Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Research Article

Effect of atomic structure on preferential oxidation of alloys: amorphous versus crystalline Cu-Zr

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ARTICLE INFO

Article history: Received 20 October 2019 Received in revised form 22 October 2019 Accepted 25 October 2019 Available online 5 November 2019

Keywords: Oxidation Atomic structure Amorphous alloys Cu-Zr HRTEM

ABSTRACT

The effect of structural order in the parent alloy substrate on the oxidation kinetics and oxide phase evolution was investigated for the thermal oxidation of amorphous Cu_{33at.} Zr_{67at.} and crystalline CuZr₂ alloys of identical compositions in the temperature range of 200–250 °C. It was found that, besides the strong preferential oxidation of Zr in both alloys, the lack of structural order in the amorphous Cu_{33at}%Zr_{67at}% alloy results in much slower oxidation kinetics, as well as in distinctly different microstructures of the oxide overgrowth and its Zr-depletion zone in the wake of the ZrO₂ overlayer growth front. The experimental findings can be rationalized on the basis of the strikingly different atomic mobilities of Cu, Zr and dissolved O in the amorphous and crystalline alloys, which also results in different nucleation barriers for crystalline oxide nucleation. The thus obtained knowledge on the underlying oxidation mechanisms provides new and profound insights into the surface engineering of metallic alloys.

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1. Introduction

Spontaneously air-formed (native) and intentionally grown oxide layers on metal and alloy surfaces are known to influence many important surface-related properties and functionalities, such as corrosion resistance, conductivity, wear, biocompatibility. [1-5]. Metal oxides not only possess high thermal and chemical stabilities considering their fully filled s-shells [6], but also own other favorable properties including high dielectric constants, wide bandgaps and fascinating electrical and optical properties, due to their partially filled d-shells [7-9]. Therefore, metal-oxide coatings are widely exploited in protective films [10], and functional devices and related components [11].

The oxidation of crystalline alloys has been intensively studied for centuries [1,2,12,13]; the unraveled oxidation mechanisms [14,15] have shown the important role of defects and grain boundaries (GBs) on the effective oxygen diffusion coefficients in the crystalline alloy and its oxide overlayer. The extended defects (dislocations and GBs) in the parent alloy and the oxide

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overlayer provide so-called short-circuit diffusion pathways for enhanced chemical (inter-)diffusion of the alloy constituents and oxygen species [16]. This implies that the thermal oxidation of an amorphous alloy of given homogenous composition should be principally different from its crystalline counterpart in light of the disordered atomic arrangement and the lack of GBs and other lattice defects.

Very recently, a first comparative oxidation study of amorphous and crystalline Al-Zr alloys was performed [17]. Because of the very similar oxygen affinities of Al and Zr, the preferential (or selective) oxidation of one of the alloy constituents during thermal oxidation could be neglected [13]. Therefore, the crucial role of structural order of the Al-Zr alloy on the oxidation kinetics and the oxide phase evolution could be isolated without any superimposed effects of preferential oxidation. Indeed, it was found that the atomic arrangement of the parent Al-Zr alloy has a strong effect on the oxidation kinetics and developing oxide composition. It is imperative and instructive to develop the comparative study on the thermal oxidation of amorphous and crystalline alloys for a given binary system exhibiting strong preferential oxidation. The Cu-Zr binary system has very different affinities of the two alloy constituents (Cu and Zr) to oxygen [18,19] (see Table 1). Moreover, the Cu-Zr binary system has been intensively studied due to its excel-

https://doi.org/10.1016/i.imst.2019.10.001

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Table 1

Gibbs energies of formation (ΔG_f) at 200–250 °C of corresponding oxide phases (unit: kJ/mol O₂). All necessary thermodynamic data were taken from [18].

Oxide	$\Delta G_{ m f}$ (kJ/mol O ₂) at					
phase	200 ° C	225 °C	250°C			
am-ZrO ₂	-943.3	-939.2	-935.0			
m-ZrO ₂	-1006.1	-1001.4	-996.6			
CuO	-224.5	-220.0	-215.5			
Cu ₂ O	-269.1	-265.3	-261.5			

lent glass forming ability [20–23], and thus is selected as a model alloy system in the present work. The thermal oxidation of amorphous $Cu_{33at,\%}Zr_{67at,\%}$ (designated as am- $Cu_{33at,\%}Zr_{67at,\%}$ below) and crystalline $CuZr_2$ (designated as $c-CuZr_2$ below) alloys has been investigated on a comparative basis by using a combinational experimental approach including X-ray diffraction, Auger electron spectroscopy depth profiling and high-resolution transmission electron microscopy. On this basis, the crucial role of structural order of the parent alloy on the oxidation mechanism (i.e. on the oxidation kinetics and developing oxide microstructure) in preferentially oxidizing binary alloy systems could be disclosed.

