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The influence of implanted chromium and yttrium on the oxidation behaviour of TiAl-based intermetallics

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The influence of implanted chromium and yttrium on the oxidation behaviour of Ti–50Al (at %) in air at 800 °C was investigated. It was found that implanted chromium and/or yttrium leads to a decrease of the oxidation rate because an alumina scale was formed on the implanted material in the early stages of oxidation, whereas a titania-based scale grew on the non-implanted material. With increasing oxidation time the difference in oxidation behaviour between the implanted and non-implanted alloy gradually disappeared. These results show that chromium and yttrium, provided their concentration is properly chosen, can have a similar positive effect on the oxidation behaviour of TiAl-based intermetallics as they have on the oxidation behaviour of conventional Fe-, Ni-, or Co-based alumina-forming high temperature alloys.

1. Introduction

Among the various potentially suitable, newly developed high temperature materials, intermetallic-based alloys are promising candidates for replacing conventional high temperature alloys in a number of applications. Materials on the basis of the intermetallic compound TiAl offer, e.g. interesting properties for turbine application due to their high temperature strength in combination with low density [1]. For this type of application however, most titanium aluminides possess insufficient oxidation resistance at the envisaged service temperatures (700–900 °C) [2–5]. The reason for this is, that the alloys generally form rapidly growing titania-based scales rather than a protective alumina layer [6]. The mechanisms of the oxidation of the TiAl-based materials, especially with respect to the effect of ternary and quaternary alloying additions, are only poorly understood and in many cases the results appear to be contradictory. For example, it is not known why additions of elements such as chromium and yttrium, which promote formation of protective alumina scales on conventional Fe-, Ni-, Co-based high-temperature alloys, are often found to decrease the oxidation resistance of TiAl-based intermetallics [7, 8].

Ion implantation is an alternative method compared to traditional metallurgical procedures for studying the effect of alloying additions on oxidation behaviour [9]. With ion implantation it is possible to produce a thin layer in the base material, in which a ternary element is enriched. In this layer the concentration of the implanted element can be higher than its equilibrium solubility in the alloy. Due to this markedly changed composition, the modified layer can strongly affect the oxidation behaviour, especially in the early stages. In the present paper the results of studies on the influence of implanted chromium and yttrium on the oxidation behaviour of Ti–50Al (at %) at 800 °C will be presented.

2. Experimental details

The studied binary titanium aluminide was produced by vacuum induction melting of the elemental mixture. The solidification of the melted alloy occurred in a ceramic mould. The composition of the alloy is listed in Table I and its microstructure shown in Fig. 1. The brighter areas consist of γ-TiAl, and the darker ones are eutectoid mixtures of γ-TiAl and α_2-Ti_3Al.

For oxidation studies specimens in the form of flat discs with a thickness of 1 mm and a diameter of 10 mm with mirror-like surfaces were prepared. SiC grid papers and 1 μm diamond powder were used for the grinding and polishing of the samples. Some of the

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TABLE I Chemical composition of the studied alloy (concentrations of Al and Ti in at %/concentration of the impurities in wt ppm)

Ti	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Zr	Nb	Sn	Sb	W	Ta	Pt
49.3	50.1	44	30	50	94.6	9	24	40	7	160	14	2.3	2.1	23	3.0	21	1.2	< 1

Figure 1 Microstructure of the studied alloy, Ti–50Al (at %)

samples were implanted with Cr and Y ions. The doses applied were 5×10^{16} and 2×10^{16} ions cm^{-2} for chromium and yttrium, respectively. For studies on the oxidation kinetics, the specimens were implanted on both sides. The edges of the samples were not implanted. The ions were accelerated to an energy of 70 keV. For scale morphology studies different implantation doses were applied to different locations of one sample, as illustrated in Fig. 2. The oxidation kinetics were studied in a ROBAL thermobalance at 800 °C in synthetic air (gas flow 10 l h^{-1}) for exposure times of 15 h. The oxidation products were studied by optical and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX).

3. Results

3.1. Oxidation kinetics

The influence of implanted chromium and yttrium on the oxidation kinetics of the studied alloy is shown in Fig. 3a and b. It follows from these plots that in all cases, both implanted elements remarkably decreased the scale growth rate. The decrease in oxidation rates was clearly visible during the first hour of oxidation, even when it was taken into account that titanium atoms in titania tie up more oxygen than aluminium atoms in alumina (Fig. 3a). After a longer oxidation time, the differences in oxidation behaviour between the differently treated samples gradually disappeared (Fig. 3b).

