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HIGH-TEMPERATURE OXIDATION OF ZrAl

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Summary

The oxidation of ZrAl in dry oxygen in the temperature range 800 - 1100 K follows a parabolic rate law. An activation energy of 86.4 kJ mol^{-1} was estimated. During the oxidation, aluminium diffuses from the oxide layer to the ZrAl bulk, thus forming a $ZrAl_2$ phase very close to the oxide–alloy interface. The excess zirconium is therefore selectively oxidized, yielding tetragonal mainly and monoclinic ZrO_2 containing no Al_2O_3.

1. Introduction

It has been found that high-temperature oxidation of Zr_3Al [1] and Zr_2Al [2] results in the formation of an oxide layer consisting of ZrO_2 with no Al_2O_3, *i.e.* zirconium is selectively oxidized. Aluminium diffuses into the bulk of the alloy accumulating at some distance from the oxide–alloy interface. This accumulation of aluminium results in the formation of the Zr_2Al phase in the Zr_3Al matrix and the Zr_5Al_3 phase in the Zr_2Al matrix. These results suggested further examination of the oxidation behaviour of ZrAl, one of the next intermetallic phases in the Zr–Al system. ZrAl is an ordered orthorhombic phase with lattice parameters $a = 0.3359$ nm, $b = 1.0887$ nm and $c = 0.4274$ nm [3]. It has a narrow compositional range and occurs at the stoichiometric composition of 22.83 mass % Al [4]. It is a brittle and relatively hard alloy.

2. Experimental details

Samples of ZrAl were prepared by arc melting appropriate amounts of iodide zirconium (zirconium refined by the van Arkel–de Boer hot-wire process) and aluminium (purity, 99.999%) in a water-cooled copper mould under a titanium-gettered argon atmosphere (pressure, 48 kPa). To ensure homogeneity, the buttons (about 3 g each) were remelted three times. They were further homogenized at 1273 K for about 40 days in evacuated sealed

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quartz tubes. X-ray and metallographic analyses confirmed that the samples consisted essentially of the ZrAl 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 oxidation of ZrAl was performed in a stream of dry oxygen at atmospheric pressure with a constant heating rate to 1273 K or isothermally in the temperature range 730 - 1100 K. The absorption of oxygen was measured using an automatic thermobalance. The surfaces of the oxidized specimens were examined using an X-ray diffraction technique. The surfaces were then ground several times and re-examined by X-ray diffraction analysis. The changes in the concentrations of zirconium, aluminium and oxygen were measured on cross-sections of oxidized specimens using electron microanalysis.

3. Results and discussion

The oxidation experiments at elevated temperatures (heating rate, 0.00788 K s^{-1}) showed that ZrAl did not oxidize noticeably below 960 K (Fig. 1), at which a measurable oxygen absorption was observed. However, the oxidation process was relatively slow until about 1120 K. The more significant weight gain took place at about 1180 K. The sample disintegrated during this period and access of oxygen to the newly formed surfaces of the sample was facilitated. Thus, the reaction became rather quick and was completed in about 6 h.

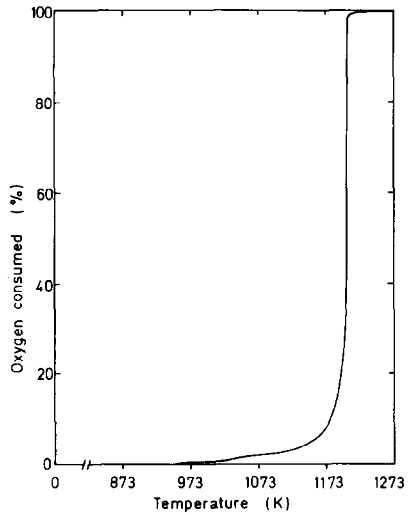


Fig. 1. TGA curve for the oxidation of ZrAl in dry oxygen at atmospheric pressure and elevated temperature (heating rate, 0.00788 K s^{-1}).

The oxidation product at 1273 K was mainly tetragonal ZrO_2 with some monoclinic ZrO_2. If this product is further heated at 1923 K in the air for 1 h, monoclinic ZrO_2, small amounts of tetragonal ZrO_2 and α-Al_2O_3 are obtained.

The isothermal oxidation of ZrAl has been investigated in the temperature range 730 - 1100 K. 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 are described by the equation

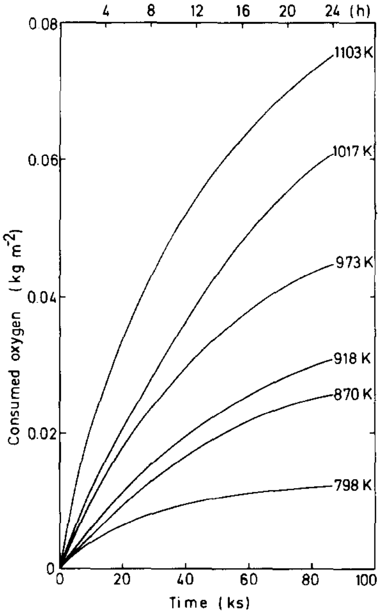
$$\Delta m^2 = k_p t + A$$

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. The activation energy for the oxidation process calculated using the least-mean-squares method at the 99% confidence level is 86.4 kJ mol^{-1}.

