

OXYGEN DIFFUSION IN THE NON-EVAPORABLE GETTER St 707 DURING HEAT TREATMENT

DIFUZIJA KISIKA V GETRU St 707 MED TOPLOTNO OBDELAVO

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The oxygen diffusion and microstructure were investigated in specimens of commercial Non Evaporable Getter under the trademark of St 707, which is an alloy of Zr(70)-V(24.6)-Fe(5.4) using EDS, AES and XRD. Specimens were in the form of tablets compressed from St 707 powder of typical particle size from 50 μm to 100 μm . To obtain an observable amount of oxygen in the bulk material, we loaded the getter specimen at 450 °C at oxygen partial pressure of $1.2 \cdot 10^{-4}$ Pa for 1 h. Using AES and EDS we investigated the distribution of oxygen in different phases of the alloy. From the concentration profile, we can see the considerable diffusion length of the oxygen into the getter. This diffusion length is much larger in the Laves phase compared to the zirconium phase. On the zirconium phase two different layers are formed, an oxide layer composed of ZrO_2 followed by a diffusion layer, while on the Laves phase only a diffusion layer can be found. In this paper, we also determined the phases present in our materials, as well as the changes of these phases after oxidation.

Keywords: diffusion, oxidation layer, getter, zirconium, Laves phase

Preučevali smo mikrostrukturo in difuzijo kisika v neuparljivih getrih St 707 (zlitina Zr(70)-V(24,6)-Fe(5,4)) z metodami EDS, AES in XRD. Preizkušanci so bili v obliki stisnjenih tablet z značilno velikostjo delcev med 50 μm in 100 μm . Pri temperaturi 450 °C smo preizkušance izpostavili kisiku pri tlaku $1.2 \cdot 10^{-4}$ Pa za 1 h. Z metodami AES in EDS smo opazili različno povečanje vsebnosti kisika v različnih fazah zlitine. Iz koncentracijskega profila je razvidna velika difuzijska dolžina za kisik v getrskem materialu. V Lavesovih fazah opazimo znatno daljšo difuzijsko dolžino kot v cirkonijevi fazi. Na površini cirkonijeve faze smo našli dve različni plasti. Na vrhu je oksidna plast ZrO_2 , ki ji sledi difuzijska plast. V Lavesovih fazah pa najdemo le difuzijsko plast. Prav tako smo ugotovili fazno sestavo materiala in spremembe zaradi oksidacije.

Ključne besede: difuzija, plast oksidacije, geter, cirkonij, Lavesove faze

1 INTRODUCTION

Getters are solid materials capable of chemisorbing gas molecules to their surface: getters are chemical pumps. Non-evaporable getters are applied in vacuum systems where a very low partial pressure of hydrogen is required, e.g., in ultra-high-vacuum (UHV) chambers⁸. Because they exhibit selective pumping, they are also used for inert-gas purification. In general, getters are classified into two main groups: evaporated getters (EGs) and non-evaporated getters (NEGs). During the handling of NEGs under usual ambient conditions their surface becomes covered with a passive layer consisting mainly of chemisorbed oxygen and carbon. But a surface phenomenon is not the only characteristic of NEGs. This passive layer must be eliminated to start the gettering action and the metal surface is less oxidized after O_2 exposure to high temperatures than at low temperatures, because the oxygen diffuses from the surface into the bulk⁷. The process of activation of the getter is described in^{1,5,11,12}. Lately, getters have found widespread application in various fields, such as ultra-high-vacuum systems of particle accelerators, sealed vacuum devices such as vacuum tubes, and field emission displays. In this study (St 707) non-evaporable getter material has been investigated. Techniques such as Energy-Dispersive Spectroscopy (EDS), Auger Electron Spectroscopy

(AES) and X-Ray Diffraction (XRD) were used for the material characterization.