2. Experimental

2.1. Specimens preparation and thermal oxidation

Amorphous Cu_{33at.%}Zr_{67at.%} alloy layers with a uniform thickness of ~2 µm (as determined by a Veeco DekTak 8 profilometer) were deposited on Si (100) wafers with an amorphous Si₃N₄ (50 nm)/SiO₂ (50 nm) buffer layer in high-vacuum (base pressure ~5 × 10⁻⁷ Pa) by magnetron co-sputtering [24]. To this end, direct-current (DC) powers of 100 W and 20 W were applied for the co-sputtered Zr (purity 98.5 wt. %) and Cu targets (purity 99.95 wt. %), respectively. The nominal composition of the as-deposited am-Cu_{33at.%}Zr_{67at.%} alloy films was calibrated and verified by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo iCAP 7400). The as-deposited wafers were cut into pieces of 10 × 7 mm² for subsequent thermal oxidation.

Crystalline CuZr₂ ingots were prepared by melting pure Cu (purity 99.9 wt. %) and pure Zr (purity 98 wt. %) under a protective Ar gas atmosphere (purity 99.995 vol. %, 0.4 bar) in a magnetic levitation melting furnace (LGX-5B) over a melting temperature of 1150 °C. To improve the alloy purity and homogeneity, the mixture was melted and slag-removed for four cycles. The as-prepared CuZr₂ ingots were cut into pieces of $10 \times 7 \times 2$ mm³, then polished by a series of SiC (#600-#7000) and diamond (0.5-0.1 µm) abrasive papers, and finally ultrasonically cleaned (in acetone and ethanol) and dried (by compressed gaseous N₂).

The as-deposited am-Cu_{33at.%}Zr_{67at.%} and as-polished c-CuZr₂ pieces were then sealed in quartz tubes for thermal oxidation in a vacuum sealing system (MRVS-3002, Partulab Technology Co. Ltd). Before sealing, O₂ gas (purity 99.999 vol. %) was introduced into the quartz tubes before sealing (base pressure ~1 Pa) to achieve an oxygen partial pressure (p_{O2}) of 1 bar at the investigated oxidation temperature (0.62, 0.59, and 0.56 bar at room temperature corresponding to 1 bar at 200, 225, and 250 °C, respectively). The Cu-Zr alloys sealed in the quartz tubes were isothermally oxidized in a tube furnace (OTF-1200X, Hefei Kejing Materials Technology Co. Ltd.). The thermal oxidations were terminated by quenching in cold water.

2.2. Optical microscopy and X-ray diffraction

The as-polished c-CuZr₂ alloy was corroded by a Kohler reagent ($H_2O:HNO_3:HCI:HF=95:2.5:1.5:1$ vol ratio) for 3 s and

then investigated by optical microscopy (OM) using an Olympus B41 M microscope. The as-deposited/as-polished and oxidized amorphous/crystalline Cu-Zr alloys were investigated by X-ray diffraction (XRD) on a Bruker D8 Advanced diffractometer equipped with a Cu X-ray anode [25]. The scanning range of the diffraction angle 2θ was 10–80°, with a step size of 0.02° and a collection time of 0.15 s/step.

2.3. Auger electron spectroscopy sputter-depth profiling

The oxidized am-Cu33at.%Zr67at.% and c-CuZr2 alloys were investigated by Auger electron spectroscopy (AES) sputter-depth profiling using a ULVAC-PHI 700Xi scanning Auger nanoprobe system (base pressure 5×10^{-7} Pa), equipped with a field-emission electron gun operated with an acceleration voltage of 5 kV. The spectra of the Cu LMM, Zr MNN and O KLL Auger spectra were recorded after each successive 2 kV Ar⁺ ion sputtering step. The sputtering rate was calibrated by sputtering oxide layers with known thicknesses on the Cu-Zr alloys (by TEM, see Section 2.4). The oxidic Zr (Zr^{ox}) and metallic Zr (Zr^{met}) depth profiles were obtained by linear least-squares (LLS) fitting of the corresponding differential AES spectra (MultiPak software, v 9.5.0.8). The quantifications of Zr^{met}, Zr^{ox}, Cu and O were carried out according to the procedure given in Ref. [26]. The determined relative sensitivity factors S with respect to Zr^{met} are: $S_{Zrmet} = 1.000$, $S_{Zrox} = 0.624$, S_{Cu} = 0.408, and S_0 = 1.336, respectively.

