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Effect of CO_2 on the oxidation behaviour of Ti–25Al and Ti–24Al–15Nb

T. K. ROY, R. BALASUBRAMANIAM, A. GHOSH
Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208016, India

In recent years Ti_3Al-based intermetallic alloys have shown promise as high temperature materials. However, the poor room temperature ductility of stoichiometric Ti_3Al and its oxidation resistance/environmental embrittlement are of concern. Ti_3Al alloyed with niobium shows improved ductility [1]. The oxidation of these alloys has been the subject of several earlier studies [2–5]. In general, the addition of Nb is beneficial in imparting oxidation resistance. The composition of the gaseous environment is an important factor that influences the oxidation behaviour of titanium aluminides. The oxidation behaviour in air could be significantly different to that in oxygen [6]. Choudhury *et al.* [7] reported that rapid oxidation rates of TiAl in air were due to N_2 and not caused by the hydrocarbons, CO and CO_2 impurities, present in air.

In a recent study [8], the oxidation and nitridation behaviour of Ti–25Al and Ti–24Al–15Nb (at%) alloys over a wide range of temperatures and gas compositions was investigated. In this letter, the interesting effect of CO_2 on oxidation of these materials at 1300 K is addressed.

The alloys in the form of arc-melted "pancakes" were obtained from the Defence Metallurgical Research Laboratory, India. The pancakes had been melted four times to eliminate inhomogeneities. Rectangular oxidation samples, approximately 16 mm × 11 mm × 1.2 mm in dimensions, were cut from the pancakes and polished up to 600 grit SiC paper, cleaned and dried. The samples were exposed in oxygen, nitrogen and a gas mixture containing $95N_2$ and $5CO_2$ (vol%). Nitrogen was passed through a BTS[1] catalyst and an Ascarite column to remove oxygen and carbon dioxide impurities, respectively. Carbon dioxide was passed through the BTS catalyst only. Anhydrous calcium chloride and Drierite were employed to remove moisture from these gases before introduction into the furnace. The weight gain of the specimen was recorded continuously using a Cahn 1000 electrobalance. The oxidation products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX).

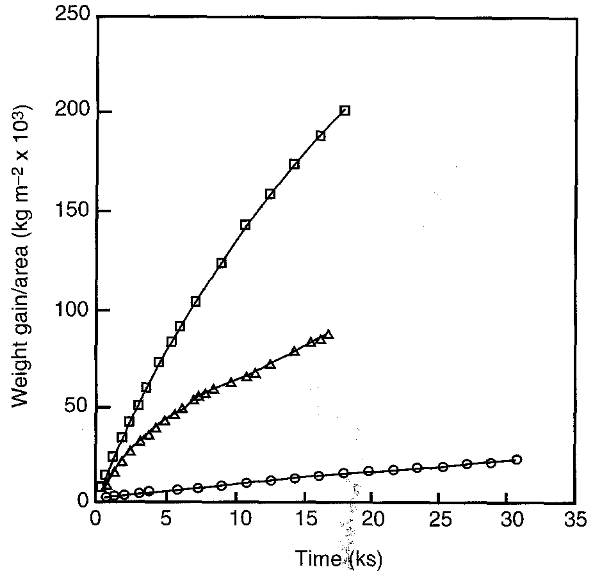

Figure 1 Weight gain plotted against time for Ti–25Al in (○) N_2, (□) N_2–CO_2 and (△) O_2 and 1300 K.

