Intermetallics xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Thermogravimetric investigation on oxidation kinetics of complex Ti-Al alloys

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ARTICLE INFO

Keywords:
A. Intermetallics
B. Thermal stability
Oxidation
C. Electron beam melting

ABSTRACT

The oxidation resistance in air of Ti-48Al-2Cr-2Nb, Ti-48Al-2Nb-0.7Cr-0.3Si, Ti-43.5Al-4Nb-1Mo and Ti-47Al-2Cr-8Nb alloys was investigated in the range of 800–1000 °C. Specimens were machined from the core of bars processed by Electron Beam Melting. Oxidation tests were performed in TGA equipment under isothermal conditions at different temperatures. The composition of the oxide layers was investigated by XRD, SEM-EDS and XPS. Layer exfoliation was observed, starting from different temperatures for the different alloys. When spallation did not happen in a significant extent the oxide layers grew according to a parabolic law. The kinetic rate constants and the activation energies were calculated. These kinetic parameters allowed to assess a rank of oxidation resistance, which can be correlated with the composition of the alloys.

1. Introduction

In the last 20 years, the titanium aluminides (TiAl) intermetallic alloys attracted significant interest in automotive and aircraft sectors because of their excellent behaviour at high temperatures. These alloys show a unique combination of properties such as low density (half of that of Ni-based superalloys), high strength in a wide range of temperature, high stiffness, good creep and fatigue resistance, rather good corrosion and oxidation behaviour. The most advanced TiAl alloys can be considered as an alternative for Ni-based superalloys as they show better specific strength up to 800 °C [1]. The replacement of Ni-based parts of gas turbines with titanium aluminides would result in the reduction of weight (20–30%) [2] and fuel consumption (20%), reduction of noise (50%) and NOx emissions (80%) [1]. The main lack of these alloys is the low ductility and fracture toughness at room temperature. Nevertheless significant improvements in microalloying, thermal treatments and manufacture processes of titanium aluminide alloys allowed to enhance the room temperature ductility, thus promoting in recent years the TiAl industrial applications. Several reviews in the literature report these achievements and the current state of the art [1–3]. The firstly developed TiAl alloys were used in automotive field for exhaust valves and turbocharger turbines [3–5]. The maximum operating temperature for turbocharger turbine ranges between 750 °C and 950 °C depending on the engine (diesel or gasoline) [5], but the exhaust gas temperature should increase up to 1050 °C in new gasoline engines designed to improve fuel efficiency. For this reason, a new Ti-31Al-8Nb-1Cr-0.5Si-0.03C wt.% alloy (DAT-TA2 by Daido) has been developed for this application [6]. GE is currently using Ti-48Al-2Nb-2Cr at.% for the low pressure turbine (LPT) blades of GEnx engine [7] and presently there are about 190,000 blades flying on Boeing 787 and Boeing 747–8. Pratt and Whitney is using instead the Ti-43.5Al-4Nb-1Mo-0.1B at.% alloy (TNM) in the LPT stage of GTF engine [8,9].

Several alloys were designed by optimizing the microstructure and exploiting the effect of alloying elements. The microstructure of the TiAl alloys of second and third generation mainly consists of two phases: ϒ-TiAl (ordered face centred tetragonal) and α_2-Ti_3Al (ordered hexagonal close packed). In addition, in some cases the β_0 -TiAl phase (body–centred cubic, disordered or ordered depending on the temperature) is present.

The composition of the TiAl alloys of second generation can be represented as follow (at.%):

Ti-(45–48)Al-(1–3)X-(2–5)Y-(< 1)Z; where: X = Cr, Mn, V; Y = Nb, Ta, W, Mo; Z = B, C, Si.

The third-generation can be classified as:

Ti-(42–44)Al-(0–10)X-(0–3)Y-(0–1)Z-(0–0.5)RE; where: X = Cr, Mn, Nb, Ta; Y = W, Mo, Hf, Zr; Z = B, C, Si; RE = rare earths.