2.4. Cross-sectional TEM specimens preparation and TEM analysis

The cross-sectional TEM lamellae of the am-Cu_{33at.\%}Zr_{67at.\%} and c-CuZr₂ alloys oxidized at 250 °C for 10 h were prepared in a focused ion beam (FIB) system (ZEISS Helios FIB/SEM crossbeam). Two protective Pt layers of \sim 200 nm and \sim 1 μ m were deposited on the area of interest by electron beam evaporation and FIB, respectively. The lamellae were cut to a thickness of \sim 1.5 μ m and then removed from the bulk using an in-situ lift-out technique. Next the lamellae were attached to a Cu grid and thinned by 30 kV/80-790 pA Ga⁺ ions, followed by cleaning with 5 kV/14 pA and 2 kV/23 pA Ga⁺ ions. The oxide layers formed on the am-Cu_{33at.}%Zr_{67at.}% and c-CuZr₂ alloys were investigated by high-resolution transmission electron microscopy (HRTEM) using a FEI Tecnai G2 F30 S-TWIN electron microscope equipped with a field emission gun operated at an acceleration voltage of 300 kV. The elemental distributions of specimens were investigated by energy dispersive X-ray spectroscopy (EDX) mapping and line scanning.

3. Results

3.1. Structure of the as-prepared and oxidized alloys by XRD

3.1.1. Amorphous Cu_{33at.%}Zr_{67at.%}

The XRD patterns of the as-deposited and oxidized am-Cu_{33at.%}Zr_{67at.%} alloys are shown in Fig. 1(a). Only a broad intensity hump in the 2 θ range of 31°-43° can be observed in the XRD pattern of the as-deposited am-Cu_{33at.%}Zr_{67at.%} alloy, reflecting its amorphous state (see Fig. 1(a)). Further cross-sectional TEM investigations (see Section 3.3) confirm the nanoscale compositional homogeneity and amorphous state of the alloy. XRD patterns of am-Cu_{33at.%}Zr_{67at.%} alloys oxidized for up to 10 h within the temperature range of 200–250 °C (see Fig. 1(a)) indicate that the am-Cu_{33at.%}Zr_{67at.%} alloy maintains its amorphous state in the studied oxidation temperature range.

3.1.2. Crystalline CuZr₂

XRD analysis of the as-polished c-CuZr₂ alloy confirms that the alloy is composed of single-phase tetragonal CuZr₂ [PDF#18-0466,



Fig. 1. XRD patterns of the as-deposited/as-polished and oxidized (a) am-Cu_{33at.%} Zr_{67at.%} and (b) c- C uZr₂ alloys, and (c) OM image of the as-polished c-CuZr₂ alloy.



Fig. 2. AES depth-profiles of am-Cu_{33at.%}Zr_{67at.%} alloys oxidized at (a) 200 °C, (b) 225 °C, (c) 250 °C for 10 h and c-CuZr₂ alloys oxidized at (d) 200 °C, (e) 225 °C and (f) 250 °C for 10 h.

I4-mmm(139)] (see Fig. 1(b)). OM image of the as-polished c-CuZr₂ alloy (see Fig. 1(c)) indicates the average grain size in the c-CuZr₂ of up to tens of micrometers. Additional reflections at 38.1° and 39.6° , pertaining to the Cu₁₀Zr₇ intermetallic phase [PDF#43-0993, C2ca(41)], emerge after thermal oxidation of the c-CuZr₂ alloy at 200–250 °C (see Fig. 1(b)).

3.2. Compositional distributions of the oxidized Cu-Zr alloys by AES

3.2.1. Amorphous Cu_{33at.%}Zr_{67at.%}

The AES depth profiles of the am- $Cu_{33at,*}Zr_{67at,*}$ alloys oxidized for 10 h at 200–250 °C are shown in Fig. 2(a–c). It follows that the preferential oxidation of Zr has resulted in the selective formation of a ZrO₂ overlayer on the top and a Zr-depleted zone in the alloy below the reaction front (i.e. below the oxide/alloy interface; see below). Moreover, the preferential oxidation of Zr is accompanied by an inward migration of the reaction front, which result in a Cu enrichment in the parent alloy below the reaction front, especially for high oxidation rates (as observed in Ref. [27]).