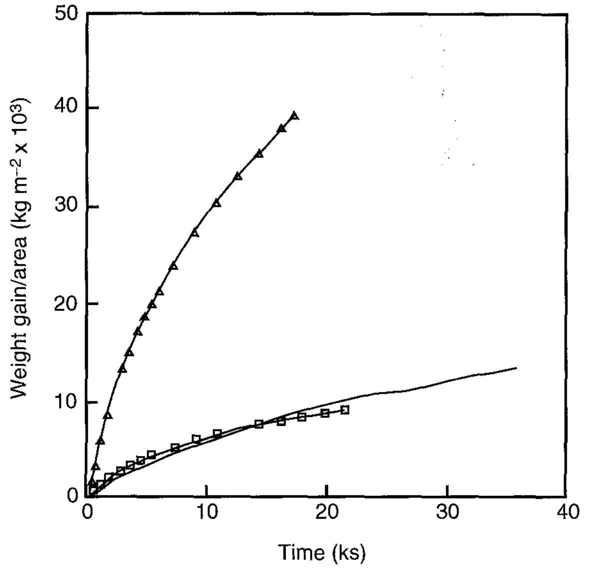

Figure 2 Weight gain plotted against time for Ti–24Al–15Nb in (—) N_2, (□) N_2–CO_2 and (△) O_2 at 1300 K.

Figs 1 and 2 show weight gain curves for both alloys exposed in O_2, N_2 and N_2–CO_2 gas mixture. The parabolic rate law was considered as the basis for data processing and interpretation of results. The parabolic rate constant (k_p) is related to weight gain per unit surface area of specimen ($\Delta W/A$) and exposure time (t) as:

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t \qquad (1)$$

k_p (expressed in $kg^2\,m^{-4}\,s^{-1}$) was obtained from the slope of the $(\Delta W/A)^2$ against t plot fitted by linear regression analysis.

For Ti–25Al, rapid oxidation with a rate constant (k_p) of 2.36×10^{-6} was obtained in N_2–CO_2 gas mixture against 1.78×10^{-8} in N_2 (Fig. 1). Inter-

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[1] BTS is the trade name of the catalyst (BASF-katalysator R 3-11) manufactured by Badische anilin and Soda-Fabrik (BASF) AG, Germany.

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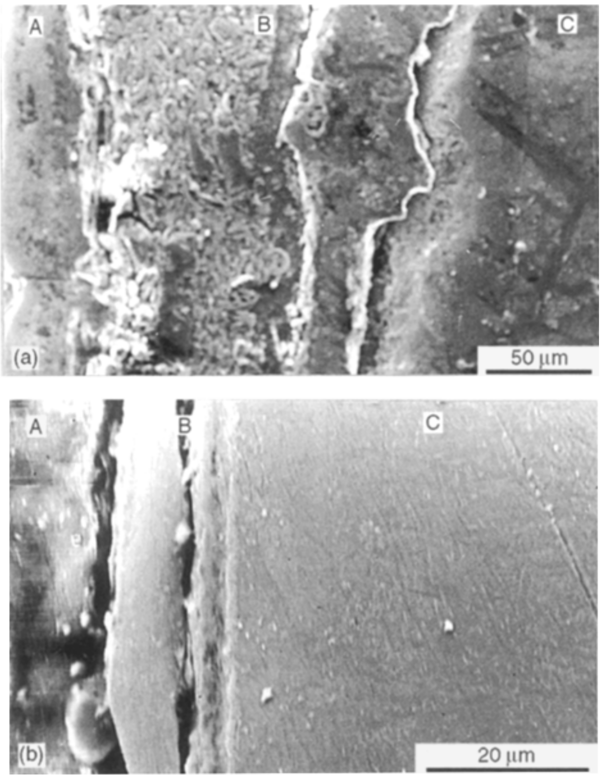

Figure 3 SEM micrographs of scale cross-sections for (a) Ti–25Al and (b) Ti–24Al–15Nb exposed to N_2–CO_2 at 1300 K. (A), Mount; (B), scale; (C), alloy.

estingly, the k_p in the gas mixture was approximately five times larger than that found in O_2 (4.50×10^{-7}) Fig. 3a is an SEM micrograph of scale formed on Ti–25Al in N_2–CO_2 gas mixture. The scale formed in the presence of CO_2 was much thicker compared to that in only O_2, and comprised a non-adherent yellow outer scale, beneath which was a cream-coloured inner scale. The outer scale spalled off considerably, exposing the metallic substrate at some edges. The inner scale was porous, with a larger pore size than the outer scale. The XRD analysis revealed the presence of TiO_2 and Al_2O_3 in the scale even on exposure in only N_2. The formation of these oxides in N_2 was due to the presence of residual oxidizing impurities in nitrogen gas and greater stabilities of oxides of aluminium and titanium as compared with those of the nitrides.

