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# Preparation, structure, and properties of an AlCrMoNbZr high-entropy alloy coating for accident-tolerant fuel cladding

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ABSTRACT

A nearly equal molar ratio AlCrMoNbZr high-entropy alloy (HEA) coating was deposited on N36 zirconium alloy substrates using magnetron co-sputtering technology to enhance the corrosion resistance of light water reactor (LWR) fuel cladding. The microstructure, mechanical properties, surface wettability and corrosion resistance of the AlCrMoNbZr coating were systematically investigated. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses showed that the AlCrMoNbZr HEA coating contained a composite of amorphous and bcc-structured nanocrystals. A nanoindentation test revealed that the coating had a high hardness of 11.8 GPa, and a scratch test indicated that the coating well adhered to the N36 substrate. The contact angle test showed that the static contact angle was 109°, which indicated the good hydrophobic property of the coating. The corrosion measurement showed that the AlCrMoNbZr coating remained effective after it was immersed in static pure water at 360 °C and 18.7 MPa for 30 days, and no N36 substrate oxides formed, which indicated a superior corrosion resistance. Furthermore, the corrosion behaviour of the coating was discussed. The weight gain measurement (8.8 mg/dm$^2$ weight gain) proved that the coating experienced an oxidation process, and during the process, protective $Nb_2Zr_6O_{17}$, $ZrO_2$ and $Cr_2O_3$ formed on the surface of the coating. Hence, the AlCrMoNbZr HEA coating is a potential candidate material for accident-tolerant fuel (ATF) coatings.

## 1. Introduction

In the event of a loss-of-coolant accident (LOCA), Zr alloy claddings will experience severe degradation from rapid oxidation due to high-temperature steam [1]. With intense neutron irradiation damage, the oxidation process of the Zr alloy claddings can be further accelerated [2], which may cause hydrogen explosions and the release of radionuclides. In the past decades, research on the high-temperature oxidation resistance of Zr alloy claddings has elicited a lot of attention, particularly after the Fukushima nuclear accident in March 2011. In 2014, a strategy for accident-tolerant fuel (ATF) was proposed to strengthen the corrosion resistance of Zr alloy claddings under off-normal high temperature conditions or a LOCA [3–5]. One of the most important ATF concepts is to develop a protective coating on the surface of the existing Zr alloy cladding. Several coating materials have been studied, including non-metallic coatings (Si) [6], metallic coatings (Cr, Mo, and FeCrAl) [7–11], and ceramic coatings (SiC, $Ti_2AlC$, TiN, and TiAlN) [12–16]. Although these coating materials exhibit good corrosion resistance in high-temperature steam tests, it remains a challenge to further develop new ATF candidate materials that can withstand the extreme service conditions in a LOCA.

A new alloy, the term “high entropy alloy” was proposed by Yeh [17], about 13 years ago. The definition of high entropy alloy (HEA) can be divided into composition-based definition, entropy-based definition and combining composition-based and entropy-based definitions [18]. For the entropy-based definition, the configurational entropy of mixing per mole could be expressed as $\Delta S = -R\Sigma_{i=1}^{n} c_i \ln c_i$, where R is the gas constant, $c_i$ the molar fraction of the ith element, and n the total number of the constituent elements. Based on the magnitude of entropy, HEA definition separates low ($\Delta S < 0.69$ R), medium ($0.69$ R $< \Delta S < 1.61$ R) and high ($\Delta S > 1.61$ R) entropy alloys. The high mixing entropy effect allows the HEA to easily form disordered solid solutions of single face-centred cubic (fcc) [19,20] or body-centred cubic (bcc) structures [19,20] instead of complex intermetallic

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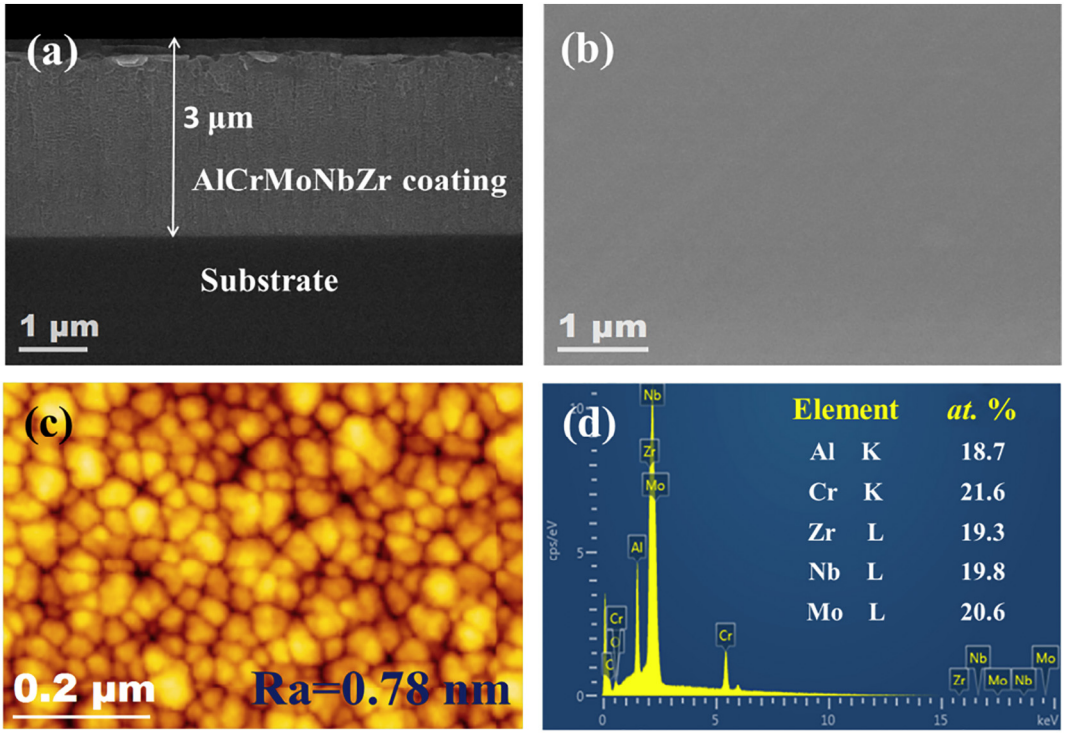


