

## Selective Oxidation of Zirconium in $Zr_2Cu^*$

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The high-temperature oxidation of  $Zr_2Cu$  in dry oxygen is characterized by selective oxidation of zirconium. The excess of copper is accumulated in the matrix alloy at the alloy-oxide interface forming the  $Zr_8Cu_5$  phase. The oxide layer consists of monoclinic  $ZrO_2$  and a small amount of  $CuO$ . Additionally, tetragonal  $ZrO_2$  appears up to 873 K at the surface, and  $Cu_2O$  is formed above 873 K, deeper in the oxide layer. The reaction kinetics obeys a parabolic rate law. An activation energy of 54.4 kJ/mol has been estimated in the temperature range 773–1123 K. An anomalous decrease of the oxidation rate occurs at 1155–1223 K, after a strong reaction at 1073–1150 K.

*Key words:* corrosion, oxidation, alloys,  $Zr_2Cu$ , high temperature, selective.

### INTRODUCTION

The oxidation behaviour of zirconium-copper alloys at high temperatures has been studied by several investigators.<sup>1–5</sup> Tests were performed with crystalline zirconium alloys containing 0.5–4.0% copper<sup>1–3,5</sup> or 0.5–15.0% (mass fractions) copper<sup>4</sup> in oxygen<sup>1</sup> and carbon dioxide<sup>2–5</sup> and with the amorphous  $Zr_{40}Cu_{60}$  alloy in laboratory air at room temperature.<sup>6</sup> Preferential oxidation of zirconium was found to occur in carbon dioxide<sup>2–5</sup> and in air<sup>6</sup>, resulting in an unusual oxidation product consisting of monoclinic

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\* Dedicated to Professor Boris Kamenar on the occasion of his 70<sup>th</sup> birthday.

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ZrO<sub>2</sub> and elementary copper.<sup>3,4,6</sup> Corrosion investigations were initiated since Zr-Cu alloys had been considered as potential fuel element cladding materials for nuclear power reactors.<sup>2-5</sup> Recent interest in the catalytic activity of Zr-Cu alloys for the oxidation of carbon monoxide,<sup>7</sup> properties of the Zr-Cu amorphous alloys<sup>8</sup> and the Zr-Cu metallic glasses<sup>9</sup> necessitates further oxidation tests.

To ensure successful detection and identification of reaction products, a well known compound with ordered structure, Zr<sub>2</sub>Cu, has been chosen for the investigation of the oxidation behaviour at high temperatures in oxygen by means of thermogravimetry, electron microscopy and X-ray diffraction analysis.

Among the phases in the Zr-Cu phase system, Zr<sub>2</sub>Cu is the intermetallic compound with the highest content of zirconium. The Zr<sub>2</sub>Cu phase is known to appear in two modifications, both of which belong to tetragonal MoSi<sub>2</sub>-type structures.<sup>10</sup> The bct MoSi<sub>2</sub>-type structure (space group I4/*mmm*) reported in the literature<sup>11</sup> is the high-temperature modification, Zr<sub>2</sub>Cu<sub>(h)</sub>, which is stable between  $\approx 1200$  K and the melting point  $\approx 1273$  K,<sup>10</sup> with lattice parameters  $a = 0.32204$  nm and  $c = 1.11832$  nm.<sup>11</sup> The low-temperature phase modification, Zr<sub>2</sub>Cu<sub>(l)</sub>, stable below  $\approx 1200$  K, is a super-structure of Zr<sub>2</sub>Cu<sub>(h)</sub>; its diffraction pattern can be indexed on the basis of primitive tetragonal unit cell with lattice parameters  $a = 1.592$  nm and  $c = 1.132$  nm.<sup>10</sup>

## EXPERIMENTAL

Zr<sub>2</sub>Cu samples with a mass of about 5 g each were prepared from the constituent elements. Appropriate amounts of zirconium crystal bar (purity 99.95%), produced by the van Arkel-de Boer hot wire process, and copper shot (purity 99.9%) were melted together using a non-consumable arc melting technique in a water-cooled copper mould under argon gettered by titanium (pressure 50 kPa). The prepared buttons were turned over and three times remelted to improve homogeneity. They were further homogenized at 1073 K in evacuated quartz tubes for a week. X-ray powder diffraction analysis showed that the as-cast alloy consisted of the high-temperature modification of Zr<sub>2</sub>Cu while the alloy homogenized at 1073 K consisted of the low-temperature modification. The buttons were then cut into small sheets of dimensions 6 mm  $\times$  4 mm  $\times$  1 mm. After grinding, they were polished using a diamond paste.

Oxidation of the specimens was performed in a stream of dry oxygen at atmospheric pressure and at a constant heating rate of 0.3 K/min up to 1373 K, or isothermally in the temperature range 773–1273 K. Oxygen absorption was monitored using a recording thermobalance.

