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

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A B S T R A C T

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-equiatomic 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-equiatomic 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-equiatomic 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 Zircaloys and stainless steels [24–29]. HEAs are a new class of alloy with four or more elements in equiatomic 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 equiatomic (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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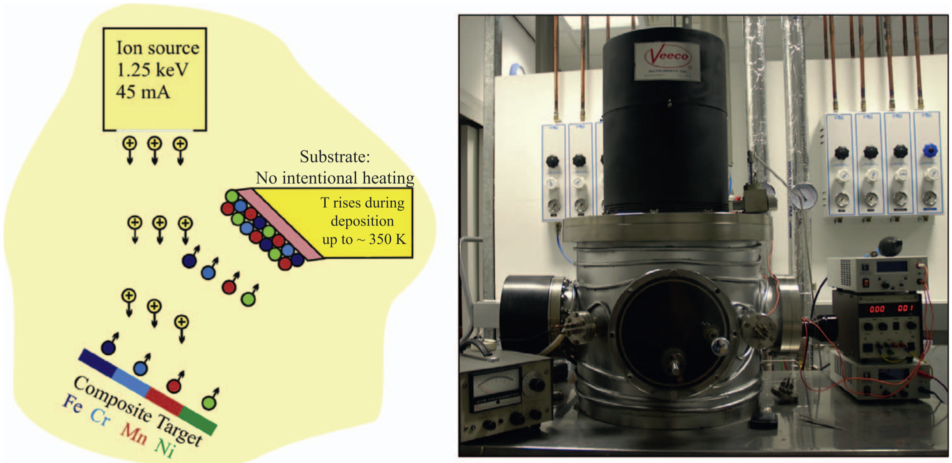


**Fig. 1.** The ion beam sputter-deposition system.

**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 |

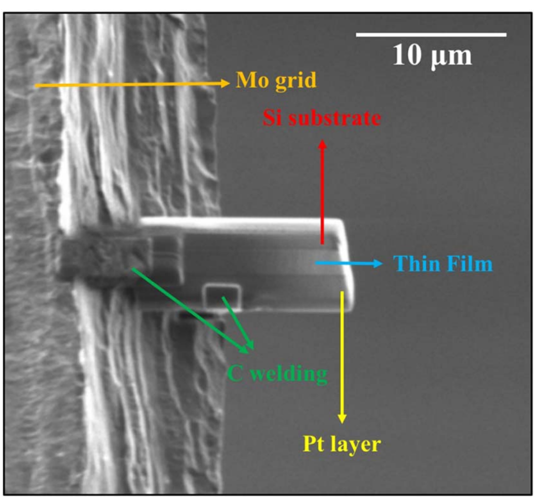


**Fig. 2.** SEM micrograph showing the HEATF TEM lamella attached to a TEM grid.

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 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.

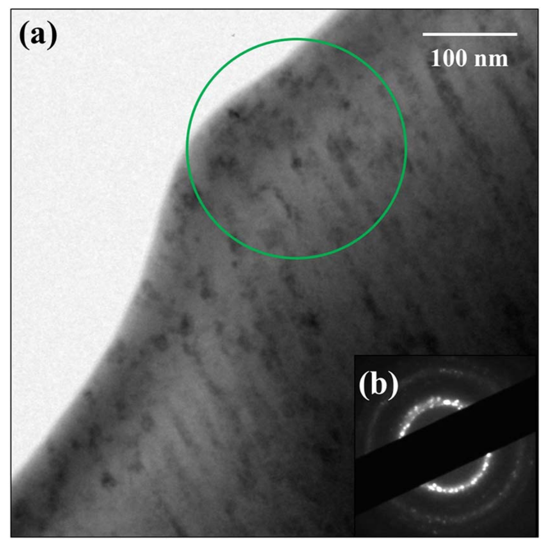


**Fig. 3.** The nanostructure of the non-equiatomic thin films. (a) is a BFTEM micrograph at focus. The SAED pattern from the area indicated by the circle in (a) is shown in (b).

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.