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Study of oxidation behaviour of Zr-based bulk amorphous alloy $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ by thermogravimetric analyser

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Abstract. The oxidation behaviour of Zr-based bulk amorphous alloy $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ has been studied in air environment at various temperatures in the temperature range 591–684 K using a thermogravimetric analyser (TGA). The oxidation kinetics of the alloy in the amorphous phase obeys the parabolic rate law for oxidation in the temperature range 591–664 K. The values of the activation energy and pre-factor as calculated from the Arrhenius temperature dependence of the rate constants have been found to be 1·80 eV and $2·12 \times 10^9$ g·cm^{-2}·sec$^{-1/2}$, respectively.

Keywords. Oxidation; (bulk) amorphous alloys; TGA.

1. Introduction

Amorphous alloys (or the so-called metallic glasses), in general, possess superior physical, mechanical and chemical properties *vis-à-vis* their crystalline counterparts (Cahn 1991). Recently, a new class of amorphous alloys has been developed which require cooling rates of about 1 K/s (Zhang *et al* 1991). These alloys, such as Zr–Ti–Cu–Al, Zr–Ti–Cu–Ni–Be etc can be processed in the bulk form (Zhang *et al* 1991; Pecker and Johnson 1993; Johnson 1996). Newly discovered Zr-based bulk multicomponent metallic glass $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ (also called as Inoue alloy) has a wide supercooled liquid region of about 100 K and a high thermal stability (Zhang *et al* 1991). Knowledge of oxidation behaviour of this alloy is important as the alloying element, specially Zr- and Al- have high reactivity with oxygen. It is, therefore, of general interest and practical relevance to study the oxidation behaviour of this alloy. Reported studies on oxidation of this alloy are very few in the literature (Sharma *et al* 1999; Triwikantoro *et al* 1999). The present study examines the oxidation behaviour of the amorphous $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ alloy in air in the temperature range 591–684 K using a thermogravimetric analyser (TGA).

2. Experimental

A small amount of the specimen was cut from the amorphous ribbon (10 mm wide × 30 μm thick) of the alloy and was put on the pan of the thermobalance of a thermogravimetric analyser (Model TGA 7, Perkin Elmer). The alloy specimen was subjected to oxidation in air environment at a given temperature (T) in the temperature range 591–684 K and the mass gain (in mg) with time (in min) during several such isothermal runs at different temperatures was continuously monitored using a computer interfaced with the system. Plots of the mass gain per unit area (g/cm^2) vs square root of time (sec$^{1/2}$) at different temperatures (591–684 K) were obtained from these experiments. The surface area is obtained from the relation

$$S = 2w_o/d_0 r,$$

where w_o is the mass of specimen before oxidation, r the density of the alloy and d_0 the thickness of the specimen (Asami *et al* 1995). The Arrhenius plot between logarithm of the slopes K (measured from the initial linear portion of mass gain per unit area vs (time)$^{1/2}$ plots) and $1/T$ was obtained, thus yielding the values of the activation energy (Q) and the pre-exponential factor (K_0). The isochronal TGA run of the specimen was also taken indicating a glass transition for the alloy at 650 K.

3. Results and discussion

Figure 1 shows typical TGA plots of the change in mass of the amorphous $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ specimen as a function of time during air oxidation at 593 K. The corresponding plot representing the mass gain (in g/cm^2) versus the square root of oxidation time (sec$^{1/2}$) is shown in figure 2, which also includes similar plots at other oxidation temperatures. The mass gain per unit area was found to agree

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reasonably well with linear variation with square root of oxidation time in the investigated temperature regime. This suggests that for the investigated temperatures and times the oxidation reaction kinetics obeys a parabolic rate law, $W = Kt^{1/2}$, where W is mass gain per unit area of the specimen, t the oxidation time in seconds and K (g cm^{-2} sec$^{-1/2}$) is the parabolic rate constant. The calculated values of the parabolic rate constant, K at various temperatures are mentioned in table 1. Figure 3 shows the Arrhenius plot between the logarithm of slopes (measured from the initial linear portion of mass gain [g/cm^2] versus square root of time [sec$^{1/2}$] plots) and $1/T$. All points except those corresponding to 681 K and 684 K lie on the straight line. From the time–temperature transformation diagram for this alloy (Busch 1998), it is found that the points at 681 K and 684 K correspond to the supercooled liquid phase (shown as unfilled points in figure 3), while all points except these two correspond to the amorphous phase of the alloy. So the data shown in figure 2 for the amorphous phase (excluding the points at 681 K and 684 K corresponding to the supercooled liquid phase) follow the Arrhenius law with the values of the activation energy, Q and the pre-factor, K_o for oxidation in air in the temperature range 591–664 K as $Q = 1{\cdot}80$ eV, $K_o = 2{\cdot}12 \times 10^9$ g cm^{-2} sec$^{-1/2}$, respectively. The oxidation kinetics obeys the parabolic growth law for the amorphous phase and is thus diffusion controlled. Evidence for diffusion controlled oxidation growth is also provided by the reported diffusion data in this alloy. In a study on self-diffusion of Ni in this alloy, an activation energy of 1·9 eV has been reported (Knorr 1999). The value of the activation energy (1·80 eV) obtained in the present study is close to the reported value for diffusion of Ni in this bulk metallic glass suggesting that the rate limiting process for the oxidation of the amorphous phase of this alloy is the diffusion of Ni. In another study (Sharma *et al* 1999) on air oxidation of this alloy no Ni was detected on the surface while Ni was present near and below the