2 EXPERIMENTAL

Our specimen is an alloy with mass fractions of Zr(70)-V(24.6)-Fe(5.4) %. In the typical procedure, specimens were prepared through grinding and polishing, and then immersing in an ultrasonic bath with alcohol for cleaning. Then the specimens were inserted into the test chamber (CH2), **Figure 1**. Then we pumped the gases out of the CH2 (through the turbomolecular pump) until the pressure in the vacuum chamber reached 10^{-7} mbar. Afterwards, the specimen was heated for activation, and simultaneously the temperature was measured by a thermocouple attached to CH2. In the experiment the specimen surface was exposed to the given partial pressure of test gas at elevated temperature. The sources of the test gases are gas cylinders. When desired temperature was reached, the regulating valve was opened and the gas (in our case pure oxygen) is permitted to flow into the system. Opening of the regulating valve was controlled to reach the pressure of $1.2 \cdot 10^{-4}$ Pa in the CH2, while, the temperature was 450 °C. The specimen was treated at this conditions, for a time of one hour. During this treatment the diffusion of

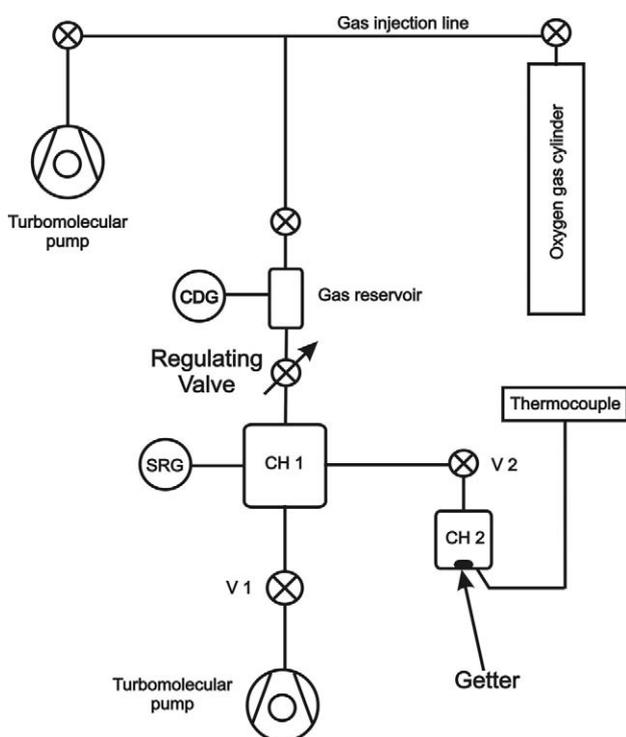


Figure 1: Experimental setup of the vacuum system. SRG is Spinning Rotor Gauge, CDG is Capacitance Diaphragm Gauge.

Slika 1: Eksperimentalna postavitev vakuumskega sistema. SRG je viskoznoštni vakuumski merilnik in CDG kapacitivni membranski merilnik.

O₂ into the specimen started. The purity of the oxygen admitted to the getter sample was better than 99.99 %.

The investigation of the diffusion depth of oxygen was performed using SEM and AES with different accelerating voltages and different magnifications. The crystal structures of the obtained specimen were characterized by powder X-ray diffraction (XRD). The specimens were characterized in both the as-received and oxidized states.

3 RESULTS

3.1 EDS analyses

The compositions of the constituents of the as-received St 707 specimen and after their oxidation in the vacuum system were investigated by EDS. The results of the EDS investigations are summarized in **Table 1** and **Figures 2a** and **3a**. The specimen in the as-received state contained particles which consisted of two different compositions of zirconium-rich phase and Laves phase, as can be seen from **Figure 2a**. Areas rich in zirconium are surrounded by those with which vanadium is the major component. It was found that iron is present only in the vanadium-rich areas². According to **Figure 2** and **Figure 3**, the bright areas in the secondary electron images could be assigned to areas rich in elemental zirconium, whereas the dark ones indicate the dominance of the Laves phase.