The estimated thicknesses of the ZrO₂ overlayer (d_{ox}) and the Zr-depleted zone within the alloy ($d_{Zrdepleted}$), as well as the average concentration of dissolved oxygen (c_0) in the interior of the Cu-Zr alloy, are given in Table 2 (as derived from the AES depth-profiling analysis). The grown ZrO₂ overlayers have thicknesses in the range of 5–13 nm. The increasing d_{ox} values after 1, 4 and 10 h of oxidation, indicate the parabolic kinetics of oxidation at 200 $\leq T \leq 250$ °C, which is characteristic for a diffusion-controlled oxidation process. The Zr-depleted zone is, on average, two to three times thicker than the respective ZrO₂ overlayer (i.e. in the range of 20–41 nm). The highest measured Cu/Zr ratio in the Zr-depleted layers is about 1.2. As expected, the concentration of dissolved O in the alloy's interior increases with increasing *T* in the range of 2.8 to 6.9 at.% (see Table 2).

Table 2

Thicknesses of oxide layers (d_{ox}) and Zr-depleted region $(d_{Zrdepleted})$ on the Cu-Zr alloys and concentration of dissolved oxygen in the Cu-Zr alloys (c_0) .

Specimen	Time	d _{ox} ±0.5 (nr	d _{ox} ±0.5 (nm)		d _{Zrdepleted} ±0.5 (nm)		c ₀ ±0.1 (at.%)			
		200 °C	225 °C	250°C	200 °C	225 °C	250°C	200 °C	225 °C	250°C
am-	1 h	5.2	9.6	11.5	14.8	14.0	15.6	2.8	3.9	4.7
	4 h	7.9	11.9	12.3	16.5	14.1	20.1	3.3	4.5	5.5
Cu _{33at.%} Zr _{67at.%}	10 h	10.7	12.6	10.9	21.8	25.8	28.4	4.4	4.9	6.9
c-CuZr ₂	10 h	13.6	16.8	22.5	19.4	24.5	26.3	5.1	5.5	10.2



Fig. 3. (a) Cross-sectional TEM image of am-Cu_{33at %Zr67at %} alloy oxidized at 250 °C for 10 h, (b) HR-TEM and (c) EDX linescan of the surficial region on the oxidized am-Cu_{33at %Zr67at %} alloy.

3.2.2. Crystalline CuZr₂

AES sputter-depth profiling of the oxidized c-CuZr₂ alloys shows a similar compositional depth distribution as in the am-Cu_{33at.%}Zr_{67at.%} alloy: i.e. preferential oxidation of Zr results in the formation of a ZrO₂ overlayer with a relative Cu enrichment (or relative Zr depletion) in the alloy underneath (see Fig. 2(d-f)). However, strikingly, the developing ZrO₂ layers on the c-CuZr₂ alloy are much thicker (i.e. d_{ox} values in the range of 13.5–22.5 nm) than those formed on the am- Cu33at.% Zr67at.% alloy under the same oxidation conditions. Also the concentration of dissolved O in the alloy interior is significantly higher (i.e. c_0 values in the range of 5.1–10.2 at.%) comparing with the am-Cu_{33at.%}Zr_{67at.%} alloy (see Fig. 2 and Table 2). This indicates the rate of oxygen dissolution in the c-CuZr₂ is much faster as compared to the am- Cu_{33at.%}Zr_{67at.%} alloy, which evidently results in a much higher oxidation rate. Consequently, also the Cu enrichment in the alloy below the alloy/oxide interface reaction front is much more pronounced for the oxidation of the c-CuZr₂ alloy (i.e. the Cu/Zr ratio in the Zr-depleted layer is roughly a factor of 2 higher). The thickness of the Zr-depleted zone in the c-CuZr₂ alloy is similar to the thickness of the corresponding ZrO₂ top layer (i.e. in the range of 19.4–26.3 nm; see Fig. 2(d-f) and Table 2): i.e. the ratio $d_{Zr-depleted}/d_{ox}$ is much smaller for the oxidized c-CuZr₂ alloy.

3.3. Microstructure of the oxidized Cu-Zr alloys by cross-sectional TEM

3.3.1. Amorphous Cu_{33at.%}Zr_{67at.%}

The am-Cu_{33at,%}Zr_{67at,%} alloy oxidized at 250 °C for 10 h was investigated by cross-sectional TEM, as shown in Fig. 3. The selected area electron diffraction (SAED) pattern shown in the inset of Fig. 3(a) evidences the amorphous state of the surface region and the bulk of the oxidized am-Cu_{33at,%}Zr_{67at,%} alloy. A homogenous amorphous ZrO₂ layer (designated as am-ZrO₂; thickness ~9 nm, in accordance with the AES measurements) has formed on top of the am-Cu_{33at,%}Zr_{67at,%} alloy, as shown in Fig. 3(a). The roughness of the oxide layer may be ascribed partly to the island-growth of the magnetron-sputtered and deposited am-Cu_{33at.%}Zr_{67at.%} alloy, but possibly also to the non-uniform growth of the oxide layer itself. Notably, many isolated spherical particles with various sizes (diameter: 7–10 nm) are distributed randomly in the Zr-depleted region between the am-ZrO₂ layer and the am-Cu_{33at.%}Zr_{67at.%} alloy substrate (see Fig. 3(a–b)). Fast Fourier transform (FFT) of the corresponding area in HRTEM, as shown in the inset of Fig. 3(b), indicates the amorphous nature of those particles, further confirmed by FFT analyses of 50 particles. EDX linescans (shown in Fig. 3(c)) identify the development of a bilayered microstructure on the oxidized am-Cu_{33at.%}Zr_{67at.%} alloy, consisting of a ZrO₂ overlayer and a Zr-depletion zone with amorphous spherical inclusions.