The phase composition of the reaction products were examined using a Philips X-ray diffractometer with proportional counter and monochromatized Cu-K $\alpha$  radia-

tion. The oxidized surfaces of the specimens were ground several times and subsequently reexamined by X-ray diffraction analysis in order to examine deeper regions of the oxide layer and subscale regions of the specimens.

The concentration profiles of zirconium, copper and oxygen on cross-sections of oxidized specimens were examined by means of energy dispersive X-ray spectrometry (EDS).

## RESULTS

### *Thermogravimetry*

Oxidation experiments at elevated temperatures (heating rate 0.3 K/min) revealed the beginning of a measurable oxygen absorption by  $Zr_2Cu$  at 673 K. The initial oxidation process was slow, up to 820 K, followed by a progressive increase of oxygen consumption up to 1073 K, at which temperature an intensive oxygen absorption began.

After this strong reaction, however, an anomalous decrease of the oxidation rate took place in the temperature interval 1155–1223 K. Thereafter, the reaction rate increased again.

The dark oxide layer consisted of monoclinic  $ZrO_2$  and  $CuO$ . Only 60% of the theoretically necessary amount of oxygen for total oxidation of  $Zr_2Cu$  into  $ZrO_2 + CuO$  was consumed up to 1373 K, which was the temperature limit of the experiment, for 60 hours. The liquid interior of the specimen above the melting point of  $Zr_2Cu$ ,  $\approx 1273$  K, was retained in the oxide shell. The specimen that was oxidized up to 1373 K was cracked and swollen, but not disintegrated.

Using the Coats-Redfern method<sup>12</sup> of evaluating the activation energy from thermogravimetric data at elevated temperatures, a value of  $54.0 \pm 0.2$  kJ/mol was estimated for the activation energy of the  $Zr_2Cu$  oxidation in the temperature range 773–1123 K.

The isothermal oxidation of  $Zr_2Cu$  was examined in the temperature range 773–1273 K in a stream of dry oxygen at atmospheric pressure for 24 hours. The mass gain-time curves are shown in Figure 1. It has been estimated that the oxidation process obeys a parabolic rate law at temperatures of: 773, 873, 973 and 1173 K for 24 hours. However, reactions at 1073 and 1123 K proceeded from the beginning according to the parabolic rate law too, but later, after 6 and 3 hours, respectively, the reaction rate increased, exhibiting breakaway phenomena due to cracks in the oxide layer that enabled oxygen to penetrate the unoxidized regions of the specimens more easily.

In contrast, oxidation at 1273 K showed an unexpected decrease of the reaction rate 3 hours after the start of the parabolic process, probably owing

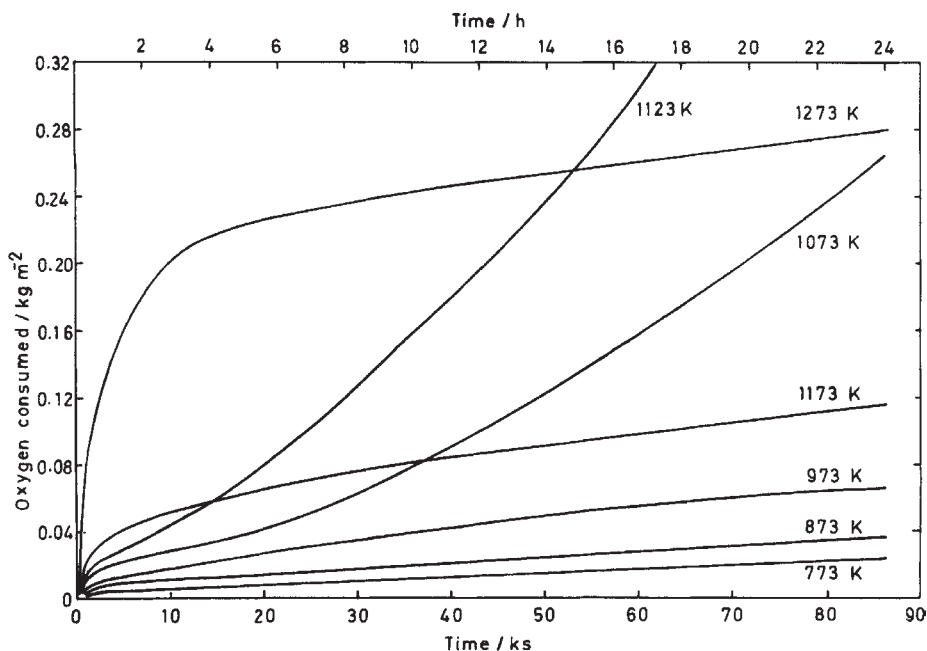


Figure 1. Typical mass gain-time curves for the isothermal oxidation of  $Zr_2Cu$  in a stream of dry oxygen at atmospheric pressure for 24 hours.

to a displacement reaction between reaction products and an alloy component.