When the getter is exposed to air, it absorbs oxygen and the gases present in the atmosphere. As consequence, a layer is formed at its surface which prevents further adsorption. For further use of the getter it should be activated, which is achieved through increasing the temperature. For this reason, a small amount of oxygen will be found in the "as-received" getter, **Figures 2a** and **3a**. The presence of oxygen in the "as-received" specimen is barely noticeable compared to the oxygen presence in the oxidized specimen **Figures 2b** and **3b**, and **Table 1**. Also in the "as-received" specimen the presence of oxygen is almost similar in all phases, the zirconium-rich phase and the Laves phase.

From the EDS spectra as well as the EDS elemental mapping images of the as-received getter material it is obvious that the amount of oxygen is almost the same in

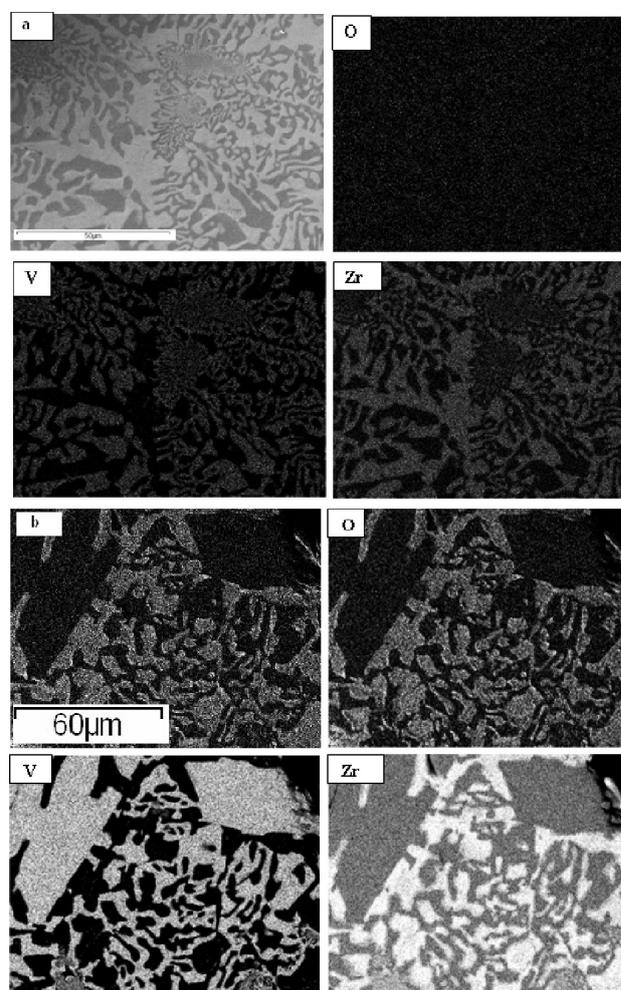


Figure 2: (a) Secondary-electron image of a polished surface of the as-received St 707 specimen and element distribution images for O, V, and Zr. (b) Secondary-electron image of a polished surface of the oxidized specimen St 707 at temperature $T = 450$ °C, pressure $P = 1.2 \cdot 10^{-4}$ Pa, and time $t = 1$ h and the element distribution images for O, V, and Zr

Slika 2: (a) Polirana površina preizkušanca St 707 in porazdelitev elementov O, V in Zr. (b) Polirana površina oksidirane preizkušanca St 707 pri temperaturi $T = 450$ °C, tlaku $P = 1.2 \cdot 10^{-4}$ Pa za čas $t = 1$ h ter porazdelitev elementov O, V in Zr

