58 \pm 0.05\ \mu\text{m}$ . Therefore, the deposition rate was roughly the same for both thin films at  $0.013\ \text{nm/min}$ .

The microstructure of the non-equiatom thin film is presented in



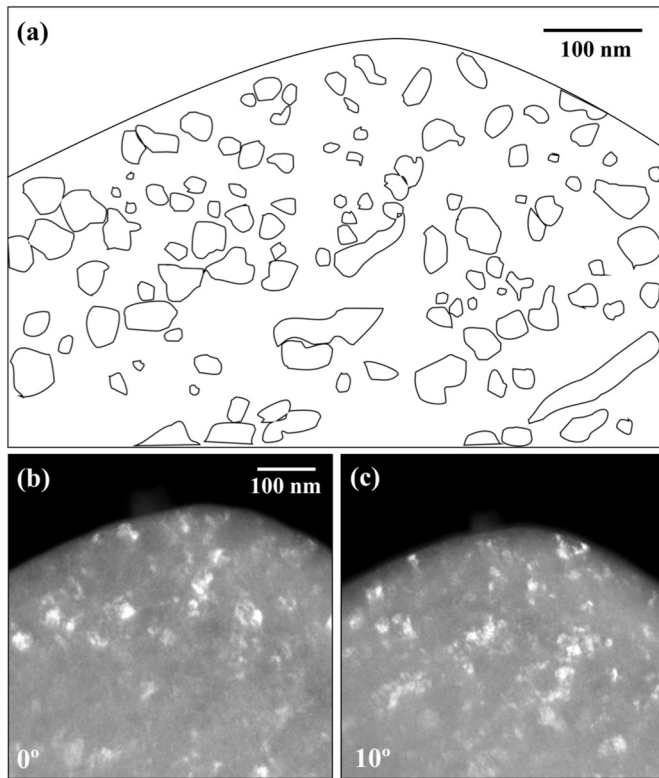


Fig. 6. (a) The nanocrystalline composite image showing the grain pattern for the images from 0° to 10° of x-axis tilting. DFTEM micrographs for (b) 0° and (c) 10° of tilting.

Fig. 3. Fig. 3(a) shows a BFTEM image at focus. Nanocrystallites are observed throughout the microstructure with sizes around of 5 nm and 50 nm. The nanocrystalline structure was confirmed with the selected-area electron diffraction (SAED) pattern exhibited in the Fig. 3(b).

Another BFTEM micrograph of a different region of the TEM lamella and at a higher magnification (40 k), Fig. 4a, shows the nanocrystallites in further detail and by defocusing the electron beam, surface roughening can be seen as “speckled” Fresnel contrast. The roughening was also observed in the HEATF to some degree as shown in Fig. 4b.

Fig. 5a–i is a set of BFTEM micrographs of the non-equiatomic thin film. When tilting around the x-axis within the TEM holder, diffraction contrast in the bright field image served to identify some of the individual grains in each case. It was thus possible to conclude that the microstructure is composed entirely of nanocrystals with sizes around of 40 nm. Fig. 6a is tracing of all the grains visible in the micrographs at the different tilt angles that were presented in Fig. 5. The area in which the analysis was carried out is represented by the dashed-rectangle in

the Fig. 5a. The dark-field TEM image (DFTEM) Fig. 6b and c also show the grain structure visible at 0° and 10°, respectively.

With respect to the HEATF, Fig. 7a features a BFTEM micrograph at focus. For this case, the SAED analysis (Fig. 7b–c) showed that the HEATF microstructure is composed of grains with sizes varying from 100 to 200 nm. The DFTEM micrograph, Fig. 7d, clearly demonstrates much bigger grain size compared with the non-equiatomic thin film. Crystallographic analysis carried out with the diffraction pattern has confirmed that the single-crystals are of face-centred cubic (FCC) structure. The microstructure of the HEATF has also revealed the presence of planar defects similar to twinning (Fig. 7a).