The parabolic rate law, based on diffusion as the rate determining process, can be described by the equation:

$$y^2 = k_p t + A \quad (1)$$

where  $y$  denotes the amount of consumed oxygen in kilograms per square meter,  $t$  is time in seconds,  $k_p$  ( $kg^2 m^{-4} s^{-1}$ ) is the parabolic rate constant and  $A$  is the integration constant.

The values of the parabolic rate constant,  $k_p$ , computed using the least-squares method, together with the oxide thickness and the phase composition of the oxide layer at relevant temperatures are given in Table I. The parabolic rate constant at 1173 K has a lower value than that at 1123 K, reflecting the anomalous decrease of the reaction rate at 1155–1223 K, found in the oxidation at elevated temperatures.

Using the Arrhenius equation for the temperature dependence of the oxidation rate constant:

$$k_p = k_0 \exp(-E_a/RT) \quad (2)$$

where  $E_a$  is the activation energy,  $R$  is the gas constant,  $T$  the absolute temperature and  $k_0$  the preexponential factor; the activation energy is determined by plotting  $\log k_p$  as a function of  $1/T$ .

TABLE I

Selected data for the oxidation of  $Zr_2Cu$  at high temperatures in a stream of dry oxygen at atmospheric pressure for 24 hours

$\frac{T}{K}$	$\frac{\delta}{\mu m}$	$\frac{k_p}{kg^2 m^{-4} s^{-1}}$	Composition of the oxide layer			
			surface phases		depth phase	
773	6	$1.202 \times 10^{-8}$	$ZrO_2(t) \ll$	$ZrO_2(m) >$	CuO	—
873	25	$1.609 \times 10^{-8}$	$ZrO_2(t) \ll$	$ZrO_2(m) >$	CuO	$Cu_2O$
973	65	$5.456 \times 10^{-8}$		$ZrO_2(m) >$	CuO	$Cu_2O$
1073	180–380	$7.673 \times 10^{-8}$		$ZrO_2(m)$	CuO	$Cu_2O$
1123	230–450	$1.806 \times 10^{-7}$		$ZrO_2(m)$	CuO	$Cu_2O$
1173	65–75	$1.483 \times 10^{-7}$	Pref. orient.	$ZrO_2(m) \gg$	CuO	$Cu_2O$
1273	90–160	$5.182 \times 10^{-6}$		$ZrO_2(m) \gg$	CuO	$Cu_2O$

$T$ : temperature,

$\delta$ : thickness of the oxide layer,

$k_p$ : parabolic rate constant.

The activation energy,  $E_a = 54.4 \pm 0.4$  kJ/mol, has been estimated for the oxidation of  $Zr_2Cu$  in the temperature interval 773–1123 K. This value agrees with the value of the activation energy found for the oxidation at elevated temperatures by the Coats-Redfern method ( $E_a = 54.0 \pm 0.2$  kJ/mol).

### X-ray Analysis

X-ray powder diffraction analysis showed that the oxide layer consisted mainly of the monoclinic modification of  $ZrO_2$  and a small amount of CuO in the whole experimental temperature range. The tetragonal modification of  $ZrO_2$  appeared at the surface of the oxide layer, *i.e.* first formed, at the temperatures of 773 and 873 K (Table I).

An oxide layer consisting of monoclinic  $ZrO_2$  with preferentially oriented crystallites and small amounts of CuO and  $Cu_2O$  was formed at 1173 K, at which temperature the anomalous decrease of the reaction rate took place. The surface of this oxide layer was covered by the monoclinic phase of  $ZrO_2$  with randomly oriented crystallites (thickness about 20  $\mu m$ ).

Successive grinding and reexamination by X-ray diffraction of oxidized specimens revealed the  $\text{Cu}_2\text{O}$  phase deeper in the oxide layer, closer to the oxide-alloy interface, and a decrease of the  $\text{CuO}$  amount at 873 K and higher temperatures.

$\text{Zr}_8\text{Cu}_5$ , a phase with a higher copper concentration than that in the matrix alloy,  $\text{Zr}_2\text{Cu}$ , was detected at the oxide-alloy interface. The excess of copper, as a consequence of preferential or selective oxidation of zirconium, accumulated in the  $\text{Zr}_2\text{Cu}$  phase close to the oxide layer forming the  $\text{Zr}_8\text{Cu}_5$  phase. The region with this phase is particularly broad in the samples oxidized at 1173 K.

The porous oxide scales at 1073 and 1123 K consisted of monoclinic  $\text{ZrO}_2$  and an increased amount of  $\text{CuO}$ .