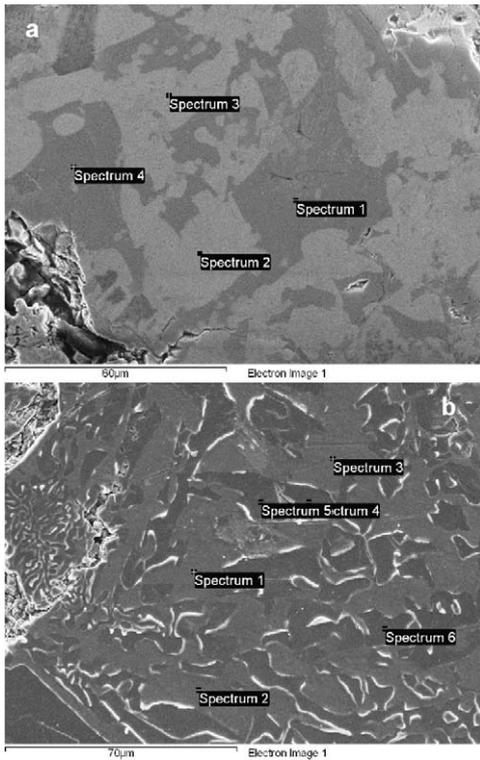


Figure 3: EDS analyses: a) as-received specimen, the presence of oxygen is almost the same in both phases b) EDS analyses for "oxidized" specimen in different phases, oxygen is more present in the zirconium than in the Laves phase

Slika 3: EDS-analize: a) začetni material, kjer je vsebnost kisika v obeh fazah podobna, b) pri oksidiranem preizkušancu je vsebnost kisika v zirkonski fazi večja kot v Lavesovi.

Table 1: Composition of "as-received" specimen and "oxidized" specimen using EDS

Tabela 1: Sestava začetnega in oksidiranega preizkušanca

	O	V	Fe	Zr	Total
Spectrum "as-received" specimen					
Spectrum 1	13.32	45.28	9.31	32.09	100
Spectrum 2	14.94	4.93	0.00	80.12	100
Spectrum 3	12.52	8.99	0.00	78.48	100
Spectrum 4	18.82	42.07	8.99	30.12	100
Spectrum "oxidized" specimen					
Spectrum 1	59.75	4.47	0.00	35.78	100
Spectrum 2	60.99	0.45	0.00	38.56	100
Spectrum 3	60.48	1.81	0.00	37.70	100
Spectrum 4	19.29	40.69	9.07	30.95	100
Spectrum 5	16.46	41.41	9.85	32.28	100
Spectrum 6	0.00	51.88	10.86	37.25	100

both phases, the zirconium-rich phase and the Laves phase **Figure 2a**. On the other hand, through the same techniques we observed a larger oxygen content in the zirconium-rich phase compared to the Laves phase (**Figure 2b**). Also from **Figure 3** and **Table 1** it is evident that there is more oxygen in the zirconium-rich phase than in the Laves phase. The spectrums 1, 2, 3 are of the zirconium-rich phase and spectrums 4, 5, 6 are of the Laves phase. Measured oxygen concentration in spectrums 1, 2 and 3 of oxidized specimen is close to 60%. This happened due to the fact that close to 500 °C

the formation of ZrO₂ bond occurs ² and also the solubility values indicate that metals of the 4th group (in our case zirconium) have higher storage capacities for oxygen than those of the 5th group (V), or, putting it another way, that hcp crystalline structures have in general higher storage capacities than the bcc ones ¹¹.

3.2 AES analyses

The surface of the getter materials is particularly difficult to analyze because of their high chemical reactivity. The results obtained can, therefore, be strongly influenced by the experimental set-up and the procedures ^{3,4}, as recently confirmed through our measurements. The AES results are also compared with complementary