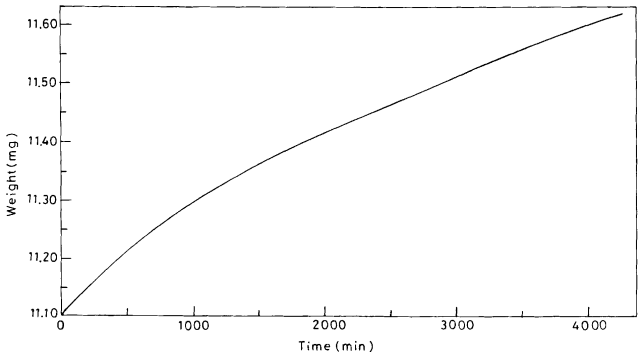

Figure 1. A typical isothermal TGA plot showing mass gain (in mg) vs time (in min) at 593 K.

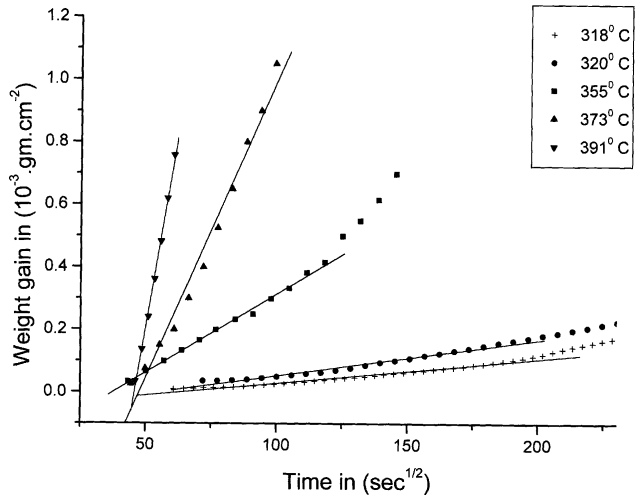

Figure 2. Plots of weight gain in g/cm^2 vs time in sec$^{1/2}$ at different temperatures.

Table 1. Variation of parabolic rate constant, K with temperature, T of an $Zr_{65}Cu_{17{\cdot}5}Ni_{10}Al_{7{\cdot}5}$ alloy.

T (K)	K (g cm^{-2} sec$^{-1/2}$)
591	$8{\cdot}13 \times 10^{-7}$
593	$1{\cdot}05 \times 10^{-6}$
628	$5{\cdot}51 \times 10^{-6}$
646	$1{\cdot}79 \times 10^{-6}$
664	$4{\cdot}47 \times 10^{-5}$
681	$8{\cdot}96 \times 10^{-5}$
684	$7{\cdot}92 \times 10^{-5}$

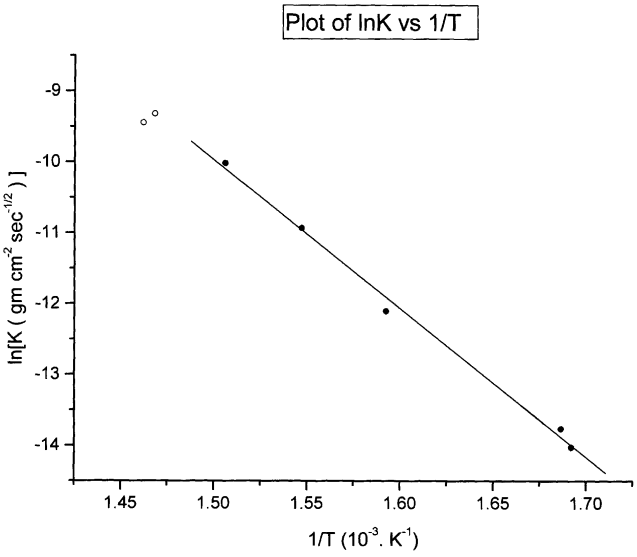

Figure 3. Arrhenius plot between ln K (g cm^{-2} sec$^{-1/2}$) and $1/T$ (10^{-3} K^{-1}). The open circles correspond to the glass being in the supercooled liquid state. The straight line has been fitted among the filled points.

oxide–alloy interface giving further support to the suggestion that the back diffusion of Ni is the rate limiting process during oxidation of the amorphous phase of the alloy $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ in air in the temperature range 591–664 K. Moreover, in another study on oxidation of this alloy in air at similar temperatures parabolic growth kinetics has been suggested (Triwikantoro *et al* 1999). Parabolic growth kinetics of oxidation has also been suggested for oxidation of amorphous $Zr_{60}Ni_{25}Al_{15}$ in dry oxygen in the temperature range 583–683 K needing an activation energy of 1·7 eV (Sun *et al* 1996).

4. Conclusions

The present study on oxidation behaviour of Zr-based bulk amorphous alloy $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ carried out in air environment in the temperature range 591–684 K using a thermogravimetric analyser (TGA) revealed the following:

(I) The oxidation kinetics of the alloy in the amorphous phase obeys the parabolic rate law suggesting a diffusion controlled growth of the oxide film.
(II) The values of the activation energy, Q and the pre-exponential factor as determined from the Arrhenius fit to $\ln K$ vs $1/T$ are 1·80 eV and $2·12 \times 10^9$ g·cm^{-2}·sec$^{-1/2}$, respectively.
(III) It is suggested that the back diffusion of Ni is the rate limiting process during oxidation of amorphous phase of the alloy $Zr_{65}Cu_{17·5}Ni_{10}Al_{7·5}$ in air in the temperature range 591–664 K.

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