### *Electron Microanalysis*

Electron microanalysis was performed on the cross-sections of oxidized specimens. The concentration profiles of zirconium and copper obtained by EDS on the specimens oxidized at different temperatures are shown in Figure 2. Concentration profiles of oxygen have been omitted to save space.

It is seen that the concentration of copper is very low in the oxide layer (left side of the diagrams). Close to the oxide-alloy interface, the copper concentration is increased and the zirconium concentration is correspondingly decreased. This region is especially wide ( $\approx 80 \mu\text{m}$ ) in the specimens oxidized at 1173 K (Figure 2e and Figure 4), where the oxide layer consists of the preferentially oriented crystallites of monoclinic  $\text{ZrO}_2$ . X-ray diffraction analysis showed that this region of increased copper concentration consisted of the  $\text{Zr}_8\text{Cu}_5$  phase. When zirconium was preferentially oxidized, excess of copper was accumulated in the  $\text{Zr}_2\text{Cu}$  phase at the oxide-alloy interface forming the  $\text{Zr}_8\text{Cu}_5$  phase.

Oxide layers are generally compact and adherent, except for the scales at 1073 and 1123 K, which are very porous (Figure 3). This porosity is manifested in the strong change of the concentration of copper and zirconium, as seen in Figure 2d.

The thickness of the oxide layer increases with temperature (Table I and Figure 2). The thickness of the porous oxide layers at 1073 and 1123 K varies greatly: from 180–380  $\mu\text{m}$  at 1073 K to 230–450  $\mu\text{m}$  at 1123 K.

The concentration of copper in the oxide layer at 1273 K is progressively increased (with a simultaneous decrease of the oxygen concentration) along the distance of 50  $\mu\text{m}$  close to the oxide-alloy interface, resulting in an increase of the  $\text{Cu}_2\text{O}$  amount (Figure 2f).

