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Effect of alloying elements on the behaviour of TiAl-based alloys

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ABSTRACT

TiAl-based alloys containing Nb, Mo and Cr have been produced by induction melting both under an Ar atmosphere and in vacuum. Fracture toughness and isothermal oxidation tests at 900 °C have been performed on a number of alloys in order to evaluate the effect of alloying elements on both fracture toughness and hot corrosion. The results highlighted that there is an alloy composition range that could allow to obtain a good compromise between high temperature oxidation resistance and fracture toughness. In fact only for a selected Al/Ti ratio and a limited content of alloying elements it is possible to attain the alloy microstructural control and, for Mo free alloys, good protectiveness against oxidation.

1. Introduction

The potential of TiAl based alloys is seen in low density, high specific yield strength, high specific stiffness, good corrosion resistance at room temperature (RT), resistance against “titanium fire”, and good creep properties up to high temperatures [1]. Because of their ordered structure, intermetallics have high mechanical strength both at RT and at high temperature [2,3]. Despite that, TiAl-based alloys cannot be used as single phase alloys since they have a very low ductility at RT. The presence of a second α_2 phase (Ti_3Al) allows control of the microstructure. As far as mechanical properties are concerned, the addition of alloying elements such as Cr, V and Mn reduces the grain size with consequent ductility improvement. Depending on alloy composition and microstructure, these alloys exhibit good workability, medium-to-good tensile properties, tensile fracture strains in the range 1–3% at RT and fracture toughness values in the range 10–25 $\text{MPa}\sqrt{\text{m}}$ [4–7]. Various TiAl-based alloys have been developed. Adding transition metals of high melting temperatures is generally beneficial to increase the high temperature strength of these alloys [8–10]. More recently, the so-called 2nd and 3rd generation alloys have been developed in order to improve their mechanical properties and high temperature properties [1]. The 4th generation alloys, also called “air-hardenable”, have been intensively studied as potential materials for investment casting of low pressure turbine blades [11]. In the production of components made of TiAl-based alloys castability is very important for industrial applications as many TiAl components are manufactured by casting. The cost of manufacturing is increased by a high number of casting defects, which makes their application difficult [12,13]. To overcome this barrier, enormous efforts [5–12] have been devoted to preparing TiAl alloys with refined and homogeneous microstructure by alloying, heat-treatment, thermo-mechanical treatment (TMP), including isothermal forging, pack forging and rolling. Some authors refined the alloy microstructure by means of boron addition but it has been suggested that grain refinement using boron can increase the number of potential crack propagation sites, due to the appearance of aciculated boride particles. Therefore, new heat treatment process based on massive transformation, that does not rely on boron, is under development as a way of achieving grain refinement and thus improved mechanical properties [14,15]. Another aspect limiting TiAl alloy applications is their poor oxidation resistance above 800 °C. When these alloys are subjected to oxidation in air the scale is not a protective Al_2O_3 layer, but a mixture of Al_2O_3 and TiO_2. Several studies indicate that the TiAl alloys oxidation resistance is increased by the formation of a pure Al_2O_3 scale on their surface. In order to obtain such a continuous protective scale, a critical Al concentration in the alloy is requested. The oxidation resistance of TiAl based alloys is known to be significantly affected by the addition of ternary elements [16–22]. In fact improvements in the oxidation resistance of gamma alloys have been achieved by modifying the alloy compositions, particularly by the addition of Mo, W and Nb [16,21]. The positive effect of Nb and Mo is generally explained in terms of the doping effect and

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increase of aluminium activity and diffusivity [23]. The doping effect refers to a reduction of oxygen vacancy concentration in rutile lattice which are responsible for oxygen diffusion, due to the higher valency of Nb than of Ti. The increase of aluminium activity and diffusion rate results in the formation of a compact and protective alumina layer in the scales. As far as the other alloying elements are concerned their action mechanism and their synergistic effect are not still completely understood.

In this work we explored the effect of some alloying elements on fracture toughness and high temperature oxidation resistance of these alloys with the aim of finding an alloy composition that could improve RT workability as well as hot corrosion resistance.

2. Experimental

The alloys used in this work were produced by induction melting after 8 vacuum-argon washing cycles both under an Ar atmosphere and in vacuum from pure Ti, Al, Cr, Nb and Mo. In fact, considering the high affinity between the alloying elements and oxygen, initially casting and pouring were performed in a centrifugal furnace under an argon atmosphere. Afterwards, in order to improve casting soundness, castings have been manufactured by means of vacuum induction melting. The used crucibles were made of vitreous silica and zirconium oxide. Table 1 shows the composition (% at.) of the considered samples. The molten metal was cast directly into the rotating mould in order to obtain compact tension (CT) specimens. In fact our purpose was to evaluate the behaviour of as-cast alloys that should not be subjected to subsequent expensive treatments.

In this work several samples fractured during cooling or showed a delayed fracture [13]. The intact specimens were used for toughness tests, while isothermal oxidation tests were carried out at 900 °C on a representative number of alloys in order to evaluate their high temperature oxidation behaviour. In order to perform metallographic examinations on the specimen surfaces, they were ground to a mirror-like surface using SiC papers up to 1200 followed by 1 μm alumina and then etched in Keller's reagent. Metallographic structure and fracture surfaces were inspected by scanning electron microscope (SEM) and microanalyses were carried out by energy dispersion spectroscopy (EDS). Image analysis for determining the quantity of β phase formed was performed on a number of representative specimens by means of Leica Application Suite software.