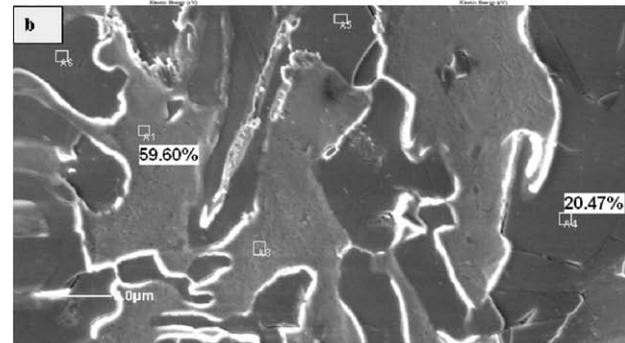
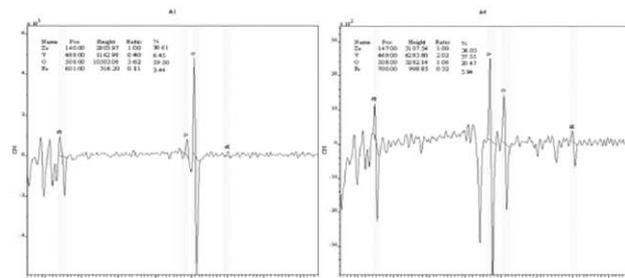
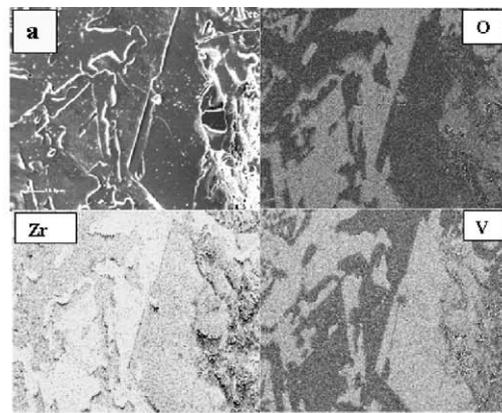


Figure 4: (a) Two-dimensional element distribution images for O, V, and Zr by Auger Electron Spectroscopy on a polished surface of the oxidized St 707 alloy, (b) AES analyses for "oxidized" specimen in different phases, more oxygen is present in Zr (spectrum A1-59.50 %) than in the Laves phase (spectrum A4-20.47 %)

Slika 4: (a) AES ploskovna porazdelitev elementov O, V in Zr na polirani površini oksidiranega St 707 (b) AES točkovna analiza oksidiranega preizkušanca v različnih fazah, kjer je razvidno, da je v Zr-fazi povečana koncentracija kisika glede na Lavesovo fazo.

EDS measurements. The results from the AES, **Figure 4**, are similar to those obtained with EDS, **Figure 3**. Again, we can observe that oxygen is more present in the Zr-rich phase than in the Laves phase. From **Figure 4** we see that the presence of oxygen in atomic percent (in the depth 41 nm) in the Zr (spectrum 1) is 59.50 %, and in the Laves phase (spectrum 4) is 20.47 %. Also, from mapping, a larger oxygen content in Zr compared to the Laves phase (**Figure 4a**) was observed. In addition, a larger amount of oxygen in the grain boundary and grain particles is observable, because the grain boundaries, as dislocations, are considered as short-circuits for atomic diffusion in metals ¹¹.

AES depth profiling measurements were made at some points of the specimen in order to be able to estimate the penetration depth of the oxygen within the getter, concretely for the zirconium-rich phase, (**Figure 5a**) and the Laves phase (**Figure 5b**). This measurement technique makes it possible to distinguish the oxidized zone (the presence of ZrO₂) and the diffused zone (the zone where oxygen is inserted). Because of the formation of ZrO₂ chemical bond in the zirconium-rich phase there is the presence of the oxidized layer. This oxidized layer is absent in the Laves phase. On the other hand, the thickness of the diffused layers is higher for the Laves phase compared to the zirconium-rich phase.