**Fig. 1.** (a) Cross-sectional SEM image of the coating; (b) surface morphology of the coating; (c) surface AFM image of the coating; (d) corresponding EDS spectra.

compounds. The random arrangement of multiple elements in a solid solution creates a particular locally disordered chemical environment [21], which endows the HEA with a high strength/hardness [22], exceptional high-temperature oxidation resistance [23], outstanding wear resistance [24], good radiation resistance [25,26], good corrosion and good oxidation resistance [27–29]. Then, HEA coatings were also developed, which exhibit similar advantages to HEA bulk materials. For example, Zhao et al. prepared the AlCrTiWNbTa HEA coating by magnetron sputtering, which displayed a high hardness of 12.1 GPa [30]. Takeshi Nagase et al. studied the radiation resistance of the CoCrCuFeNi HEA coating and showed that the coating had a high phase stability over a wide temperature range of 298–773 K and could withstand a high damage of 40 displacements per atom (dpa) [31]. The FeAlCuCrCoMn HEA coating exhibited superior corrosion resistance and decreased the corrosion current by 40 times compared to that of 201 stainless steel in salt solutions [32]. Another HEA alloy system, the AlCoCuFeNiV coating, was fabricated by magnetron sputtering with a homogeneous fine grain, and it had a good corrosion-resistant ability in acid, alkali and salt environments [33]. The combined good corrosion and irradiation resistances make HEAs potential candidates for ATF coatings.

In this study, an HEA coating was used as the protective coating for a zirconium alloy cladding. Considering the service environment requirements of coatings, five elements (Al, Cr, Mo, Nb and Zr) were selected to prepare an HEA coating using magnetron co-sputtering technology. The selection of these elements was based on the following unique relationships: (i) these elements have low thermal neutron absorption cross sections, i.e., passivating elements or high melting point elements: Al (0.22 b, 660 °C), Cr (3.05 b, 1850 °C), Mo (2.4 b, 2425 °C), Nb (1.1 b, 2415 °C), and Zr (0.18 b, 1850 °C). (ii) Nb, Mo, and Cr exist in a bcc structure in their entire solid-state range, and Zr has a bcc phase in the high-temperature region; thus, a bcc structure easily forms. The single bcc structure materials have a better resistance to void swelling and low-irradiation-induced chemical separation than multi-phase alloys, and they can be used as structural materials for advance nuclear reactors [34]. (iii) The addition of Zr improves the adhesion between the coating and the N36 substrate. This work mainly focuses on the microstructural, mechanical, wettability and high-temperature corrosion resistance properties under normal conditions (360 °C, 18.7 MPa) of the HEA coating that contains five elements (Al, Cr, Mo, Nb, Zr) and was prepared using co-sputtering technology.

## 2. Experimental

### 2.1. Coating deposition

The AlCrMoNbZr HEA coatings were deposited on N36 Zr alloy (Zr-1Sn-1Nb-0.3Fe in wt%) substrates by magnetron co-sputtering. Five types of single-element metal targets of Al, Cr, Mo, Nb and Zr with a purity of 99.999% were used. Before the deposition, the Zr alloy substrates were first polished to obtain a mirrored surface and ultrasonically cleaned with acetone and ethanol in a bath. Then, the substrates were cleaned with 600 V $Ar^+$ ions for 10 min. As a supplement, a single-crystalline Si substrate was used to structurally characterize the coatings. During the deposition, the base pressure was $2 \times 10^{-4}$ Pa. The samples were placed on a water-cooled copper substrate holder, and the sample holder was rotated at 30 rpm to ensure a uniform thickness. The target-to-substrate distance was 9 cm for all the metal targets. The Ar gas flow rate was fixed at 30 sccm, and the work pressure was maintained at 0.4 Pa by controlling the throttle valve. The sputtering powers of the Al, Cr, Mo, Nb, and Zr targets were 50, 70, 70, 80, and 90 W, respectively, which assured the formation of AlCrMoNbZr coatings with near-equal molar ratios. The deposition time of the coatings was approximately 4 h, which could yield a coating with a thickness of approximately 3 μm.

### 2.2. Coating characterization

The phase structure of the coating was characterized by glancing incidence X-ray diffraction (GIXRD, Empyrean, PANalytical). The surface morphology of the coating was investigated by atomic force microscopy (AFM, MFP-3D-BIO, Asylum Research) and field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL). The microstructure of the coating was analysed by FESEM and spherical