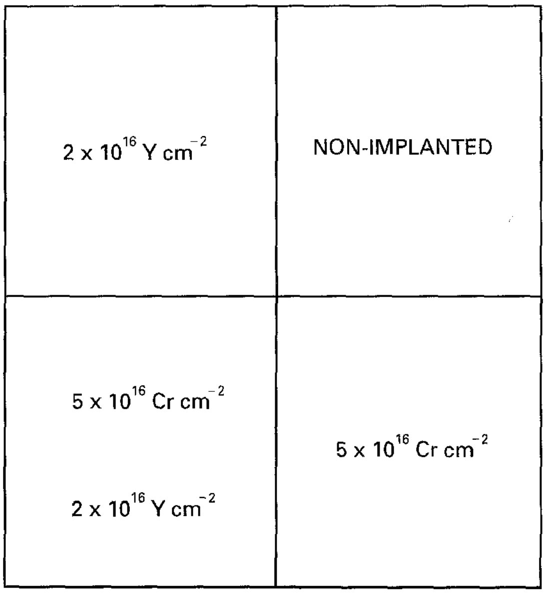

Figure 2 Schematic illustration of implantation areas on the specimens for morphology studies

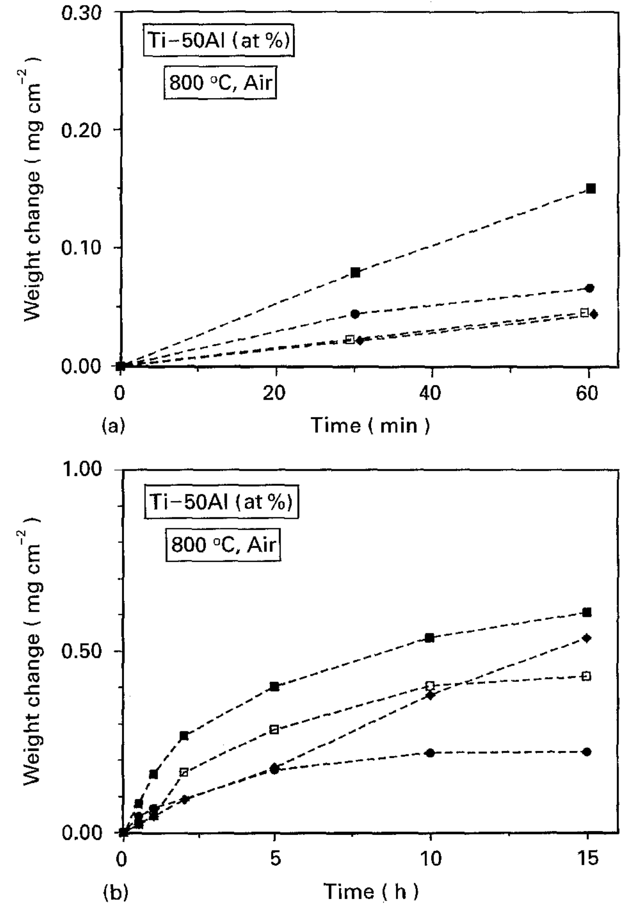

Figure 3 Influence of implanted chromium and/or yttrium on the weight change of Ti–50Al during isothermal oxidation in air at 800 °C. Weight changes (a) during the first hour of oxidation, and (b) during 15 h. -■- Non-implanted (CEC124); -□- Cr implanted (CEC104); -◆- Y implanted (CEC013); -●- Cr + Y implanted (CEC110).