3.3.2. Crystalline CuZr₂

The c-CuZr₂ alloy oxidized at 250 °C for 10 h was also investigated by cross-sectional TEM, as shown in Fig. 4. The SAED, as shown in the inset of Fig. 4(a), indicates that the substrate is singlephase crystalline CuZr₂. A uniform and homogenous ZrO₂ layer (thickness \sim 17 nm, in accordance with the AES results) has formed on top of the alloy (see Fig. 4). A second continuous and uniform Zrdepleted layer, with a thickness similar to that of the ZrO₂ top layer, is formed between the ZrO₂ layer and the c-CuZr₂ alloy substrate, as shown in Fig. 4(a). Interestingly, the ZrO_2 overlayer is not amorphous (in striking contrast with the amorphous oxide overlayer formed on the am-Cu33at.%Zr67at.% alloy), but constituted of monoclinic ZrO₂ (designated as m-ZrO₂; see FFT analysis in Fig. 4(b-I)). Also the Zr-depleted zone is completely crystalline (i.e. it does not contain amorphous particles as for the oxidized am-Cu_{33at.%}Zr_{67at.%} alloy; see Fig. 4(b)) and consist of Cu₁₀Zr₇ nanograins (see FFT analysis in Fig. 4(b–II)). Moreover, the accumulation of Cu below the oxide/alloy interface is much more pronounced for the same oxidation conditions (as compared to the am-Cu_{33at.%}Zr_{67at.%} alloy). High angle annular dark field (HAADF) combined with cross-sectional EDX elemental analysis (see Fig. 4(c)) confirms the formation of a bilayer structure on the oxidized c-CuZr₂ alloy, consisting of a ZrO₂ overlayer and a crystalline Zr-depletion zone composed of



Fig. 4. (a) Cross-sectional TEM image of c-CuZr₂ alloy oxidized at 250 °C for 10 h, (b) HR-TEM of the oxide layer region (rectangle in (a)), and (c) the corresponding EDX elemental linescan of the surface oxide region.

Cu₁₀Zr₇ nanograins (without any detectable inclusions with a different composition).

4. Discussion

The experimental findings reported in Section 3 show that the thermal oxidation of the am- $Cu_{33at,\%}Zr_{67at,\%}$ and c-CuZr₂ alloys in the temperature range of 200-250 °C proceeding by the preferential oxidation of Zr from the parent alloy, results in the formation of a pure ZrO₂ overlayer. As a result, a Zr-depletion zone is formed in the parent alloy directly beneath the growing ZrO₂ overlayer. Interestingly, three striking differences can be observed between the oxidation behaviours of the crystalline and amorphous Cu-Zr alloys with the same nominal composition of 33 at.% Cu and 67 at.% Zr: First of all, the oxidation kinetics are much slower for the oxidation of the am-Cu_{33at.%}Zr_{67at.%} alloy than for c-CuZr₂ under the same conditions (see Fig. 2 and Table 2). Secondly, the developing ZrO₂ overlayer is amorphous for the oxidation of the am-Cu_{33at,%}Zr_{67at,%} alloy, whereas a crystalline m-ZrO₂ oxide phase is formed on the c-CuZr₂ alloy. Thirdly, the Zr-depletion region consists of isolated amorphous nanoparticles for the oxidation of the am-Cu33at.%Zr67at.% alloy, whereas the Zr-depletion layer is a continuous crystalline layer composed of Cu₁₀Zr₇ nanograins for the oxidation of the c-CuZr₂ alloy. These strikingly different oxidation behaviors for the amorphous and crystalline Cu-Zr alloys with the same nominal composition can be rationalized as follows.