The alloy is covered by a very thin reddish coating at a temperature of 730 K, but no weight gain was registered in a period of 24 h. The measurable oxygen consumption was observed at a temperature not lower than



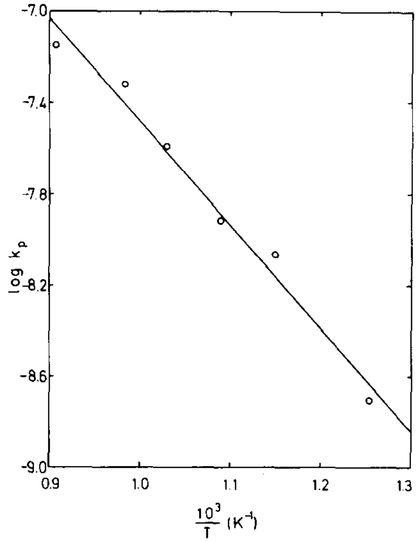


Fig. 2. Typical weight-gain–time curves for the isothermal oxidation of ZrAl in a stream of dry oxygen at atmospheric pressure.

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

TABLE 1

Selected data for the oxidation of ZrAl at high temperatures in a stream of dry oxygen at atmospheric pressure

Temperature (K)	*Parabolic rate constant* k_p ($kg^2\ m^{-4}\ s^{-1}$)
798	1.9667×10^{-9}
870	8.6586×10^{-9}
918	1.2071×10^{-8}
973	2.5325×10^{-8}
1017	4.7292×10^{-8}
1103	6.9778×10^{-8}

798 K. At this and higher temperatures, the colour of the oxide layer changed to grey. X-ray diffraction analysis showed that the surface oxide layer consisted of a mixture of the tetragonal (mainly) and the monoclinic phases of ZrO_2. No ZrO_2 was found by X-ray analysis at 730 K, although the alloy was covered by the reddish coating. In contrast the oxidation products of Zr_3Al and Zr_2Al, cubic or tetragonal ZrO_2 respectively, only were formed at lower temperatures [1, 2], the oxidation product of ZrAl consisted of both tetragonal and monoclinic ZrO_2 in the whole temperature range (798 - 1100 K) studied. The degree of crystallinity of both phases increased with temperature. No Al_2O_3 was detected in the oxide layer, as in the case of the oxide layers on Zr_3Al and Zr_2Al.

As ZrAl contains 50 at.% Al, it is to be expected that the oxidized specimen will contain aluminium. It has been found that Al_2O_3 is mostly insoluble in ZrO_2 [5 - 8], but a eutectic of the composition 57.4 mass % Al_2O_3 and 42.6 mass % ZrO_2 with a melting point of 1983 K is formed [8]. Thus, if Al_2O_3 had been formed during the oxidation of ZrAl, it would have been found in the oxide layer using X-ray analysis, supposing it had sufficient crystallinity. However, X-ray analysis revealed no information about the presence of Al_2O_3 in the oxide layer formed in 24 h and electron microanalysis showed that the concentration of aluminium in the oxide layer had undergone a significant decrease (Fig. 4). After the oxide layer had been removed by grinding, $ZrAl_2$ phase was detected. This phase, richer in aluminium than ZrAl, accumulated in the matrix of ZrAl 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 ZrAl matrix very close to the oxide–alloy interface. Consequently, the remaining zirconium is selectively oxidized to form ZrO_2.

The same phenomenon was observed in the oxidation of Zr_3Al and Zr_2Al [1, 2]. The oxide layer in both cases consisted of ZrO_2 only. Diffusion of aluminium from the oxide layer into the alloy resulted in the formation of Zr_2Al in the Zr_3Al matrix and Zr_5Al_3 in the Zr_2Al matrix.

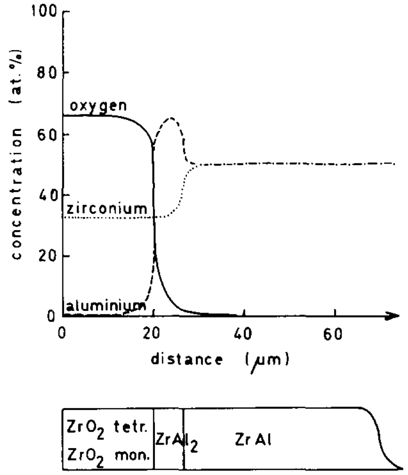


Fig. 4. Concentration profiles across the ZrAl alloy and oxide scale formed after 24 h in oxygen at 1017 K.

According to Wagner theory of selective oxidation [9 - 11], 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.

Under any set of conditions selective oxidation will take place only above a critical concentration of the active alloy component. It is obvious that this critical concentration for zirconium in the system Zr–Al is less than 50 at.%.

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