Journal of Alloys and Compounds, 191 (1993) 27–29
JALCOM 448

Selective oxidation of Zr_2Al_3

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(Received 22 July, 1992)

Abstract

The oxidation of Zr_2Al_3 in dry oxygen in the temperature range 875–965 K obeys a parabolic rate law. An activation energy of 270 kJ mol^{-1} has been estimated. During the oxidation, aluminium diffuses from the oxide layer into the Zr_2Al_3 bulk, thus forming the $ZrAl_2$ phase very close to the oxide–alloy interface. The excess zirconium is therefore selectively oxidized, giving tetragonal and monoclinic ZrO_2 containing no Al_2O_3.

1. Introduction

Among the phases in the Zr–Al system, some uncertainty about the existence of Zr_2Al_3 has been reported [1]. It has been stated that a phase which might be represented by either of the formulae Zr_2Al_3 (30.73 mass% Al) or Zr_3Al_4 (28.28 mass% Al) is formed by a peritectic reaction between the phase $ZrAl_2$ (37.17 mass% Al) and a melt containing about 30 mass% Al at 1868 K. The evidence then available suggested that the designation Zr_2Al_3 can be tentatively adopted. The other investigations [2–4] have confirmed the composition of 30.73 mass% Al and 69.27 mass% Zr for the Zr_2Al_3 phase.

Zr_2Al_3 has an orthorhombic structure with lattice parameters $a = 5.572$ Å, $b = 9.599$ Å and $c = 13.879$ Å [3]. The space group is *Fdd*2, with eight formula units per cell [2, 3].

As examinations of high temperature oxidation of Zr_3Al, Zr_2Al, ZrAl and $ZrAl_2$ [5, 6, 7, 8] have shown that zirconium is selectively oxidized to ZrO_2 and aluminium diffuses into the bulk of the alloy, forming there a phase richer in aluminium than the matrix alloy, an investigation of the oxidation behaviour of Zr_2Al_3 has been undertaken in order to complete the picture of the oxidation behaviour in the Zr–Al system.

2. Experimental details

Samples of Zr_2Al_3 with a mass of about 3 g each were prepared from the constituent elements. Appropriate amounts of zirconium, refined by the van Arkel–de Boer hot wire process, and aluminium ingots (purity, 99.999%) were melted together using a non-consumable arc melting technique in a water-cooled copper mould under argon (pressure, 50 kPa). The samples were turned over and remelted three times to help to ensure homogeneity. They were further homogenized at 1373 K for 2 months in evacuated quartz tubes. X-ray powder diffraction analysis showed that the samples consisted essentially of the Zr_2Al_3 phase.

The specimens were then cut into small flat pieces of dimensions 6 mm × 4 mm × 1 mm. After grinding, they were polished using a slurry of Cr_2O_3 and water with the addition of few drops of 0.5% HF solution. The Cr_2O_3 is freshly prepared by the ignition of ammonium dichromate [9].

Oxidation of Zr_2Al_3 was performed in a stream of dry oxygen at atmospheric pressure with a constant heating rate up to 1273 K, or isothermally in the temperature range 875–965 K.

The absorption of oxygen was monitored using a recording thermobalance. Reaction products were examined using a Philips X-ray diffractometer with proportional counter and monochromatized Cu Kα radiation. The oxidized surfaces of the specimens were ground several times and re-examined by X-ray diffraction analysis.

3. Results and discussion

The oxidation experiments at elevated temperatures (heating rate 0.3 K min^{-1}) showed that Zr_2Al_3 did not oxidize noticeably below 820 K at which temperature measurable oxygen absorption was observed (Fig. 1). However, the oxidation was relatively slow until 1000 K. Strong oxygen consumption took place at 1100 K. The sample disintegrated in this process and the newly