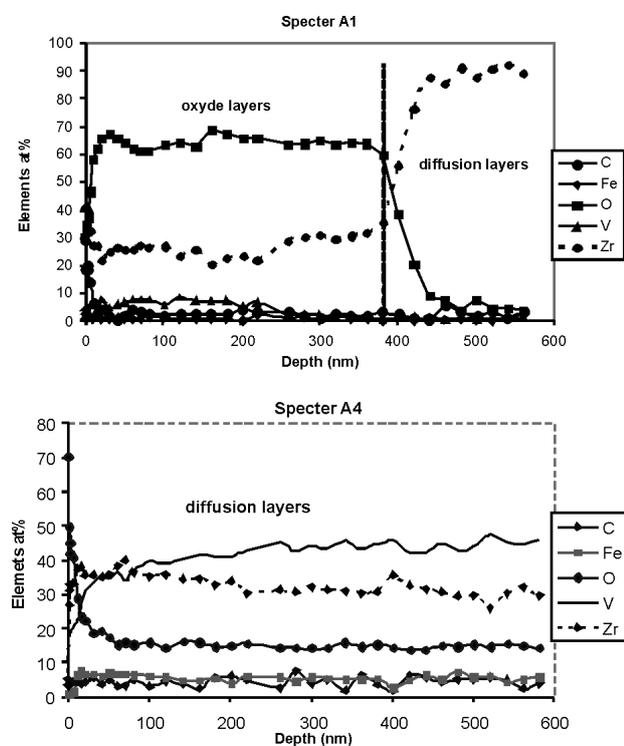


Figure 5: AES depth profiles for a) Zr phase and b) Laves phase at 450 °C for 60 min

Slika 5: AES globinski profil za a) Zr-fazo ter b) Lavesovo fazo. Preizkušane je bil oksidiran pri temperaturi 450 °C, 60 minut.

3.3 X-ray diffraction analysis

XRD analyses were carried out in order to determine the phases present in the materials. We confirmed that the as-received alloy is biphasic at room temperature (300 K), consisting of hexagonal α -Zr and the cubic Laves phase Zr(V_{1-x}Fe_x)₂ as shown in **Figure 6a** and indicated in references ^{2,10}. We can see in **Figure 6b** that for the sample treated at 450 °C under oxygen partial pressure of $1.2 \cdot 10^{-4}$ Pa the intensity of the Laves phase will decrease and, at the same time, a new phase of ZrO₂ will emerge. This new phase comes as consequence of ZrO₂ bond formation at high temperatures. The ZrO₂ has a monoclinic structure. The as-received specimen exhibits narrower XRD peaks, while with the oxidized specimen a certain broadening of the peaks (mainly Laves phase) due to lattice strains and distortions can be observed.

4 DISCUSSION

The diffusion length during the time t at temperature T is given by ¹³:

$$L = \sqrt{D(t) \cdot t}$$

where L/cm is the thickness, $D/(cm^2 s^{-1})$ is the diffusion coefficient and t/s is the time. The diffusion coefficient (or diffusivity) in the metal at temperature T is:

$$D = D_0(t) \cdot \exp\left(-\frac{E}{RT}\right)$$

D_0 is a constant, E is the activation energy for diffusion, and R is the universal gas constant. In the literature ¹⁵ we have found following values for hexagonal α -Zr (mean of two data): $D_0 = 0.21 \text{ cm}^2/\text{s}$ and $E = 184.1 \text{ kJmol}^{-1}\text{K}^{-1}$, and for cubic V: $D_0 = 0.013 \text{ cm}^2/\text{s}$ and $E = 121.3 \text{ kJmol}^{-1}\text{K}^{-1}$. Using these values we get for Zr: $D(T = 723 \text{ K}) = 1.3 \cdot 10^{-14} \text{ cm}^2/\text{s}$ and for V: $D(T = 723 \text{ K}) = 2.6 \cdot 10^{-11} \text{ cm}^2/\text{s}$.