Some alloying elements (Cr, Mn, V) are used to increase the ductility while Nb, Ta, W and Mo are added to improve the creep resistance [3]. In addition Nb and Mo are β stabilizers and the formation of this further phase, which shows an ordered structure at high temperatures, facilitates hot extrusion and hot forging [1]. It is recognized that the third generation TiAl alloys can operate up to 850 °C [1,10], but further improvements in terms of oxidation and creep resistance should be achieved in case there is a need to use these alloys at higher

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http://dx.doi.org/10.1016/j.intermet.2017.09.020
Received 31 May 2017; Received in revised form 26 September 2017; Accepted 28 September 2017

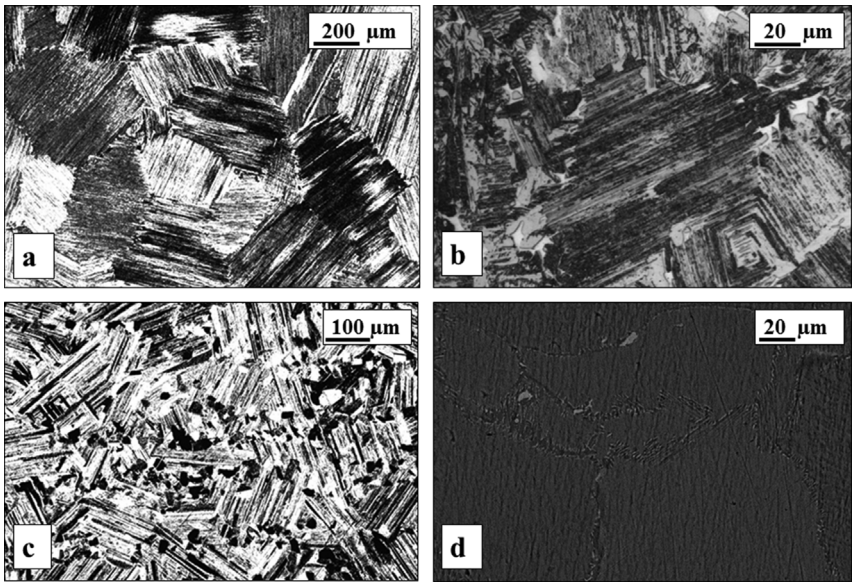

Fig. 1. Optical microscopy images: (a) Ti-48Al-2Cr-2Nb, (b) Ti-47Al-2Cr-8Nb, (c) Ti-48Al-2Nb-0.7Cr-0.3Si; (d) SEM image of Ti-43.5Al-4Nb-1Mo.

temperatures. Therefore, oxidation resistance still represents a strong limitation for their more extensive application in automotive and aerospace fields. Both coating adoption [10,11] and alloy composition changes can be used for improving oxidation resistance. However, to date, the long-term stability of the coatings and then their usability in service has not yet been proved. Also surface modification was investigated giving some encouraging results, for instance fluorination can appreciably improve for a long period the oxidation behaviour of TNM and Ti-48Al-2Nb-2Cr alloys [12].

