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Getter potentialities of some intermetallics: $ZrAl_2$, $ZrAl_3$ and $CeNi_5$

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Abstract

The oxidation kinetics of single phases $ZrAl_2$, $ZrAl_3$ and $CeNi_5$ have been studied as a function of temperature and fugacity of oxygen to investigate the getter potentialities of these intermetallics. These measurements have been performed using a technique developed in our laboratory for measuring the kinetics of very low oxygen ($\geq 10^{-9}$ moles) consumption by a given sample. Powder samples of $ZrAl_2$ and $ZrAl_3$ were thermally cycled first at 8 ppm (0.8 Pa) of oxygen then at 90 ppm (9 Pa). Each cycle was performed with a soak at 1063 K; the results of oxygen consumption rate and the actual oxygen consumption show that $ZrAl_2$ has greater reactivity when compared to $ZrAl_3$. Furthermore, $ZrAl_2$ becomes reactive at lower temperatures (320°C). Small pieces of $CeNi_5$ were studied at 6 ppm (0.6 Pa) of oxygen. More than one isotherm was performed during each experiment to investigate the oxygen consumption of the intermetallic as a function of temperature. Oxygen consumption data and the relatively low reaction temperature (>300°C) show good potentialities as getter of this intermetallic. In particular, the decrease of the oxygen content in the gas mixture was found to be five orders of magnitude, producing a minimum oxygen partial pressure of 2×10^{-6} Pa in the Ar stream for several hours.

Keywords: Getter; Intermetallics; Aluminides; Oxidation

1. Introduction

There are several high-technology applications and laboratory operations which require a very neutral gas environment or UHV conditions. In both cases, the use of a getter material is still the most adequate way to achieve the high quality performances required. Since the beginning of the vacuum tube era, getters have been used to overcome the difficulty at that time to attain satisfactory low pressures. When the vacuum technology improved, getters continued to be utilized to remove residual gases produced, for instance, in outgassing of the device and/or to preserving on time the physico–chemical properties of the surfaces in order to maintain the electronic characteristics of the device.

Metals and alloys have been particularly used as getters for a long time, some alloys are patent commercial products and more recently the intermetallic compounds also have been considered for the same purpose.

While the literature concerning the reactivity of intermetallics to hydrogen is wide and abudant and it covers theoretical [1], experimental and application aspects [2], unfortunately only a very limited literature concerns the whole field of the reactivity of intermetallics to oxygen [3] and other oxidising species. In the area of our interest, the field becomes even more restricted due to the specific experimental conditions in which the reactivity should be studied: very low partial pressures and temperatures as low as possible down to the room temperature. All this requires dedicated on line analysis systems with very low detection limits such as the apparatus designed and realized in our laboratory.

In the framework of an Italian National Research Project entitled 'Alloys and Intermetallic Compounds: Thermodynamic Stability, Physical Properties and Reactivity' our group, in collaboration with the Professor Ferro group at the University of Genoa, has been recently involved in the study of the reactivity of some intermetallics, especially oxygen, at partial pressures and temperatures in the appropriate ranges for the application of the intermetallics as getters.

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Table 1
Main features of the experimental apparatus

Operating temperature (°C)	25–1500
Operating pressure (bar)	1–3
O_2 partial pressure range (Pa)	Up to 20[a]
Sensitivity at 700°C ($mVPa^{-1}$)[b]	42(0.5)–1(20)
Noise (μV)	≈50
Detection limit (as O_2 consumed) (mol)	1×10^{-9}
Detection limit (as O_2 change rate) (mol s^{-1})	$\approx1\times10^{-11}$
In situ resistivity measurements	4×4 relays matrix
by van der Pauw method	PC controlled
Flow rate (sccm)	1–50
Data acquisition	On-line multichannel

[a] The lowest value is fixed by the O_2 content in the carrier gas.

[b] Values in brackets are the oxygen partial pressure values in Pa.