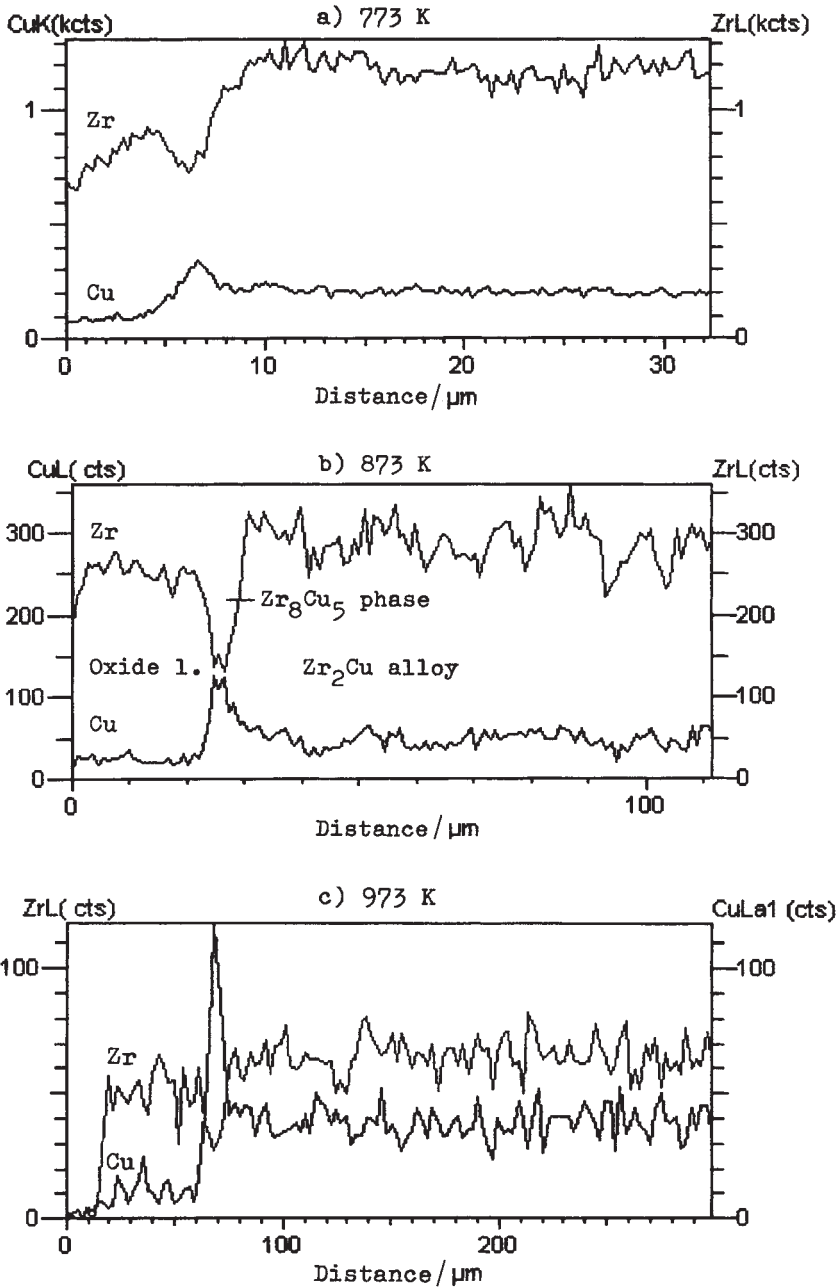
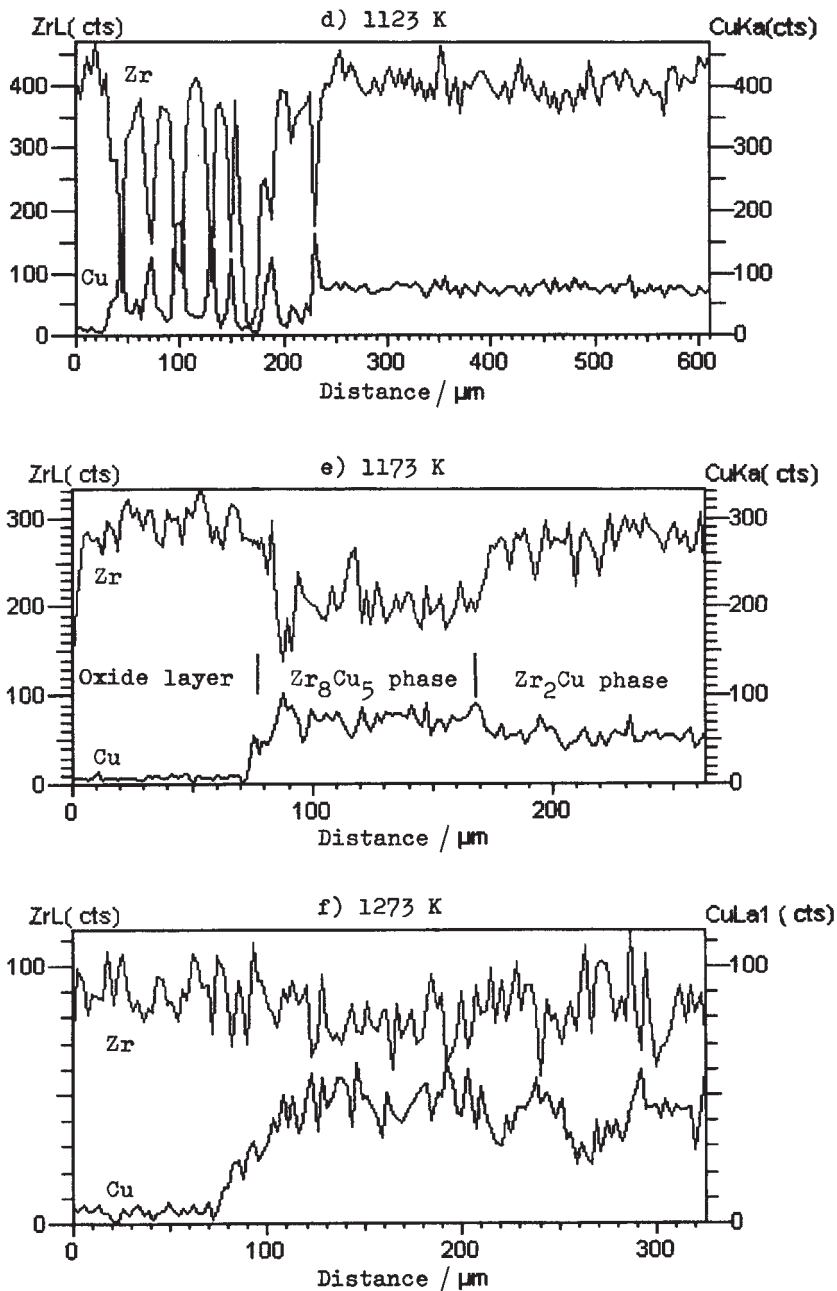


Figure 2. Scanning concentration profiles of zirconium (upper line) and copper (lower line) across the oxide layer (left) and the  $Zr_2Cu$  alloy oxidized in dry oxygen for 24 hours at the temperatures of: a) 773 K, b) 873 K and c) 973 K, obtained by energy dispersive X-ray spectrometry. (Continued; 2d, 2e, 2f on the next page.)



(Figure 2, cont.) Scanning concentration profiles of zirconium (upper line) and copper (lower line) across the oxide layer (left) and the  $\text{Zr}_2\text{Cu}$  alloy oxidized in dry oxygen for 24 hours at the temperatures of: d) 1123 K, e) 1173 K and f) 1273 K, obtained by energy dispersive X-ray spectrometry.