#### 4. Discussion

##### 4.1. The dynamics of nucleation and the Gibbs free energy

The microstructural differences between the HEATF and the non-equiatomic thin film can be discussed using current HEA theory. It has been established that the maximum configurational entropy in a metallurgical system is reached when the alloying elements are mixed in equal amounts [42]. Despite the fact that in a thermodynamic system the mixing entropy is subdivided into four different types, e.g. configurational, vibrational, magnetic dipole and electronic randomness, Fultz [43] concluded that the configurational contribution is the dominant part of the mixing entropy. In terms of statistical mechanics, this can be expressed using the classical Boltzmann entropy theory which states that for  $N$  different alloying elements, the general form of the entropy of mixing is:

$$\Delta S = -k_B N_a \sum_{i=1}^N x_i \ln x_i \quad (1)$$

Where  $k_B$  and  $N_a$  are Boltzmann's constant and Avogadro's number, respectively and the variable  $x_i$  corresponds to the molar fraction of each alloying element present in the system with the boundary condition of  $\sum_{i=1}^N x_i = 1$ . Thus, in Eq. (1), the maximum configurational entropy is a condition where the all the alloying elements  $N$  have equimolar fractions implying that the Gibbs free energy will be minimum (eq. 2) as the entropy overcomes the contribution of the enthalpy. The condition of minimum also holds for the temperature range to which the alloy may be subjected: as the higher  $T$ , the lower is the  $\Delta G$ .

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Due to their equiatomic nature, the HEAs possess major features that establish a new category of metallic alloy. The high-entropy effect favours the formation of a single-phase solid solution instead of the clustering of atoms or the precipitation of secondary phases in the microstructure as this would reduce the configurational entropy [42,44].

In the case of the non-equiatomic thin film, the TEM microstructural

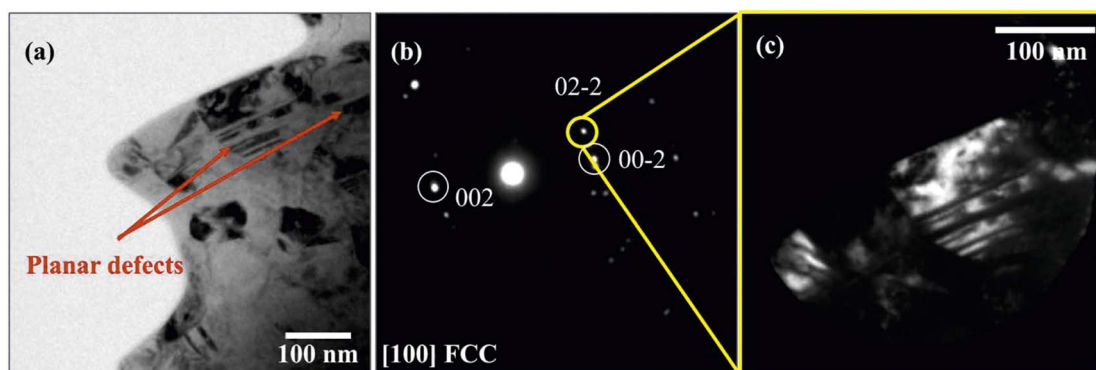


Fig. 7. TEM characterisation of the HEATF. Figure (a) is a focused BFTEM image, (b) is the diffraction pattern corresponding to (a) and (c) exhibits the dark-field image of the studied region.

analysis showed the presence of nanocrystallites while the grains in the HEATF case have grown under the same deposition conditions. Comparing the diffraction patterns of the non-equiatomic thin film with the HEATF, the latter case resembles a typical crystalline pattern. For the non-equiatomic thin film, the diffraction pattern is of a nanocrystalline alloy (grain-sizes smaller than 100 nm according to the definition proposed by Jang [45]). The diffraction patterns are consistent with the grain-size analysis carried out in the TEM as showed in the Figs. 6 and 7. The major difference between the two thin films is that in the HEATF the grains are bigger. With respect to the FCC crystal structure observed for the HEATF, the results are in agreement with previous works in the literature for the same HEA system [46,47].