3. Results and discussion

In our experiments the alloy composition was changed (Table 1) in order to evaluate the effect of alloying element concentration on fracture toughness and oxidation resistance.

Over the last few years our research group produced and studied many TiAl intermetallic alloys with the aim of optimising both high temperature oxidation behaviour and fracture toughness. The difficulty of doing so is that alloying elements that are beneficial for improving oxidation resistance are usually detrimental for fracture toughness.

In order to achieve reliable results a number of specimens has been produced and tested. To understand the effect of the considered alloying elements on fracture toughness, oxidation resistance and residual stresses, experimental results are reported in Fig. 1, where each alloy is positioned in a graph according to its Al/(Al + Ti) ratio and to its content of β-stabilising elements. Considering that the alloying elements have different β-stabilising effect that could be quantified by using the molybdenum equivalent [24], the data in Fig. 1 could be reported as a function of it. Despite that the use of the Mo equivalent in the plot is not useful for discussions on the oxidation behaviour at high temperature of these alloys. In fact this behaviour is strictly related to the actual content of Mo, Nb and Cr that have different effect on the hot corrosion resistance.

Fig. 1 highlights that for a percentage of β-forming elements higher than 11% at. the produced alloys are going to break up either during or after cooling, while for a β-forming element percentage lower than 11% at. the alloys are going more likely to crack during the production process as far as the aluminium concentration increases.

K_{IC} values characterising the tested alloys vary over the range 11.3–23.8 MPa$\sqrt{m}$, the highest values being reached with alloys containing 5% at. of β-forming elements on average. This behaviour can be understood by observing Fig. 2 that shows some representative SEM micrographs. In fact TiAl based alloys produced in this research are characterised by different microstructures. Alloy 10, containing 2.6% at. Cr and 3.1% at. Nb, shows a lamellar microstructure and a K_{IC} value of about 21.8 MPa$\sqrt{m}$. Alloy 21, containing 11.9% at. of β-stabilising elements, is characterised by uniformly distributed fine lamellar colonies and a small quantity of residual β phase distributed around colony boundaries (bright phase in Fig. 2b). This microstructure determines a quite low fracture toughness (11.3 MPa$\sqrt{m}$). Alloy 22 containing a quantity of β-forming elements even higher than Alloy 21 shows β phase precipitated around colonies and from lamellar interfaces (Fig. 2C). Generally speaking the disordered bcc structure of β phase is softer than α and γ phases at elevated temperature and it is expected to facilitate thermomechanical processing of TiAl alloys. However, it has been reported that both the coarse β particles existing in colony boundaries and excessive β phase precipitating from lamellar interfaces deteriorate room-temperature ductility, while the precipitation of very fine β particles is considered as intrinsic toughening

Table 1
Chemical composition and fracture toughness of the tested specimens (BM = specimen broken in the mould, MC = specimen broken during machining, NF = specimen not subjected to fracture toughness test).

	Al (% at.)	Ti (% at.)	Cr (% at.)	Nb (% at.)	Mo (% at.)	K_{IC} (MPa$\sqrt{m}$)		Al (% at.)	Ti (% at.)	Cr (% at.)	Nb (% at.)	Mo (% at.)	K_{IC} (MPa$\sqrt{m}$)
Alloy 1	48.1	47.1	2.5	0.1	2.0	23.8	Alloy 15	45.8	47.2	2.7	2.0	2.3	21.3
Alloy 2	47.8	47.5	2.1	0.4	2.2	16.6	Alloy 16	48.0	44.0	2.0	6.0	–	NF
Alloy 3	49.1	45.8	2.4	0.3	2.3	15.3	Alloy 17	44.3	46.4	–	7.4	1.2	14.9
Alloy 4	48.0	47.0	2.0	3.0	–	NF	Alloy 18	42.8	47.7	2.4	5.1	1.1	22.0
Alloy 5	44.4	50.6	2.4	0.2	2.5	21.3	Alloy 19	45.9	45.1	3.0	4.2	1.6	MC
Alloy 6	48.8	45.9	2.8	0.6	1.9	16.9	Alloy 20	48.3	42.0	1.8	2.8	5.1	BM
Alloy 7	48.1	46.2	2.6	0.3	2.4	15.9	Alloy 21	42.4	45.6	2.8	5.2	3.9	11.3
Alloy 8	47.3	47.3	2.7	0.5	2.2	15.5	Alloy 22	46.7	40.3	4.2	3.5	5.2	MC
Alloy 9	47.9	46.6	2.8	0.5	2.2	23.8	Alloy 23	38.9	48.2	4.6	2.9	5.5	MC
Alloy 10	44.2	50.0	2.6	3.1	–	21.8	Alloy 24	39.2	47.4	4.8	3.3	5.0	BM
Alloy 11	48.4	45.5	–	4.3	1.5	MC	Alloy 25	43.4	42.2	5.7	5.7	2.3	BM
Alloy 12	44.3	49.8	2.6	3.3	–	19.6	Alloy 26	38.2	47.5	4.5	3.5	6.1	BM
Alloy 13	46.9	47.3	3.5	0.4	2.0	21.3	Alloy 27	32.0	52.7	5.8	5.4	4.2	BM
Alloy 14	52.1	41.2	–	4.7	1.6	BM	Alloy 28	44.9	38.3	3.9	5.9	7.0	BM