4.1. Oxidation kinetics

The growth of an amorphous or crystalline ZrO₂ layer on a pure Zr metal or a Zr- based alloy surface by thermal oxidation is known to proceed by an O vacancy diffusion mechanism [28,29]. In this case, the oxidation rate is governed by the coupled fluxes of O anions and their vacancies under influence of the chemical potential gradients across the developing ZrO₂ layer. New O vacancies are injected into the ZrO₂ layer at the oxide growth front by continuous dissolution of O into the parent Cu-Zr substrate. The interstitially dissolved O can diffuse and redistribute in the alloy until the solubility product K_{sp} for the formation of ZrO_2 is locally exceeded (i.e. $a_{Zr} \times a_0 > K_{sp}$, where a_{Zr} and a_0 are the activities of Zr and O at a given distance from the oxide growth front [26]). Hence the oxide/alloy interface progressively migrates inwards due to continuous oxide formation in the wake of the oxide growth front [29,30]. Continuous oxide formation in the wake of the growth front will be associated with the expulsion (segregation) of Cu out of the forming ZrO₂ phase. This implies that continuous formation of ZrO₂ in the O-saturated alloy region not only necessitates a certain atomic mobility and critical concentration of interstitially dissolved O in the Cu-Zr alloy, but also requires a certain atomic mobility of Cu in the surrounding Cu-Zr alloy matrix. The resulting oxidation kinetics can thus be rate-limited (or co-determined) by:

- (i) the rate of injection of O vacancies in the developing oxide by continuous dissolution of O from the oxide into the parent alloy substrate. If O dissolution is the slowest step in the oxidation process (i.e. slower than the diffusion of O within the ZrO₂ layer and the combined atomic mobilities of O, Zr and Cu in the parent alloy), the oxidation process would be interface-controlled, resulting in linear oxidation kinetics [17,29].
- (ii) the combined atomic mobilities of O, Zr and Cu in the alloy in the wake of the oxide growth front. If the combined atomic mobilities of O, Zr and Cu are much slower than the O dissolution step and the diffusion of O within the ZrO₂ layer, the oxidation process would be diffusion-controlled, resulting in parabolic oxidation kinetics.

The oxidation kinetics of the am-Cu_{33at.%}Zr_{67at.%} alloy at 200-250 °C practically follows a parabolic oxidation law (see Table 2), in accordance with a diffusion-controlled oxidation process. Previous studies on the thermal oxidation of Cu-Zr-based amorphous alloys at intermediate temperatures of, say, up to 300 °C have also reported parabolic oxidation kinetics [31-38]. Also, at more elevated oxidation temperatures, Cu-Zr crystalline alloys typically exhibit parabolic oxidation kinetics [39,40]. As very recently demonstrated for the thermal oxidation of amorphous Al_{68at.%}Zr_{32at.%} (am- Al_{68at.%}Zr_{32at.%}) and crystalline Al₂Zr (c-Al₂Zr) alloys of similar composition [17], the O dissolution rate and diffusivity of dissolved-O within the alloy both strongly depend on the atomic arrangements in the parent alloy. While O dissolution and diffusion within the alloy are relatively fast for the c-Al₂Zr alloy due to the existence of energetically-favorable interstitial hexahedral and crowdion sites, these processes are suppressed in the amorphous counterpart alloy due to the lack of long-range order. Consequently, the oxidation kinetics of the c-Al₂Zr alloy obeys a fast interface-controlled linear law, distinctively different from the slow parabolic oxidation kinetics of the am-Al_{68at.%}Zr_{32at.%} alloy [17]. Analogously, the tetragonal interstitial sites in the c- CuZr₂ alloy provide well-defined, energetically-favorable interstitial sites for fast O diffusion, which are non-existence in the respective am- $Cu_{33at.\%}Zr_{67at.\%}$ alloy due to the lack of long-range order. Hence O dissolution and diffusion of dissolved-O within the alloy are retarded in the am-Cu_{33at.%}Zr_{67at.%} alloy at the wake of the reaction



Fig. 5. Schematic illustration of structure of thermal oxidized (a) am-Cu_{33at.%}Zr_{67at.%} and (b) c- CuZr₂ alloys.

front, resulting in a much lower steady-state O vacancy concentration at the oxide/alloy interface and thus a lower oxidation rate in comparison to the c-CuZr₂ alloy (see Table 2). Moreover, due to the lack of long-range order, it may be argued that the effective diffusion coefficient of O in am-ZrO₂ is slower than in the m- ZrO₂ layers, as is also the case for amorphous Al₂O₃ and its respective crystalline (α/γ -) Al₂O₃ polymorphs [41,42].