2. Experimental

The technique, based on the measure of the kinetics of oxygen consumption by the sample, has been successfully utilized for the oxidation study of various forms of carbon [4] and metal refractory carbides [5–9]. The sample is placed in the reaction chamber at a given temperature in the range from 25 to 1500°C and exposed to a flux of a gas mixture at 1 bar in which the range for oxygen partial pressure can be set from 0.1 mPa to 20 Pa. Both the oxygen partial pressure in the gas mixture and the reactivity of the sample to oxygen are measured through the emf of solid electrolyte oxygen sensors. A detailed description of the apparatus is reported elsewhere [5,8]. The main characteristics of the system are reported in Table 1.

Three intermetallic compounds were studied: $ZrAl_2$, $ZrAl_3$ and $CeNi_5$. The first two compounds are two out of eight of the intermetallic phases belonging to the Zr–Al system and they are the ones richest in Al. Both the intermetallics, as pellets obtained by isostatic pressing at 2500 atm of the stoichiometric powder mixture, were prepared by self-sustaining high-temperature synthesis (SHS) in high purity Ar. The starting powders Zr (>98%) and Al (99.8%) were used as received. Their dimensions were in the range from 20 to 40 μm. X-ray diffraction (XRD) revealed the features of ZrO_2 as major impurity. Due to the preparation technique both the intermetallics appear as coarse powders.

$CeNi_5$ has been prepared by melting the metals using an RF furnace maintained at 500°C for 15 days then quenched in water. The product prepared was found as a single phase by metallographic microscopy and XRD. The scanning electron microscopic (SEM) microanalysis confirmed the expected composition Ni 83at.% and Ce 17at.%. Samples used were small grains of a few milligrams.

3. Results

Data reported below on zirconium aluminides refer to a typical set of experiments each one based on thermal cycles between room temperature and 790°C. In each cycle, the temperature reaches the maximum value at the rate of 2°C/min and it holds that value for 3 h then decreases rapidly up to the room temperature. At the beginning of the experiment, the oxygen partial pressure (OPP) in the Ar stream is maintained at 0.8 Pa (O_2 impurity in the Ar bottle used) and, after some thermal cycles in these conditions, the OPP is changed at 9 Pa by using the computer controlled mixing system of the experimental apparatus. Throughout the experiments the flow-rate of the Ar stream has been fixed at 35 sccm (standard cubic centimeter per min; 1 sccm$=1.6667\times10^{-8}$ m^3 s^{-1} at 273 K and 1 bar).

Fig. 1 shows the typical behavior observed for both aluminides when exposed to the two selected values of OPP. The mass of samples of $ZrAl_2$ and $ZrAl_3$ were, respectively, 28.94±0.01 mg (1.99×10^{-4} moles) and 10.92±0.01 mg (6.34×10^{-5} moles). Depending on cycling, the temperature at which the gettering action of the aluminide becomes detectable, the minimum temperature of the getter activity (MTGA), changes as reported in Fig. 2. We define the getter capacity, G_c, as the ratio of the moles of O_2 consumed to the moles of O_2 consumable assuming the stoichiometric formation of both the oxides ZrO_2 and Al_2O_3. The quantity G_c calculated in a whole experiment is reported in Fig. 3 for both aluminides. The figures pointed by the arrows are the OPP values. The oxygen partial pressure in the gas stream after the reaction with getter, OPP_g, is also an important parameter to consider in evaluating the gettering properties of the material under study. Fig. 4 shows the OPP_g quantity

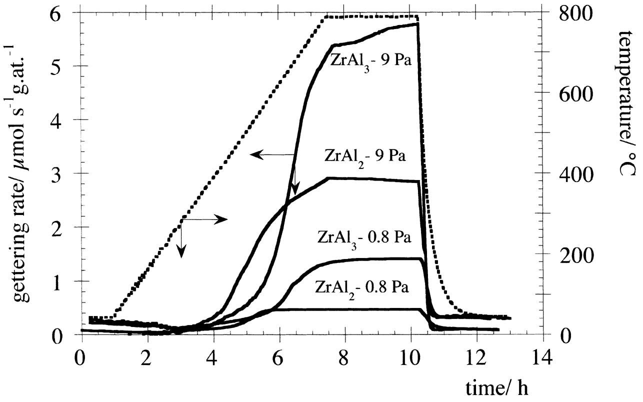

Fig. 1. Left ordinate: specific O_2 gettering rate in a thermal cycle for $ZrAl_2$ and $ZrAl_3$. Right ordinate: thermal cycle.