An important issue here is more extensive scale cracking, porosity and spallation in N_2–CO_2 as compared to that in oxygen. Carbon dioxide is much less stable compared to titanium and aluminium oxides. Therefore, carbon dioxide is as much an oxidizing agent as O_2. Due to scale cracking and porosity, carbon dioxide can diffuse to the interior of the scale and come in contact with the alloy, and thus react with it. Its reaction with the allloy also gives rise to the formation of carbon or carbides. The formation of reaction products in the interior of the scale may cause generation of additional stresses, resulting in cracking and spallation of the scale and subsequently an abnormal enhancement of rate.

In contrast, the effect of CO_2 on oxidation of Ti–24Al–15Nb was negligible (Fig. 2). k_p in N_2–CO_2 gas mixture was 3.97×10^{-9} as compared to 5.09×10^{-9} in N_2. The scales were thin, adherent and compact in both cases. Fig. 3b shows the cross-section of the scale on this alloy after exposure in N_2–CO_2 gas mixture. XRD results indicated that the scales on Ti–24Al–15Nb in both N_2 and N_2–CO_2 consisted of minor quantities of TiN and Al_2O_3 in addition to TiO_2, which was the principal constituent.

Carbon dioxide was not able to penetrate the scale and react directly with the alloy in the case of Ti–24Al–15Nb. Therefore, its role as an oxidant was restricted near the outer surface of the scale. The oxygen potential in the gas due to the presence of CO_2 may be estimated approximately as follows.

The dissociation of CO_2 into CO and oxygen is represented by:

$$CO_2(g) = CO(g) + \tfrac{1}{2}O_2(g) \qquad (2)$$

and the equilibrium constant (K) for the reaction is given by:

$$K = \frac{p_{CO}\,p_{O_2}^{1/2}}{p_{CO_2}} \qquad (3)$$

At high temperature, equilibrium of the above reaction may be assumed. From free energy data at 1300 K [9], $K = 1.47 \times 10^{-7}$. Assuming that the gas did not have any oxygen before introduction into the furnace, $p_{CO} = 2p_{O_2}$ from stoichiometry of Reaction 2. This gives us a value of equilibrium p_{O_2} in the gas equal to 2.38×10^{-6} atm (1 atm $= 1.013 \times 10^5$ Pa).

For experiments carried out in only nitrogen, from the flow rate of nitrogen and the weight gain of the sample, approximate oxygen balance calculations were performed for each experiment. This revealed that the gas train was not able to remove impurity oxygen from nitrogen to a level as low as the above value of p_{O_2} in N_2–CO_2 mixture. Hence, addition of CO_2 to N_2 was not expected to increase oxygen potential in nitrogen. Since the scale was dense and adherent, CO_2 molecules were not able to penetrate through the scale and react with the alloy directly. Therefore, the effect of CO_2 was restricted to the outer surface of the scale, and the arguments presented above explain why CO_2 behaved as an inert species in the case of Ti–24Al–15Nb.

In general, niobium-containing alloy showed improved oxidation resistance with dense and adherent scale, in this investigation. Although niobium oxide was not detected by XRD in any of the experiments, EDX elemental concentration maps revealed the presence of Nb along with Ti in the scale. Therefore, Nb seems to have acted as a dopant in the oxide scale, resulting in lowering of the defect concentration in TiO_2. This is expected to retard the motion of ions through the oxide scale, thus promoting oxidation resistance, and is one of the explanations proposed in the literature for the improved oxidation resistance of Nb-containing titanium aluminides [3].

In summary, rapid oxidation of Ti–25Al was caused by the presence of carbon dioxide in nitrogen, whereas it did not affect the rate in Ti–24Al–15Nb alloy.

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