Differences in composition were found to be influential in the final microstructures: both morphology and crystal structure indicate that for the HEATF, the grains started to nucleate and grow at the early stages of deposition while in the non-equiatomic case, although the nucleation rate was higher, the formation of smaller crystals was due to suppressed growth kinetics. As studied by Hollomon and Turnbull [48,49], the Gibbs free energy of a material plays a major role in the formation of *embryos* which affect the overall nucleation kinetics. The authors reported an inversely proportional relationship between the Gibbs free energy and the critical radius for nucleation: as the HEATF has a lower Gibbs free energy than the non-equiatomic thin film, in the latter case the critical radius for an *embryo* in the heterogeneous nucleation is smaller. We speculate that in the HEATF, the high-entropy effect may act in favour of a uniform nucleation rate for the most stable phase in the given equiatomic composition, although the configurational entropy for the non-equiatomic thin film and the HEATF are very similar when Eq. (1) is used:  $1.32k_B N_a$  and  $1.38k_B N_a$ , respectively. These observations are in agreement with previously reported results on thin solid films [50], but further studies are needed in order to better understand the nucleation kinetics of HEA thin films as the current lack of experimental data in equiatomic alloy systems, such as latent heat and surface energy, poses challenges for deeper analytical calculations. Additionally, the influence of configurational entropy, regarded as the most influential component of the high-entropy effect, should be investigated in greater depth as small differences in calculated entropies were observed to be significant in the final microstructures of the synthesised thin films in this work.

It is worth emphasising that both the temperature of the substrate and the deposition conditions were equal for the two thin films:  $\sim 350$  K (probably equal to  $0.2 T_m$ ,  $T_m = 1685$  K for Si [51]). As studied by Thornton [52], for substrate temperatures within the range of  $0.3$ – $0.5 T_m$ , surface mobility is sufficiently high to promote grain boundary migration and even recrystallisation. While the deposition temperature reported in this work is outside of this region, some ion assistance by ions backscattered from the targets during the film growth will promote the surface mobility of solute atoms. The nucleation but lack of growth of grains in the non-equiatomic thin film is probably rather a feature of the non-equiatomic condition which affects the overall nucleation kinetics rather than due to lack of atomic diffusion [53].

#### 4.2. Surface roughening and planar defects

Another difference between the HEATF and the non-equiatomic thin film lies in the observation of planar defects in the first case, although as a recent subject of research some authors have reported such defects in nanocrystalline materials [45,54,55]. In both thin films, surface roughening was also observed in underfocused micrographs (Fig. 4a and b). As studied previously by Roitburd [56], the ion beam sputter-deposition of a thin film on a substrate induces the generation of residual stresses that can be the cause of deposition-related effects such as thermal expansion mismatch, epitaxy and phase transitions. It has been shown that these stresses can be a significant fraction of the shear modulus [57]. Dislocation motion, cracking, surface roughening,

twinning and stacking faults are some possible mechanisms by which the residual stresses are relieved [7,56].

The whole-solute matrix in the HEATF is a multicomponent solid solution formed from elemental targets with slightly different atomic sizes [47]. This atomic size difference creates a “severe distorted lattice” that was confirmed using X-ray diffraction analysis (XRD): the distorted Miller planes generates X-ray peak a with decreased intensity [24]. The observation of planar defects throughout the microstructure of the HEATF may indicate that they are being formed in order to reduce the elastic strain energy mismatch by the mixing of the different kind of solute atoms in equimolar proportion in combination with the residual stresses induced by the deposition method, but these facts highlight the need for further research to evaluate the impact of planar defects in both the tribological and mechanical properties of the HEATFs.

## 5. Conclusions

Metallic alloys with nanometre-sized grains have attracted the attention of the materials science community due to their superior properties for a wide range of applications. Recently, ongoing investigations in high-entropy alloys have already established a new paradigm [28,29] for materials applications at high temperatures with increased mechanical strength. These superior properties of HEAs are commonly attributed to the thermodynamic stability of the single-phase crystal structure at equiatomic compositions.

In this work, we have demonstrated the viability of producing nanocrystalline thin films using ion beam sputter-deposition from elemental targets of Fe, Cr, Mn and Ni. Two thin films were produced under the same deposition conditions: a non-equiatomic thin film and a HEATF. The TEM analysis revealed that in the HEATF, the thin film at close equiatomic composition, the grains have grown significantly and their sizes were on the order of 100–200 nm. Conversely, in the far from equimolar composition, the thin film exhibits nanocrystals whose growth has been less than those in the HEATF. Differences in the composition and in the Gibbs free energy states were used to discuss the observed results regarding the evolution of the microstructures.

Owing to the potential high radiation hardness of the high-entropy alloy systems, its potential high corrosion resistance and metallic nature [32], we propose the FeCrMnNi HEA in thin film form as a candidate material for future research within the scope of accident tolerant nuclear fuel systems. Further work is needed to investigate the properties of such HEATFs particularly those relevant to nuclear environments such as corrosion behaviour, mechanical resistance and compatibility with nuclear fuel cladding alloys.

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