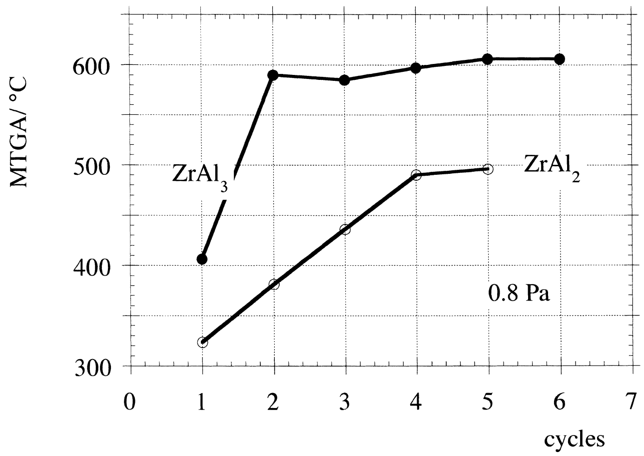

Fig. 2. Minimum temperature of the getter activity (MTGA), as function of the number of the thermal cycles for both the aluminides exposed at $P_{O_2} = 0.8$ Pa.

recorded along the isotherms in whole experiments with both the aluminides.

The behavior of $CeNi_5$ is shown in Fig. 5. In panel A, left ordinate, the integral quantity of O_2 gettered by the sample is compared with the integrated quantity of oxygen, carried by the Ar stream, passed in the reaction chamber during the whole experiment. The measured final quantity of gettered oxygen is compared with the weight change (1.71 mg) of the sample found at the end of the experiment. The agreement between these two quantities, which were independently measured, is excellent. During the experiment some changes in the Ar stream flow-rate have been performed in order to testing the dependency of the gettering rate (see below). On the right ordinate of the same panel A is reported the temperature path followed in the experiment. The procedure was to increase the temperature only when the OPP_g became too high as shown in the right ordinate of the panel C. Both the specific gettering rate and the specific gettered O_2 are reported in panel B, respectively, in the left and right ordinate. The sample mass in this experiment was 16.69 mg corre-

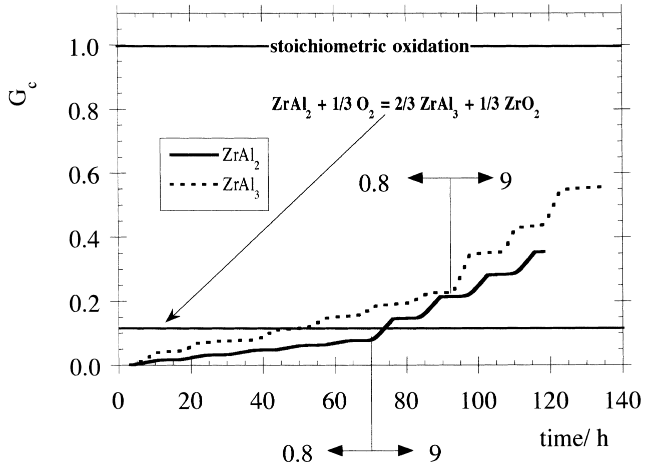

Fig. 3. Getter capacity as a function of time. The figures pointed by the arrows are the P_{O_2} values.