Lee et al. [43] calculated the hydrogen diffusivity $(D_{\rm H})$ in am-Cu33at.%Zr67at.% and c-CuZr2 alloys using molecular dynamics simulations. The calculated $D_{\rm H}s$ at 227 °C are as follows: $1.02\times 10^{-10}\,m^2/s$ for 0.1 at.% H and $1.32\times 10^{-10}\,m^2/s$ for 10 at.% H in the am-Cu_{33at.} $Zr_{67at.}$ alloy, and 5.87 \times 10⁻¹⁰ m²/s for 0.1 at.% H and $9.76 \times 10^{-10} \text{ m}^2/\text{s}$ for 10 at.% H in the c-CuZr₂ alloy [43]. Hence the calculated $D_{\rm H}$ at 227 °C is much lower for the am-Cu_{33at.}%Zr_{67at.}% alloy. Besides, the value of $D_{\rm H}$ strongly increases with increased dissolved-H content in the c- CuZr₂ alloy, while the respective value of $D_{\rm H}$ for the am- Cu_{33at %}Zr_{67at %} alloy is largely unaffected by dissolved-H content. These findings have been attributed to lattice expansion of c-CuZr₂ upon H dissolution, which lowers the migration barrier of H within the c-CuZr₂ alloy and thus enhances the H diffusivity. Notably, a higher H solubility in the crystalline state (as compared to its amorphous polymorph) has also been reported for e.g. Fe-Ti [44]. The concentration of dissolved oxygen (c_0) in c-CuZr₂ is up to 10.2 at.%, which is much higher than that in the am-Cu_{33at.%}Zr_{67at.%} alloy (2.8–6.9 at.%) (see Table 2 and Fig. 2). For the c-CuZr₂ alloy, 10 at.% O atoms only occupy 1/6 of all the Zr₄ tetrahedral sites in c-CuZr₂ [43]. Hence, it may be assumed that, analogously to the study on the hydrogen diffusivity $(D_{\rm H})$ in am-Cu_{33at.%}Zr_{67at.%} and c-CuZr₂ alloys [43], the higher O solubility for the c-CuZr₂ alloy induces an expansion of the intermetallic lattice and thereby enhances the diffusivity of interstitially-dissolved O within the c-CuZr₂ alloy (in comparison to the respective amorphous alloy).

It should be noted that the amorphous samples studied in the present work were prepared by sputtering. The amorphous Cu-Zr alloys can also be prepared by casting or melt spinning considering their good glass forming ability [20]. The cast bulk or the spun ribbon likely has a lower defect density comparing with the sputtered film, which thus should be more corrosion resistant than the crystalline Cu-Zr alloys.

4.2. Oxide structure

Besides the distinct difference in the oxidation kinetics (and O solubility) between the am- $Cu_{3at,*}Zr_{67at,*}$ and c-CuZr₂ alloys, different ZrO₂ polymorphs are formed on the alloy surfaces during thermal oxidation: i.e. amorphous and monoclinic ZrO₂ overlayers are formed on the am- $Cu_{3at,*}Zr_{67at,*}$ and c-CuZr₂ alloys, respectively. This suggests that the lattice expansion of the intermetallic c-CuZr₂ alloy during O-dissolution not only enhances the

O diffusivity, but also lowers the energy barrier for the nucleation of m-ZrO₂. Indeed lattice parameters of a typical oxide unit cell are generally larger than the lattice parameters of the respective parent metal or alloy: i.e. lattice parameters of m-ZrO₂ (a=5.3129 Å, b=5.2125 Å, c=5.1471 Å) are larger than those of $CuZr_2$ (*a*=*b*=3.2204 Å, *c*=11.183 Å) and Zr (*a*=*b*=3.232 Å, *c*=5.147). According to the empirical Ostwald's Rule of Stages [45,46], the oxide phase initially formed on a bare alloy surface by thermal oxidation is not necessarily the most stable one, as preferred by bulk thermodynamics, but can be an intermediate state which is nearest in stability to the original state. Accordingly, from a kinetic point of view, it may be argued that the oxide phase which is most easily derived from a local atomic arrangement of the parent phase (here: the expanded c-CuZr₂ lattice) and its reactants (here: interstitially dissolved O) will form first. From a thermodynamic point of view, a low structural mismatch between a parent and product phase will result in favorable interface energy and thus in a relatively low activation barrier for phase formation according to classical nucleation theory [45,47]. Due to the lack of long range order in the am- Cu_{33at.%}Zr_{67at.%} alloy, specific local atomic rearrangements will be required to nucleate m-ZrO₂, which appears to be kinetically hindered for the moderate oxidation temperatures up to 250 °C, thus resulting in the formation of an amorphous oxide overlayer. Besides, the formation of am-ZrO₂ thin film is preferred at low temperatures due to the negligible misfit-strain and the lower surface and interface energies [48]. Indeed, for the thermal oxidation of c-CuZr₂ alloys, m-ZrO₂ has also been reported to form at higher oxidation temperatures of 500-800 °C [40]. Schematic illustrations of the microstructures of the thermally oxidized am-Cu_{33at.%}Zr_{67at.%} and c-CuZr₂ alloys are shown in Fig. 5.

