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High entropy alloys deposited by magnetron sputtering

Vincent Dolique, Anne-Lise Thomann, Pascal Brault

***Abstract* - We have studied the deposition of AlCoCrCuFeNi high entropy alloy (HEA) thin films on Si (100) substrates by DC magnetron sputtering process. Three mosaic targets have been used for easily tailoring the film composition. Chemical composition can be modified around the nominal value by tuning the ratio of the powers applied to the magnetron targets. The deposition rate is directly related to the power sum. Moreover, various surface morphologies have been evidenced by scanning electron microscopy and correlated to the crystalline phases present in the films. Morphology and crystalline structure have been found to depend on the chemical composition.**

High Entropy Alloys (HEA) are metallic compounds containing six to 13 metallic elements in equimolar ratios. Their mixing entropy is high, leading to the formation of random solid solutions during solidification, rather than inter-metallic compounds. They exhibit very interesting properties: hydrophobicity, good temperature stability [1], high stiffness, strength and toughness, high hardness, corrosion resistance, superplasticity and high-strain-rate superplasticity.

To synthesize HEAs, different techniques are employed at present, such as rapid solidification, spray forming or mechanical alloying [2]. All these techniques lead to the formation of bulk or thick films of HEA (> 1mm). In this study, HEA thin films have been synthesized by magnetron sputtering of mosaic targets (Patent N° WO/2008/028981). This technique allows to synthesize HEA films in a wide range of chemical compositions [3]. The composition can be easily controlled by varying the magnetron powers and the relative surface of each element on the targets. Three magnetron targets are focused onto rotating Si (100) substrates. The six chemical pure elements are fixed on the targets (Fig.1): Fe, Co and Ni are on target 1, Cu and Cr on target 2 and Al on target 3. This distribution has been chosen for the following reasons. Al sputtering yield being the lowest, a large area, corresponding to the size of a whole target, is necessary to reach the required ratio. The presence of a single magnetic element in a target would have led to local perturbation of the permanent magnetic field. To avoid the phenomenon of perturbation by the magnetic elements, we have chosen to build a target with the three magnetic elements: Fe, Co and Ni. To ensure an efficient sputtering process of this target, a thin thickness (1 mm) is required. Finally, the last target is composed of the remaining elements: Cr and Cu. In a first approximation, the following equation has been used to calculate the relative exposed area *Ai* of each element and to obtain the equimolar stoichiometry AlCoCrCuFeNi:

$$X_i = \frac{Y_i \times A_i \times 100}{\sum Y_i \times A_i}$$

where, Y_i is the sputtering yield, A_i the surface area and X_i the percentage of element *i*. The X_i value required to obtain an equimolar alloy with six elements is 16.7 %. The power (on each target) is varied to achieve composition near the equimolar one. The same argon pressure is used (1 Pa) during deposition runs. The substrate temperature remains floating and stays below 100 °C. The targets-to-substrate distance is kept constant, equal to 90 mm.

It is known that the crystalline structure of bulk HEAs synthesized by melting depends on the chemical composition and the processing route [2]. In the following we will evidence what is driving the structure of HEA thin films.

In the present study, the powers of the three targets are varied, corresponding to target voltages in the range 200V to 500V, voltage which determines the argon ion sputtering energy (accelerating voltage minus plasma potential). Calculations show that, in our experimental conditions the kinetic energy of the depositing metallic atoms does not depend on the argon ion sputtering energy but rather on the argon pressure and the target to substrate distance, that have not been modified [4]. The kinetic energy of the metal atoms is thus constant and can be not responsible for the morphology changes. Moreover, the substrate being located far away from the targets, there is no interaction with the sputtering plasma and thus, a modification of the energetic level of the Ar plasma (kinetic energy and flux of energetic species) will not drastically influence the deposition process.

From the literature [2], it appears that a complex relationship exists between crystalline structure and composition. For instance, the presence of copper, which crystallizes into a FCC structure, is found to promote the formation of a FCC solid solution. This is also the case for Co and Ni, whereas, Cr and Fe, crystallizing into BCC structure, induce the formation of a BCC solid solution [1]. However, pure Al having also a FCC structure, leads to the formation of a FCC solid solution if the concentration is below 15 % and a BCC solid solution if the concentration is higher than 15 % [2]. In this study, three film families have been evidenced exhibiting three surface morphologies and main crystalline structures: BCC, FCC solid solutions and a disordered state. The relationship between composition and structure has been evidenced, and general trends have been drawn in good agreement with bulk HEAs. BCC structure seems to be