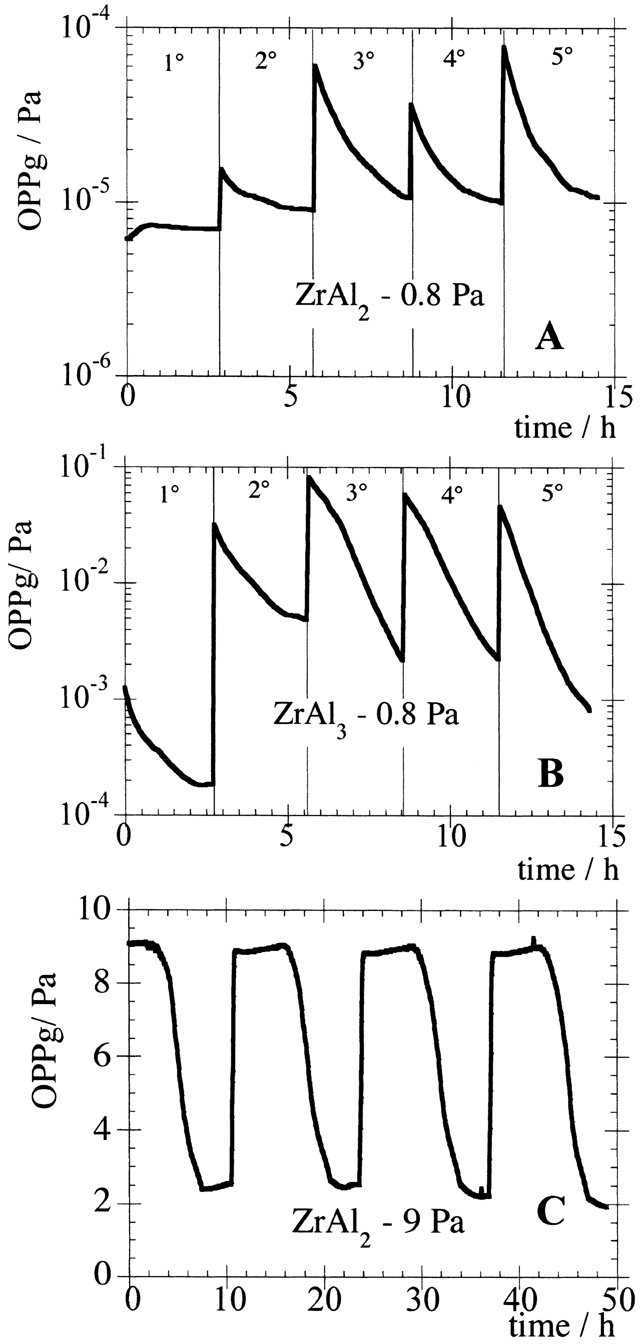

Fig. 4. Oxygen partial pressure (OPP_g) after reaction with getter as detected during repeated thermal cycles as reported in Fig. 1. Panel A: $ZrAl_2$ at $P_{O_2} = 0.8$ Pa; Panel B: $ZrAl_3$ at $P_{O_2} = 0.8$ Pa; Panel C: $ZrAl_2$ at $P_{O_2} = 9$ Pa.