The corresponding diffusion lengths for 1 h treatment at 450 °C are 70 nm for Zr and 3050 nm for V. We can

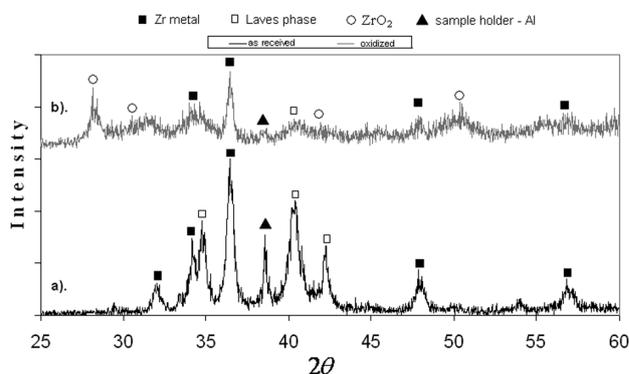


Figure 6: X-Ray diffraction spectra: a) as-received specimen, b) oxidized specimen at 450 °C for 1 h

Slika 6: XRD-spektri: a) začetni preizkušaneec, b) oksidiran preizkušaneec pri temperaturi 450 °C in času 1 h

see from **Figure 5a** that in the diffusion layer in Zr the drop of oxygen concentration from 66 % to nearly zero occurs in approximately 100 nm. Because of almost 50 times larger diffusion length in V we can not see in **Figure 5b** a considerable change of oxygen concentration in Laves phase over the investigated depth of 600 nm.

The data for the diffusivity and the solubility limit from the literature give us a global view about the diffusivity and solubility limit in single-crystal pure metals. However, the NEG materials under investigation are alloys. The diffusivity and the solubility-limit values that can be found in the literature are valid for single crystals, so they are not very helpful to evaluate the diffusivity and the solubility limit in the case of alloy. It is known that the diffusivity and the solubility limit increase in the presence of grain boundaries. From the literature we find that metals of the 5th group (in our case vanadium) have a higher diffusivity for oxygen than elements of the 4th (in our case zirconium) group, whereas the solubility limit values indicate that metals of the 4th group (Zr) have higher storage capacities for oxygen than those of the 5th group¹¹. This can be clearly seen from the results of our measurements, which are presented in **Figure 5**. There are two layers in the zirconium-rich phase, the first one is the oxidized layer, and the second is the diffused layer. On the other hand, in the Laves phase there is only the diffused layer. The appearance of the oxidized layer in the zirconium-rich phase is the consequence of the affinity of Zr to form chemical bonds with O₂ at elevated temperatures. As a consequence of the composition of ZrO₂, the presence of oxygen in the zirconium-rich phase in mole fractions (%) can be twice that of the zirconium atoms at most, which is evident in **Figure 5a**. By increasing the temperature or time of oxidation, we will observe an increase in the thickness of the oxidized layer, whereas the structure of diffused layer will remain similar. Thus we have a saturation of the zirconium-rich phase with oxygen in the oxidized layer. On the other hand, in the Laves phase the oxidized layer practically does not exist. Only the diffused layer is present there, which is in accordance with theory¹¹. According to theory, the elements of the 5th group have a greater affinity for oxygen diffusion compared to those of the 4th group, whereas the solubility in these elements is quite small.

5 CONCLUSION

According to the results reported in this paper, it can be stated that:

- The XRD together with EDS and AES confirms that the as-received alloy is biphasic.
- The hexagonal zirconium and cubic Laves phases coexist in this material.
- The presence of oxygen in the oxidized specimens is more observable in the zirconium than in the Laves phase, whereas in the as-received specimen, the

presence of oxygen is almost the same in both phases.

- XRD analysis of the sample oxidised at 450 °C showed a decrease in the intensity of the Laves phase reflections and the formation of ZrO₂ was indicated.
- With AES depth profiling it is possible to determine the size of the zones affected by the oxygen. The presence of the oxide layer composed of the ZrO₂ was confirmed on the Zr phase.

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