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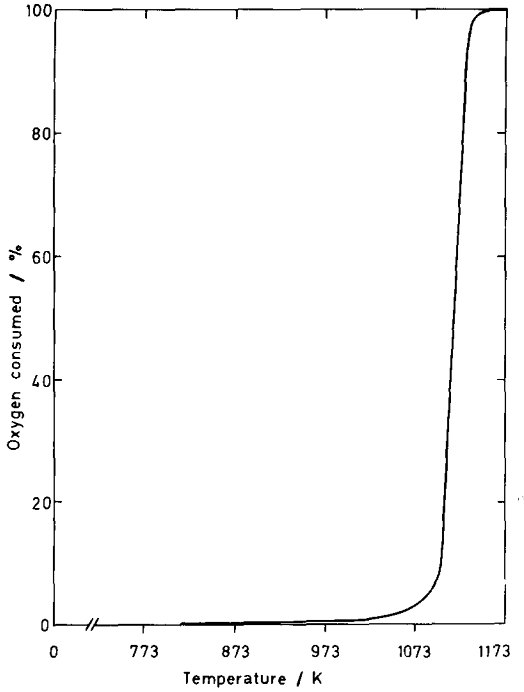

Fig. 1. Thermogravimetry curve for the oxidation of Zr_2Al_3 in dry oxygen at atmospheric pressure and elevated temperature (heating rate, 0.3 K min^{-1}).

formed surfaces of the alloy became available for reaction with oxygen. The reaction accelerated in this way and was completed in about 3 h until a temperature of 1150 K had been reached. The reaction product consisted of weakly crystallized tetragonal ZrO_2 and small amounts of monoclinic ZrO_2. Further heating of this product in air at 1873 K for 1 h resulted in monoclinic ZrO_2, small amounts of tetragonal ZrO_2 and α-Al_2O_3. Tetragonal ZrO_2 was transformed to the monoclinic form.

The isothermal oxidation of Zr_2Al_3 has been investigated in the temperature range 875–965 K for 24 h. The mass gain–time curves are shown in Fig. 2. The oxidation process obeys a parabolic rate law which suggests that the rate-determining process is thermal diffusion. The oxidation curves can be described by the equation

$$\Delta m^2 = k_p t + A$$

where Δm is the amount of absorbed oxygen in kilograms per square metre, t is the time in seconds, k_p ($kg^2\ m^{-4}\ s^{-1}$) is the parabolic rate constant and A is a constant.

The values of the parabolic rate constant k_p at various temperatures T computed using the least-squares method are given in Table 1.

An Arrhenius plot of log k_p against $1/T$ is shown in Fig. 3. A value of 270 kJ mol^{-1} was estimated for the activation energy of oxidation of Zr_2Al_3 in the temperature range 875–965 K.

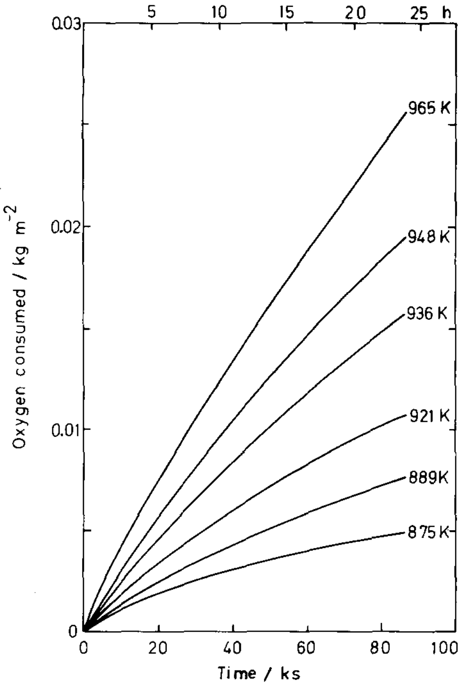

Fig. 2. Typical mass gain–time curves for the isothermal oxidation of Zr_2Al_3 in a stream of dry oxygen at atmospheric pressure.