4.3. Zr-depletion zone and associate bilayered structure

The Zr-depletion zone in the alloy at the wake of the oxide growth front occurs as a result of the selective oxidation of Zr (see Sec. 3). For the oxidized am-Cu_{33at.%}Zr_{67at.%} alloy, the Zr-depleted region is amorphous and has an average composition of Cu_xZr_{1-x} ($x = 0.49 \pm 0.05$) (see Fig. 2(a–c)). This compositional range of the Cu_xZr_{1-x} alloy has a higher thermodynamic (glass-forming) stability [49,50] than the original am-Cu_{33at.%}Zr_{67at.%} alloy. The structural disorder in the am-Cu_{33at.%}Zr_{67at.%} alloy leads to relatively sluggish atomic mobilities of Cu, Zr and dissolved O and thereby a heterogenous chemical composition in the Zr-depleted zone, forming isolated Zr-depleted particles (see Figs. 3 and 5(a)).

For the c-CuZr₂, preferential oxidation of Zr results in a Zrdepletion zone in the alloy with an average composition of Cu_xZr_{1-x} ($x = 0.64 \pm 0.09$) (see Figs. 2(d–f) and 4). According to the binary phase diagram of Cu-Zr system [51], the crystalline phase closest to the resulting alloy composition of Cu_xZr_{1-x} ($x = 0.64 \pm 0.09$) corresponds to the $Cu_{10}Zr_7$ phase. Indeed, the Zr and Cu atomic mobilities are relatively higher in the c-CuZr₂ alloy as compared to that of the am-Cu_{33at.%}Zr_{67at.%} alloy, thus enabling a much higher diffusivity of metallic ions to equalized any compositional (and structural) heterogeneities in the Zr-depletion zone. As a result, a continuous c-Cu₁₀Zr₇ layer with a uniform thickness is formed in the case of the c-CuZr₂ alloy, as shown in Fig. 5(b).

5. Conclusions

- (1) The thermal oxidation of c-CuZr₂ and am-Cu_{33at.%}Zr_{67at.%} alloys have been studied comprehensively on a comparative basis.
- (2) The ion diffusion-controlled oxidation rate of c-CuZr₂ alloy is much higher than that of the am-Cu_{33at.%}Zr_{67at.%} alloy, due to the higher atomic mobilities of the alloy constitutions and of dissolved oxygen in the well-defined, energetically-favorable interstitial sites of the c-CuZr₂ alloy (which are non-existence in the am-Cu_{33at,%}Zr_{67at,%} alloy). The lattice expansion associated with the dissolution of O in the alloy is much larger for the c-CuZr₂ alloy because of the much higher oxygen solubility, which further enhances the diffusivity of the interstitially-dissolved oxygen in the parent alloy during oxidation (thereby enhancing the oxidation rate).
- (3) The ZrO₂ layer formed on top of am-Cu_{33at %} $Zr_{67at \%}$ alloy by selective oxidation of Zr is fully amorphous, because the nucleation of a crystalline oxide phase is hindered by the high structural mismatch between the parent and product phases. A crystalline m-ZrO₂ layer is formed on top of the c-CuZr₂ alloy, since the enhanced O-dissolution is associated with an expansion of the alloy in the wake of the oxide growth front, which not only increases the O diffusivity but also reduces the barrier for nucleation of m-ZrO₂.
- (4) Amorphous Zr-depleted particles are formed between the top am-ZrO₂ layer and the am- $Cu_{0.33}Zr_{0.67}$ alloy due to the enhanced thermodynamic (glass-forming) stability of amorphous state in the Zr-depletion zone (as compared to the am-Cu_{33at.%}Zr_{67at.%} alloy; i.e. ΔG_f (Zr-depleted) < ΔG_f (am-Cu_{33at.%}Zr_{67at.%})) in combination with a relatively sluggish atomic diffusion in the am- $Cu_{0.33}Zr_{0.67}$ alloy. In contrast, a continuous crystalline $Cu_{10}Zr_7$ layer is formed between the top m-ZrO₂ layer and the cryst-CuZr₂ alloy, as aided by the relatively high atomic mobilities of Zr, Cu and dissolved O in the c-CuZr₂ alloy.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51571148) and the National Key Research and Development Program of China (No. 2017YFE0302600).

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