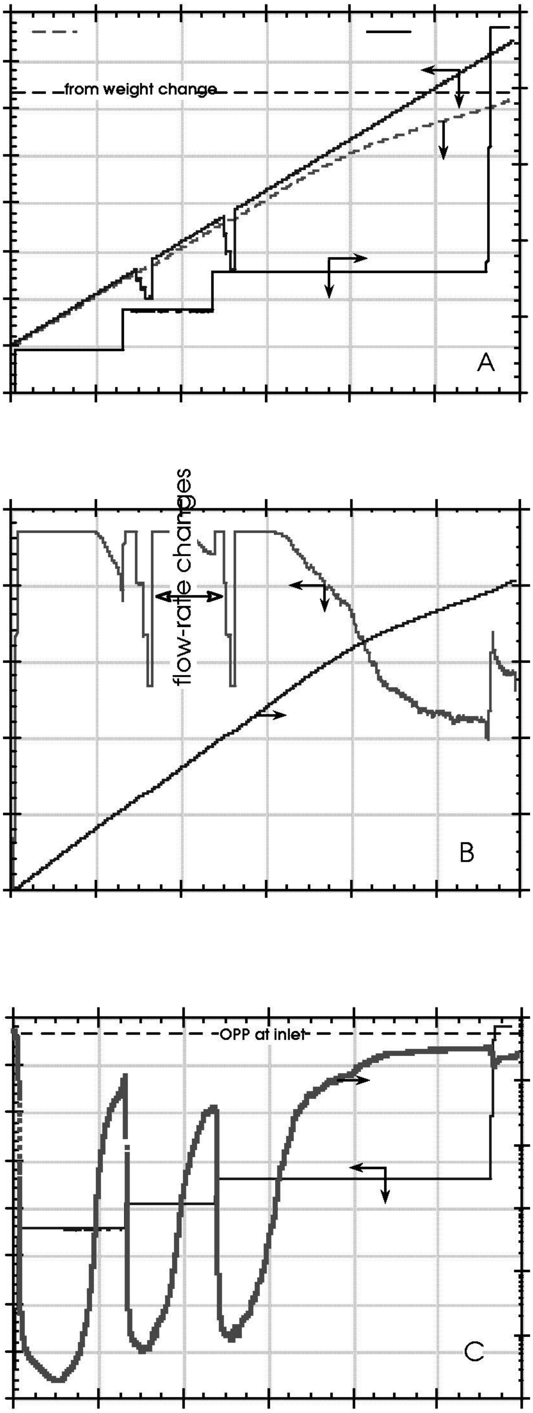

Fig. 5. Panel A (left ordinate): integral quantity of O_2 consumed by the $CeNi_5$ sample; right ordinate: temperature. Panel B(left ordinate): specific O_2 gettering rate; right ordinate: specific O_2 gettered. Panel C(left ordinate): temperature; right ordinate: oxygen partial pressure after reaction with getter (OPP_g).

sponding to 3.84×10^{-5} moles or $3.84\times10^{-5}/6$ g·atoms. The final gettering capacity, G_c, is therefore $5.54\times10^{-5}/1.344\times10^{-4}=0.41$. The quantity 1.344×10^{-4} refers to the moles of oxygen consumed by the sample in the case of a complete and stoichiometric transformation of $CeNi_5$ in CeO_2 and NiO.

4. Discussion

It is useful at the beginning of this section to give some information on how the reaction rate has been calculated starting from the experimental data supplied by our apparatus. The oxygen consumption rate, r, is given by the equation:

$$r\ (\mathrm{mol\ s^{-1}}) = aJ_{\mathrm{Ar}}x_{\mathrm{O_2}}\{1-\exp[(E^*_2-E_2)/bT_2]\} \tag{1}$$

where:

$a = 7.435795\times10^{-7}\ \mathrm{mol\ s^{-1}\ sccm^{-1}}$;

J_{Ar} = flow-rate of the Ar stream in sccm;

$x_{\mathrm{O_2}} = x^{\mathrm{ref}}_{\mathrm{O_2}}\exp[(E_1-E^*_1)/bT_1]$ = molar fraction of O_2 in Ar. E_1 is the emf of the solid electrolyte oxygen sensor and $x^{\mathrm{ref}}_{\mathrm{O_2}}$ the O_2 molar fraction in the gas stream flowing in one of the two sides of the electrolyte tube. $x^{\mathrm{ref}}_{\mathrm{O_2}}=1$ because pure O_2 is used and $b=R/4F$.