The effect of alloying modification on the oxidation resistance has been well reviewed in the literature [10,13,14]. The oxidation resistance of TiAl alloys mainly depends on the aluminium content [14,15], because the bulk concentration of this element determines the ratio between alumina and titanium oxides within the oxide layer. In fact, alumina layers show a passivating behaviour and then they grow much slower than those made of titanium oxides [16]. For this reason the activation energy for oxidation increases with the Al to Ti atomic ratio in the TiAl alloy [17]. In addition, the aluminium content rules the ratio between γ and α_2 phases in the alloy microstructure. This ratio also affects the oxidation resistance, since aluminium diffusion occurs more quickly in γ-TiAl than in α_2-Ti_3Al (diffusion coefficients at 650 °C are equal to 1×10^{-21} m^2 s^{-1} and 1×10^{-23} m^2 s^{-1} respectively) [18]. It is recognized that some alloying elements (Nb, Mo, Si, W, Zr) can display a beneficial effect on the oxidation resistance of TiAl [2,3,10,13,19]. The addition of Nb enhances the oxidation resistance of TiAl, Ti_3Al [20] and Ti-48Al alloy [21] under both isothermal and cyclic oxidation conditions, even though a Nb content exceeding 10% at. becomes detrimental owing to the formation of Ti-Nb and Al-Nb mixed oxides [20]. The mechanism of growth for the oxide layer formed on TiAl is dominated by the inward diffusion of oxygen and the outward diffusion of aluminium [16,21], and Nb is able to hinder the diffusion of these two elements [22]. The beneficial effect of Mo has been attributed to its capability of increasing the alumina content in the external part of the oxide layer and decreasing contemporaneously the oxygen solubility in the bulk alloy [13,23]. The presence of silicon slows down the oxidation process owing to a barrier effect exerted by both silicides and silica [19,23,24], but the Si addition also causes the drawback of promoting the layer exfoliation [24]. The effect of other elements (e. g. Cr, Y) seems to depend on several factors: content in the alloy, general alloy composition and conditions adopted for the oxidation test [13,17]. For instance, in the ternary alloys, Cr has a detrimental effect if its content is below 4% at., but Cr displays a beneficial effect when its content increases over 8% at [17]. It has been also observed that Cr can display a synergistic effect with Nb in quaternary alloys [25]. A similar beneficial synergy was observed when using contemporaneously Nb (5–10% at.) and Si (1–5% at.) in quaternary Ti-Al-Nb-Si alloys [26]. In beta alloys like TNM the oxidation resistance can be positively affected by a synergy between Mo and Nb [12,27]. On the other hand beneficial effects on the oxidation resistance were not found when using contemporaneously Nb, Mo and Cr alloying elements [15], which is not consistent with the positive synergy provided separately by the couples of elements Nb-Cr and Nb-Mo. Therefore, it seems that both synergistic effects and not favourable interferences between different alloying elements can occur. On one hand, some useful indications about the action of the single alloying elements are given in the literature but, on the other hand, it is very difficult to foresee the oxidation behaviour of TiAl alloys with complex composition and different microstructures. In addition the oxidation response very likely depends also on several other factors like: experimental set-up used for oxidation study, temperature, kind of atmosphere, oxygen impurity formerly present inside the alloy [17] etc. For these reasons the kinetic parameters reported in the literature such as the parabolic rate constant [16,19] are spread in a wide range of values, also in the case of parabolic rate constants calculated for rather similar alloys. In this work, the oxidation kinetics of some of the most promising TiAl alloys was investigated under the same experimental conditions.

2. Material and methods

The alloys under investigation have been produced by electron beam melting; details about the processing path were given in previous papers [28–30]. In order to obtain a balanced set of mechanical properties the TiAl alloys are usually submitted to thermal treatments which result in optimized microstructures [28–30]. In this paper, the comparison of oxidation behaviour was carried out by submitting to TGA test different alloys showing microstructures that are currently selected for their applications (Fig. 1). The Ti-48Al-2Cr-2Nb (Ti-33.3Al-2.7Cr-4.8Nb wt.%) showed a fully lamellar microstructure (Fig. 1a), which is believed to grant the best creep resistance [31]. Near lamellar Ti-47Al-2Cr-8Nb (Ti-30.4Al-2.5Cr-17.8Nb wt.%) and Ti-48Al-2Nb-0.7Cr-0.3Si (Ti-33.5Al-4.8Nb-0.9Cr-0.2Si wt.%) alloys [29, 30], were investigated (Fig. 1b and c). The microstructure of Ti-43.5Al-4Nb-1Mo (Ti-28.6Al-9.1Nb-2.3Mo wt.%) [31], [32], consisted of lamellar γ/α_2 colonies with globular β_0 and γ grains at the grain boundaries, that can be clearly distinguished from the darker γ/α_2 colonies when using SEM [11,31,32] (Fig. 1d).