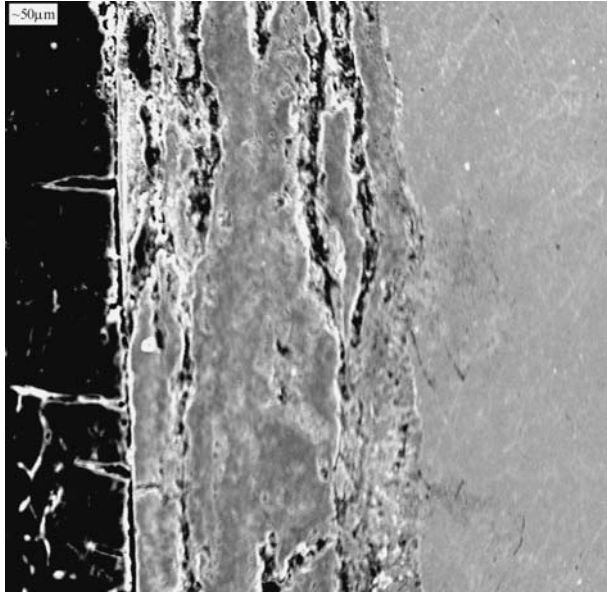


Figure 3. Scanning electron micrograph of the cross-section of the  $Zr_2Cu$  specimen oxidized in dry oxygen at 1073 K for 24 hours. The porous oxide layer is formed.

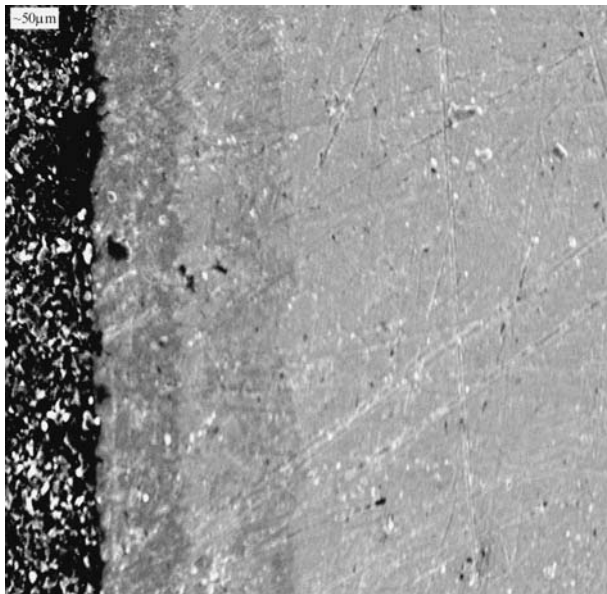


Figure 4. Scanning electron micrograph of the cross-section of the  $Zr_2Cu$  sample oxidized in dry oxygen at 1173 K for 24 hours. The middle dark zone between the compact oxide layer (left) and the  $Zr_2Cu$  alloy is the  $Zr_8Cu_5$  phase.

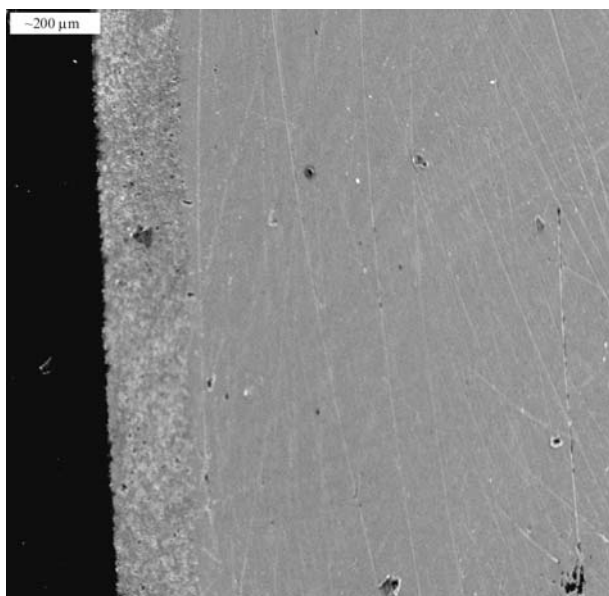


Figure 5. Scanning electron micrograph of the cross-section of the  $Zr_2Cu$  specimen oxidized in dry oxygen at 1273 K for 24 hours. The formed oxide scale is compact and adherent.