E_2 is the emf of a second O_2 sensor working in differential mode. On one side of the sensor the Ar stream circulates before entering the reaction chamber, where the sample is positioned, and the other side is exposed to the same gas stream outgoing from the reaction chamber. If the sample does not react or the reaction chamber is empty $E^*_2=E_2$ and $r=0$. Due to the way in which the oxygen sensors are connected both to the multichannel voltmeter and gas lines, $E_2>E^*_2$ means oxygen consumption and vice versa if oxygen is released by the sample. The OPP at outlet of the reaction chamber or OPP_g, as indicated in this paper, is given by the equation:

$$\mathrm{OPP_g}\ (\mathrm{Pa}) = P_t x_{\mathrm{O_2}}\exp[(E^*_2-E_2)/bT_2] \tag{2}$$

where P_t is the total pressure (10^5 Pa). From inspection of Eq. (1), it is easy to observe that since the sample is an oxygen getter $E^*_2-E_2<0$ and if $|E^*_2-E_2|\gg bT_2$, $r\cong r_{\max}=aJ_{\mathrm{Ar}}x_{\mathrm{O_2}}$. In this condition, the system is 'blind' in determining the rate changes whereas it is powerful for detecting very low levels of oxygen through Eq. (2). In this way, some apparent discrepancies are easily explained. Consider, for example, Fig. 5 panels B and C. In panel B, the gettering rate is practically constant for more than 60 h (apart from the periods where different flow-rate settings have been performed) while changes of some orders of magnitude appear in the OPP_g value. The gettering rate variation becomes appreciable when the reactivity of the getter is sufficiently low just to reduce the inlet OPP of less than two decades. The same reasoning could apply for aluminides by comparing the isothermal part of the gettering rate curve, shown in Fig. 1, with any of the isothermal trends of the respective cycles reported in Fig. 4. Further support that the gettering rate is at the maximum value, $r_{\max}$, comes from the linear dependency of r from J_{Ar} of slope ax_{O_2} as expected by the above-mentioned considerations. Therefore, to evaluate finely the behavior of the getter, the $\mathrm{OPP_g}$ trend instead of the gettering rate trend has to be considered. In fact, the changes of $\mathrm{OPP_g}$ as a function of the experimental variables are strictly dependent on the kinetics of the gas–solid reaction operating on the getter. At constant temperature and flow-rate, the trend of $\mathrm{OPP_g}$ vs. time is quite characteristic and reproducible as also found in commercial getters. This trend is also influenced by the procedure adopted. In the present study, two procedures have been used which are normally encountered in the on-line application of getters: discontinuous and continuous procedures. The first procedure has been applied here to the aluminides. The continuous procedure is shown for $\mathrm{CeNi_5}$ by increasing the temperature for simulating an application where an $\mathrm{OPP_g}$ threshold should be maintained at the outlet. From Fig. 4, it appears that, in the case of $\mathrm{ZrAl_2}$, an $\mathrm{OPP_g}$ value of 10^{-5} Pa (0.1 ppb) can be repeatedly obtained probably only for relatively short times. This would be not feasible if the getter were $\mathrm{ZrAl_3}$. In the case of $\mathrm{CeNi_5}$, where a continuous procedure has been adopted, the 10^{-5} Pa threshold could be maintained even more than 60 h if the temperature had been controlled in such a way as to be increased just to the value sufficient for avoiding to overcome the preset $\mathrm{OPP_g}$ level.

It is however evident in all the cases examined that the getter function of the intermetallic tends to vanish after a certain time though the total gettered oxygen is still below the expected oxygen quantity consumable by the sample. Many efforts have been made to improve the oxidation resistance in alloys through the addition of an element that will oxidise selectively and produce a protective surface oxide. The formation of this surface layer requires that the oxide be more stable than the lowest oxide of the base metal. On the contrary, the ideal way in which an intermetallic getter should operate must be completely different: the growing oxide layer should not be protective. Its peculiar characteristic should be to allow a rapid outward mass transfer to ensure the continuous growth of the oxide external layer. Even better than this would be a mechanism in which the continuous external growth were associated with a spontaneous detachment of the oxide layer, just as a very thin layer is formed. In this way, a fresh surface of the intermetallic would allow a high gettering rate associated to its complete reaction. Several strict and simultaneous conditions would be necessary for the occurrence of the above mechanisms. Some of them are: relative thermodynamic stability of the respective oxides by considering also the activities of the inter-