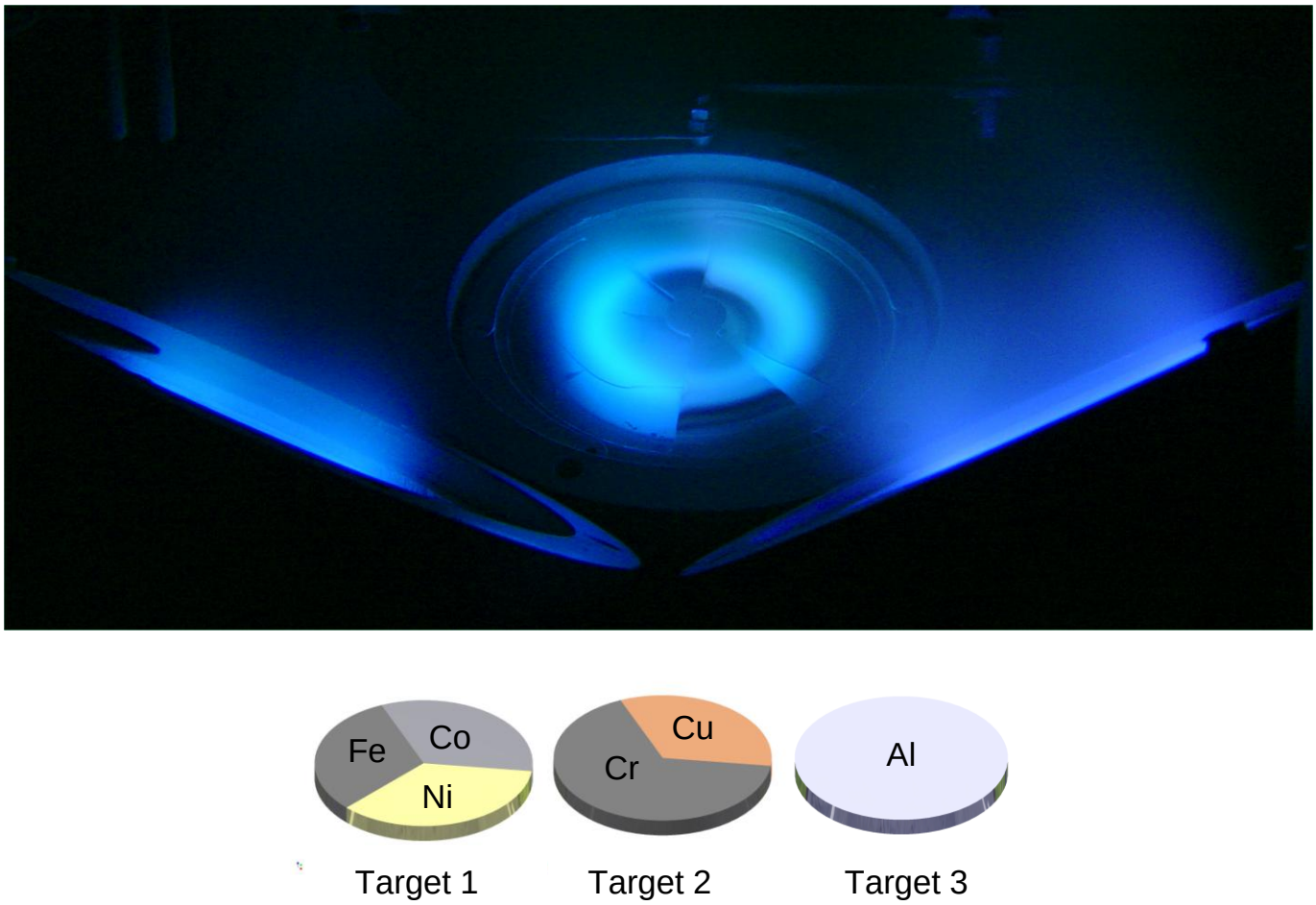

Fig. 1. Plasma characteristics for a magnetron sputtering process to deposit high entropy alloy and the schematic of the three mosaic targets focused on the substrate.

stabilized by the presence of Cr and Al in higher concentrations than the other elements. Low Al contents associated with high Cu, Co and Ni concentrations promote the formation of FCC solid solution. However, it appears that very small variations of the chemical composition can induce lattice distortion and leads to a disordered state, which make difficult anticipation of the structure from the deposition parameters. Moreover, the detection of a single phase by XRD attributed to the HEA, even for films with a chemical composition far from the equimolar one (30% to 50% of one of the elements), indicates that an amorphous phase is formed that coexists with the AlCoCrCuFeNi solid solution. This confirms that the relationship between structure and composition is complex as proved by Yeh et al that has reported two different crystalline structures for a bulk HEA synthesized in the same experimental conditions [5, 6].

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