## DISCUSSION

According to electron microanalysis and X-ray powder diffraction analysis, the oxide layer consists of  $ZrO_2$  and small amounts of  $CuO$  and  $Cu_2O$ . During the reaction of  $Zr_2Cu$  with oxygen, zirconium is preferentially oxidized to  $ZrO_2$ . Excess of copper is accumulated in the matrix alloy at the alloy-oxide interface forming  $Zr_8Cu_5$ , an alloy with a higher copper concentration than in the  $Zr_2Cu$  phase. According to the Wagner theory of selective oxidation,<sup>13-16</sup> in which the least noble constituent of the alloy is selectively or preferentially oxidized, zirconium is less noble and copper more noble in the  $Zr_2Cu$  alloy. A similar phenomenon was observed in the high-temperature oxidation of Zr-Al alloys<sup>17</sup> where zirconium was selectively oxidized too and aluminium was accumulated in the matrix phase near the oxide alloy interface forming there the adjoining phases in the phase diagram Zr-Al, having higher aluminium concentration than the matrix alloy.

In general, the components of alloys have different affinities for oxygen, and the reacting atoms do not diffuse at the same rates either in the oxide or the alloy phases. As a result, oxide scales on alloys will not contain the same relative amounts of alloy constituents as does the alloy phase.

The thickness of the oxide layers increases with temperature for equal durations of oxidation. Due to compressive strain at a certain oxide thickness, these oxide scales crack and become porous. The cracks enable oxygen to penetrate the unoxidized regions of the specimen more easily, causing the reaction to proceed at a faster rate. The oxide layers formed for 24 hours at the temperatures of: 773, 873 and 973 K are compact and adherent. The scales at higher temperatures, 1073 K and particularly 1123 K, are cracked, very porous and non protective. This is understandable. However, the oxide layers at even higher temperatures, 1173 and 1273 K, are unexpectedly compact and protective again. At the same time, the oxidation rate is decreased (at 1173 K) or decreases after the rapid initial process (at 1273 K).

As a rule, high-temperature parabolic oxidation signifies that a thermal diffusion process is rate-determining. Studies of diffusion in metals<sup>18</sup> have indicated that, as an approximate rule, the activation energy for grain boundary diffusion is about half of that for lattice diffusion.

The low activation energy of 54.4 kJ/mol in the temperature range 773–1123 K suggests that the grain boundary diffusion is the predominant, rate determining process in the oxidation of  $Zr_2Cu$ .

It may be stated qualitatively that grain boundaries represent regions of lattice mismatch and disorder that cause enhanced diffusion. The grain boundary is assumed to be a narrow region having a high rate of diffusion, as compared to the adjacent grains. The material moves rapidly along the grain boundary and simultaneously also diffuses into the grains from the grain boundary by lattice or volume diffusion. Diffusion along grain boundaries depends on the grain size and boundary orientation. At small orientation differences,  $\theta < 10^\circ$ , the grain boundary diffusion approaches and equals volume diffusion, but at higher values of grain boundary diffusion increases with misorientation.<sup>18</sup>

In the case of the preferred orientation of crystallites, very small orientation differences are conceivable.

The adherent compact oxide layer on  $Zr_2Cu$  at 1173 K consisted of preferentially oriented monoclinic  $ZrO_2$  and small amounts of  $CuO$  and  $Cu_2O$ . The  $ZrO_2$  crystallites in the interior of the oxide scale were oriented in such a way that their  $\{011\}$  planes were parallel to the surface of the specimen sheet. While the intensities of the X-ray diffraction lines of the randomly oriented crystallites of monoclinic  $ZrO_2$  are related as:  $I_{(11\bar{1})} : I_{(011)} : I_{(022)} = 100 : 18 : 18$ ,<sup>19</sup> the intensities of the reflections from  $ZrO_2$  obtained on the  $Zr_2Cu$  sheet oxidized at 1173 K, and produced by rotating about an axis normal to its face, were related as:  $I_{(11\bar{1})} : I_{(011)} : I_{(022)} \approx 18 : 33 : 100$ .

The preferred orientation of the oxide grains might effect the »transformation« from grain boundary diffusion to volume diffusion and thus the de-

crease of the reaction rate. The parabolic rate constant at 1173 K had a lower value than that at 1123 K (Table I). Taking into account the oxidation examination at elevated temperatures and the observed anomalous decrease of the oxidation rate in the temperature interval 1155–1223 K, it might be stated that preferred orientation of the crystallites of monoclinic  $\text{ZrO}_2$  predominated in the temperature range 1155–1223 K. This preferred orientation might be caused by the phase transformation of the low-temperature modification of  $\text{Zr}_2\text{Cu}$  to the high-temperature modification.<sup>10</sup>

The relative oxide growth rate and the thickness of the layers are determined by the relative diffusion rate through the layers. The oxide layers at 1073 K and 1123 K were thicker than that at 1173 K (Table I) because of the quicker oxide growth, as a consequence of the grain boundary diffusion. Due to compressive strain, at a certain oxide thickness, these oxide scales cracked, thus leading to the breakaway oxidation 6 and 3 hours after the beginning of the reactions at 1073 K and 1123 K, respectively (Figure 1). The cracks enable oxygen to penetrate the unoxidized regions of the specimens more easily, causing the oxidation to proceed at a higher rate. One would expect that the breakaway oxidation at higher temperatures would arise earlier, but there were no breakaway phenomena at 1173 K and 1273 K.