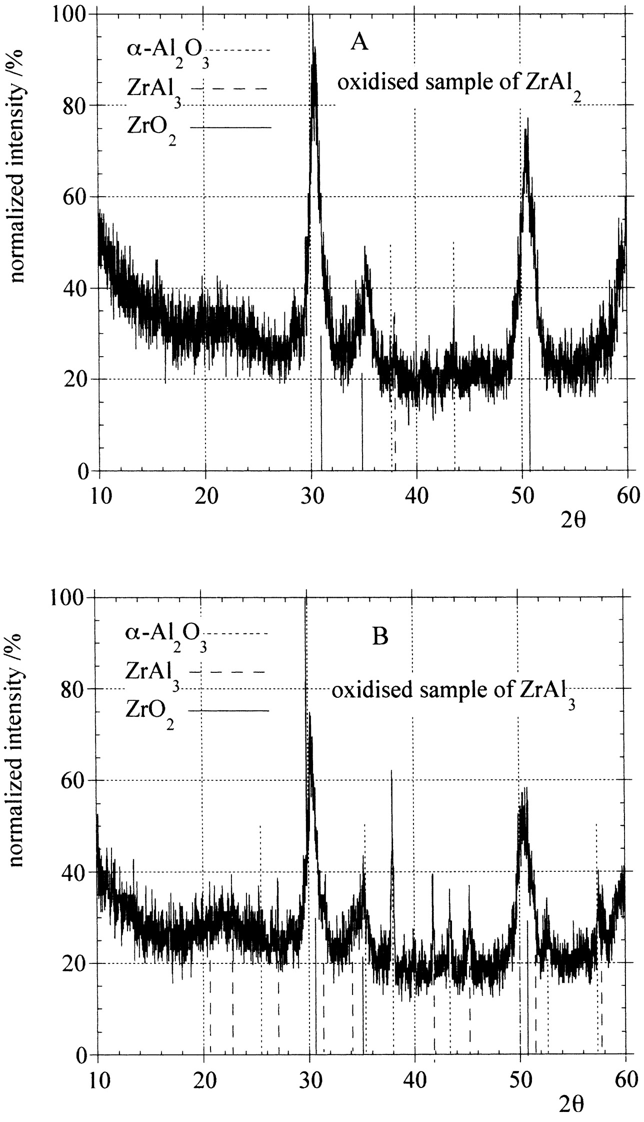

Fig. 6. Panel A: XRD of $\mathrm{ZrAl_2}$ sample at the end of experiment; Panel B: XRD of $\mathrm{ZrAl_3}$ sample at the end of experiment.

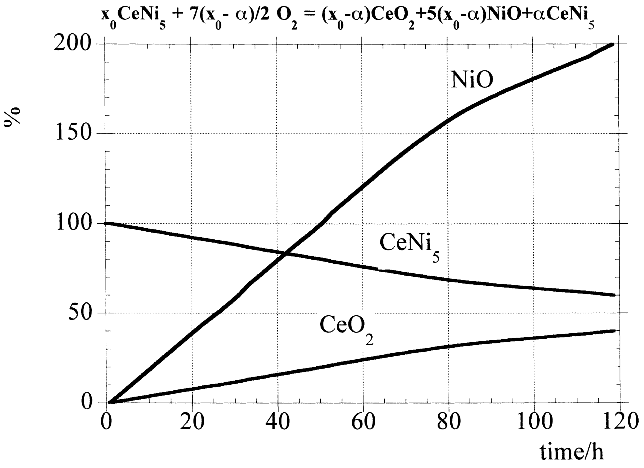

Fig. 7. Calculated time profiles in the oxidation of $\mathrm{CeNi_5}$ sample.

metallic components [10–12]; high values of the diffusion coefficient even at moderate temperature; structural compatibility between the growing oxide and intermetallic substrate in such a way that the adhesion is favorite (this only when the other parameters for the continuous oxide growth are favorable); omogeneity range of the intermetallic, etc. Consider the intermetallics examined in this paper starting from the experimental evidences reported in Figs. 3 and 6, for the aluminides, and Fig. 7 for $CeNi_5$.