TABLE 1. Selected data for the oxidation of Zr_2Al_3 at high temperatures in a stream of dry oxygen at atmospheric pressure for 24 h

Temperature T (K)	Parabolic rate constant k_p ($kg^2\ m^{-4}\ s^{-1}$)
875	2.499×10^{-10}
889	5.012×10^{-10}
921	1.511×10^{-9}
936	2.993×10^{-9}
948	4.554×10^{-9}
965	8.066×10^{-9}

The oxide covers the alloy surface as a dark layer at lower temperatures. At higher temperatures the colour changes to grey and finally becomes white. X-ray diffraction analysis showed that the surface oxide layer consisted of a mixture of weakly crystallized tetragonal (mainly) and monoclinic phase of ZrO_2. The oxide layer is generally thin. X-ray diffraction examination detected no oxide phase on the surfaces of specimens oxidized at temperatures below 950 K for 24 h, although the alloy surface was tarnished and covered with a dark oxide film. However, diffraction lines of $ZrAl_2$ were found in addition to the lines of matrix alloy, Zr_2Al_3. These lines of $ZrAl_2$ disappeared on subsequent grinding. The samples of Zr_2Al_3 oxidized at 1000 K and higher temperatures for 24 h were disintegrated and crumbled.

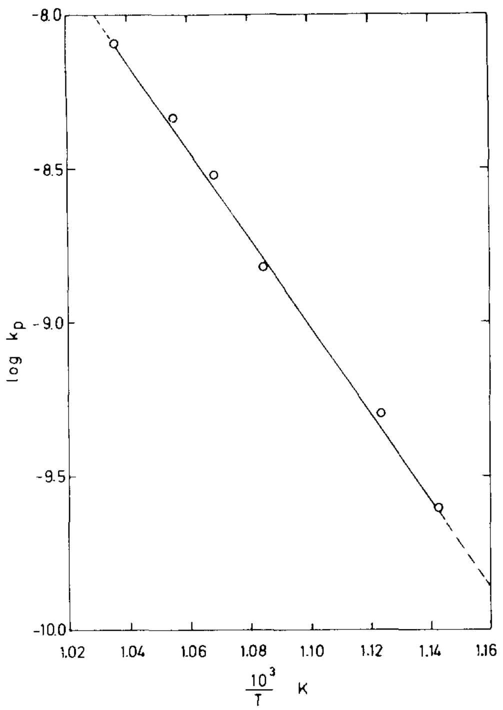

Fig. 3. Arrhenius plot of log k_p *vs.* $1/T$ for the oxidation of Zr_2Al_3.

The oxidation product on the surface of Zr_2Al_3 is ZrO_2 containing no Al_2O_3. It is known [10] that Al_2O_3 is almost insoluble in ZrO_2, and a eutectic at 57.4 mass% Al_2O_3 is formed. Successive grinding and X-ray examinations of oxidized Zr_2Al_3 specimens revealed the $ZrAl_2$ phase under the oxide film. The $ZrAl_2$ phase, which contains more aluminium than the matrix phase, Zr_2Al_3, accumulated in the matrix phase very close to the oxide–alloy interface.

Thus, after the oxide film is formed, both oxygen and aluminium diffuse through the film to the alloy. Aluminium avoids oxidation in this way and forms $ZrAl_2$, an aluminium-rich phase, in the Zr_2Al_3 matrix very close to the oxide–alloy interface. Consequently, the remaining zirconium is selectively oxidized to form ZrO_2.

The same phenomenon of selective oxidation was observed in the oxidation of other phases in the Zr–Al system. Thus Zr_3Al, Zr_2Al, ZrAl and $ZrAl_2$ are oxidized to yield tetragonal and monoclinic ZrO_2 as the oxidation product, during which aluminium escapes oxidation by diffusion into the bulk of the alloy and forms there Zr_2Al, Zr_5Al_3, Zr_2Al_3 and $ZrAl_3$ respectively [5–8]. The newly formed phases with higher aluminium content than the matrix phase are the adjoining phases in the phase diagram of the Zr–Al system.

According to the Wagner theory of selective oxidation [11–13], aluminium is a "more noble" and zirconium a "less noble" metal in the Zr–Al system. The more noble metal escapes oxidation diffusing from the oxide layer into the bulk of the alloy, and the less noble metal is selectively oxidized forming an outer oxide layer.

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