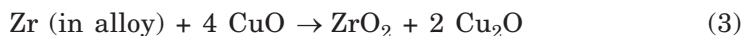
In contrast, the reaction rate at 1273 K decreased suddenly 3 hours after the beginning of the parabolic oxidation (Figure 1). Dissociation of  $\text{CuO}$  could not be the cause of the reaction rate decrease because  $\text{CuO}$  did not decompose below 1299 K in air and 1370 K in oxygen.<sup>20</sup> The process which slowed down the reaction rate might be a displacement reaction between the reaction products and an alloy component. Taking into account the free energy of formation at 1273 K:

$$\Delta_f G^\circ (\text{ZrO}_2) = -854.60 \text{ kJ/mol}^{21}$$

$$\Delta_f G^\circ (\text{Cu}_2\text{O}) = -71.13 \text{ kJ/mol}^{22}$$

$$\Delta_f G^\circ (\text{CuO}) = -41.01 \text{ kJ/mol}^{23}$$

it is seen that the free energy of formation of  $\text{ZrO}_2$  is less than the free energy of formation of  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ . Therefore, one would expect that two reactions could proceed toward the formation of zirconium dioxide:



Since no free copper was found in the oxide scale, the reaction (3) is more probable. A similar effect was found in the oxidation of some Cu-Zn alloys.<sup>24</sup>

It is evident from the present examinations that poor resistivity of  $Zr_2Cu$  against oxidation is in the temperature range 1073–1150 K, and surprisingly better resistivity occurs at higher temperatures, 1155–1223 K, and even at 1273 K.

## CONCLUSION

Essentially, the high-temperature oxidation of  $Zr_2Cu$  in dry oxygen is characterized by preferential or selective oxidation of zirconium and by an anomalous decrease of the reaction rate in the temperature interval 1155–1223 K.

Zirconium as a less noble metal is oxidized preferentially giving  $ZrO_2$ , and excess copper is accumulated in the matrix alloy at the oxide-alloy interface forming there  $Zr_8Cu_5$ . Copper is only partly oxidized, contributing small amounts of  $CuO$  and  $Cu_2O$  into the oxide scale. The main component of the oxide scale is monoclinic  $ZrO_2$ . Tetragonal  $ZrO_2$  appears at the surface of the oxide scale, *i.e.* first-formed, up to 873 K and  $Cu_2O$  is formed in the interior of the oxide layer closer to the oxide-alloy interface. The oxide layer is compact and adherent except at the temperatures 1073–1123 K.

The reaction kinetics obeys a parabolic rate law followed by an increase of the reaction rate, breakaway, at 1073 K and 1123 K due to cracks created in the oxide layer, and by a decrease of the reaction rate at 1273 K due to a displacement reaction.

An activation energy of 54.4 kJ/mol has been estimated in the temperature interval 773–1123 K. Such a low activation energy suggests that grain boundary diffusion is the rate-determining process.

An anomalous decrease of the oxidation rate takes place in the temperature range 1155–1223 K due to preferred orientation of the crystallites of monoclinic  $ZrO_2$  forming a compact and protective oxide layer.

Poor oxidation resistivity of  $Zr_2Cu$  was found in the temperature interval 1073–1150 K, and surprisingly good resistivity was observed in the temperature range 1155–1223 K.

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## SAŽETAK

### Selektivna oksidacija cirkonija u $Zr_2Cu$

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Visokotemperaturnu oksidaciju  $Zr_2Cu$  u suhom kisiku karakterizira selektivna oksidacija cirkonija. Preostali se bakar nakuplja ispod oksidnog sloja na rubu slitine u obliku faze  $Zr_3Cu_5$ . Oksidni se sloj sastoji pretežito od monoklinskog  $ZrO_2$  i male količine  $CuO$ . Na površini oksidnog sloja do temperature od 873 K pojavljuje se tetragonski  $ZrO_2$ , a iznad 873 K u dubini oksidnog sloja nastaje i  $Cu_2O$ . Kinetiku oksidacije opisuje parabolična funkcija. Energija aktivacije od 54,4 kJ/mol određena je u temperaturnom području od 773–1123 K. Nakon jake reakcije pri temperaturi od 1073–1150 K slijedi neobičan pad brzine oksidacije u temperaturnom području od 1155–1223 K.