Below 1100°C, Al_2O_3 is thermodynamically more stable than ZrO_2 when the activity of the respective metals is considered unity. Suppose that the activity of Al is greater than Zr in both aluminides, then the formation of an external alumina layer should be favorite with respect to zirconia. If so, it is expected that the composition of the intermetallic at the oxide–intermetallic interface should move to the intermetallic compound more as Zr reaches Zr_2Al_3 in the case of $ZrAl_2$, and $ZrAl_2$ in the case of $ZrAl_3$ as given by the Zr–Al phase diagram [13]. In the case of growth of a contnuous zirconia layer, the expected composition beneath the oxide layer moves in the opposite direction in the phase diagram. Therefore, $ZrAl_3$ from $ZrAl_2$ and we have to expect ZrO_2 and Al_2O_3 as final products in the case of $ZrAl_3$. However, for both the intermetallics, the final products of the oxidation would be anyway ZrO_2 and Al_2O_3. The G_c trend in Fig. 3 for both aluminides, before increasing the OPP, suggests that we have to expect for $ZrAl_2$ the reaction: $ZrAl_2+1/3\ O_2=2/3\ ZrAl_3+1/3\ ZrO_2$ to which the reaction $ZrAl_3+13/2\ O_2=ZrO_2+3/2\ Al_2O_3$ follows. The XRD spectra at the end of the experiment for both the aluminides are reported in Fig. 6. According to the reactions before, it is expected to find ZrO_2, Al_2O_3 and a residue of $ZrAl_3$ in agreement with Fig. 3. The spectrum of Fig. 6A shows the features of ZrO_2 and α-Al_2O_3 but no clear evidences of $ZrAl_3$ due to the superimposition of its features with α-Al_2O_3. No evidences of $ZrAl_2$. In the case of the $ZrAl_3$ sample, the spectrum in Fig. 6B shows ZrO_2 and Al_2O_3 as expected. Similar results were already reported in the literature [14,15] for the oxidation of $ZrAl_2$.

Concerning $CeNi_5$, the large difference in the thermodynamic stability of CeO_2 with respect NiO allows to assume that CeO_2 is the continuous external oxide layer and, differently from the Zr-aluminides, no intermetallic compound at lower Ce/Ni ratio than $CeNi_5$ is present in the Ce–Ni phase diagram. Accordingly, at the end of the experiment, only NiO, CeO_2 and $CeNi_5$ should be found as confirmed by the XRD spectrum. From the gettered oxygen data reported in Fig. 5B, it is possible to derive the time trend of all the species involved in the oxidation of $CeNi_5$ by considering the mass balance in the reaction: $x_0CeNi_5+7(x_0-\alpha)/2\ O_2=(x_0-\alpha)CeO_2+5(x_0-\alpha)NiO+\alpha CeNi_5$ where x_0 and α are, respectively, the initial number of moles of the intermetallic compound and $CeNi_5$ unreacted. Since the gettered oxygen $[7(x_0-\alpha)/2]$ is measured on time and x_0 is known, the plot of Fig. 7 has been obtained where the values are given with respect to x_0. In the experiment considered, only 40% of the intermetallic reacted.

5. Conclusions

The performances of a getter should be evaluated through the values of MTGA, OPP_g and operating time at a given OPP_g. In terms of these parameters, $ZrAl_3$ has to be discarded because it does not satisfy any of them. $CeNi_5$ seems more promising on the basis of a lower OPP_g which can be maintained for a longer time in the experimental conditions adopted. A more systematic study will be required to explore the potentialities of these intermetallics to getter other molecules as CO, CO_2 and H_2O.

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