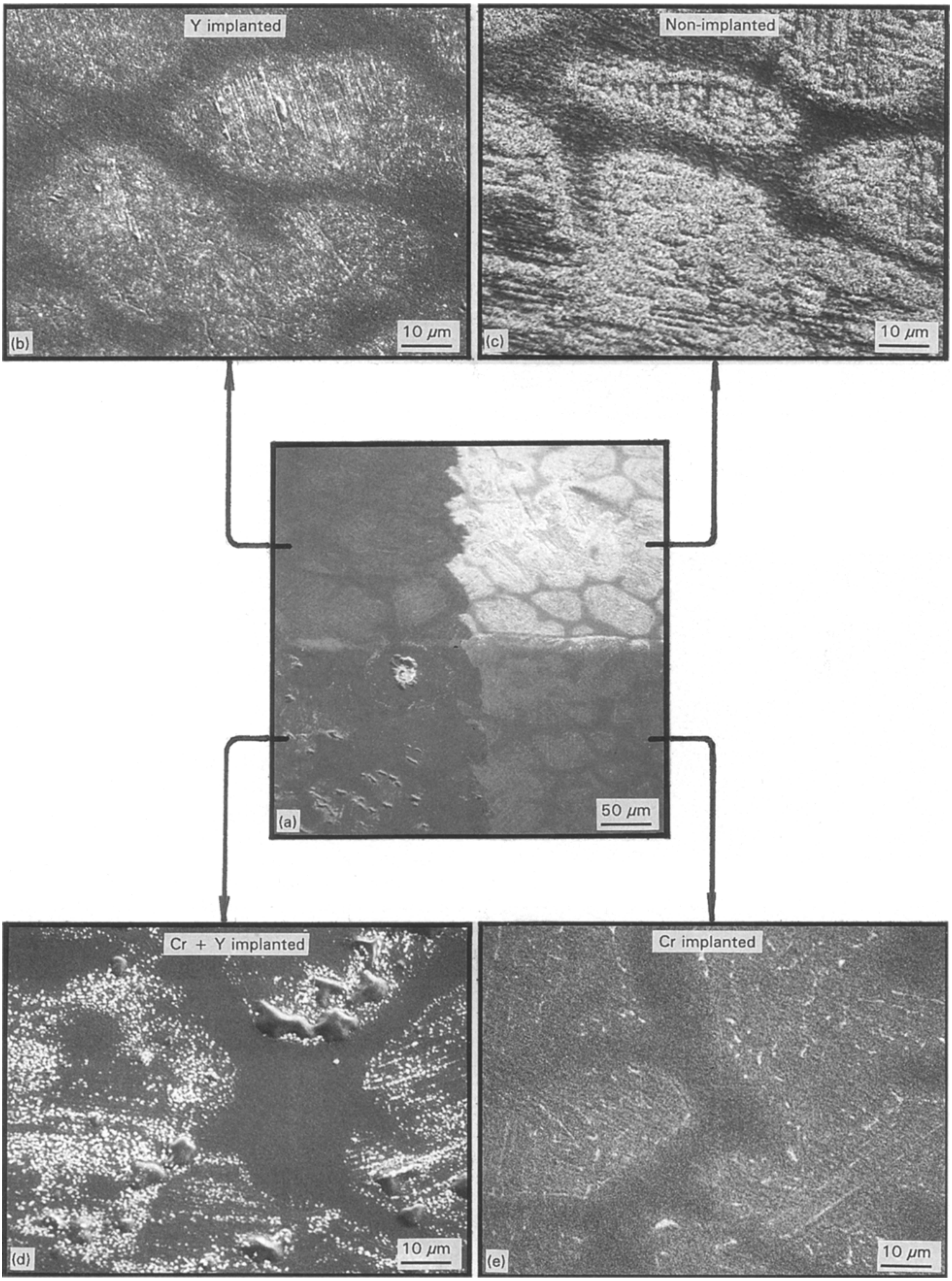

Figure 4 Oxide surface morphology (SEM) of sample implanted with different elements after 1 h exposure in air at 800 °C.

3.2. Scale composition and structure

Investigations with SEM and optical microscopy were carried out on specimens exposed for 1 and 24 h at 800 °C. For easier comparison of the scale morphologies on the non-treated materials with those of the implanted ones, different areas on one sample were implanted with the two elements (Fig. 2).

The oxide morphology studies confirmed the gravimetric results, showing that implantation leads to a decrease in the oxide thickness. It was shown

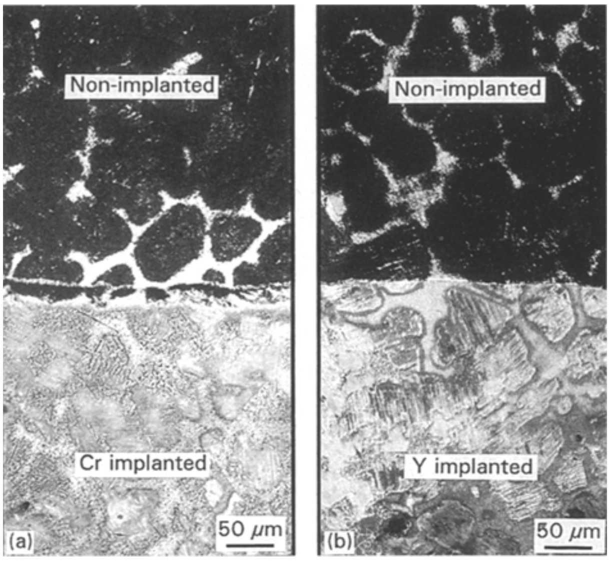

Figure 5 Scale morphology of the various regions on the implanted sample (as Fig. 4) in light microscopy.

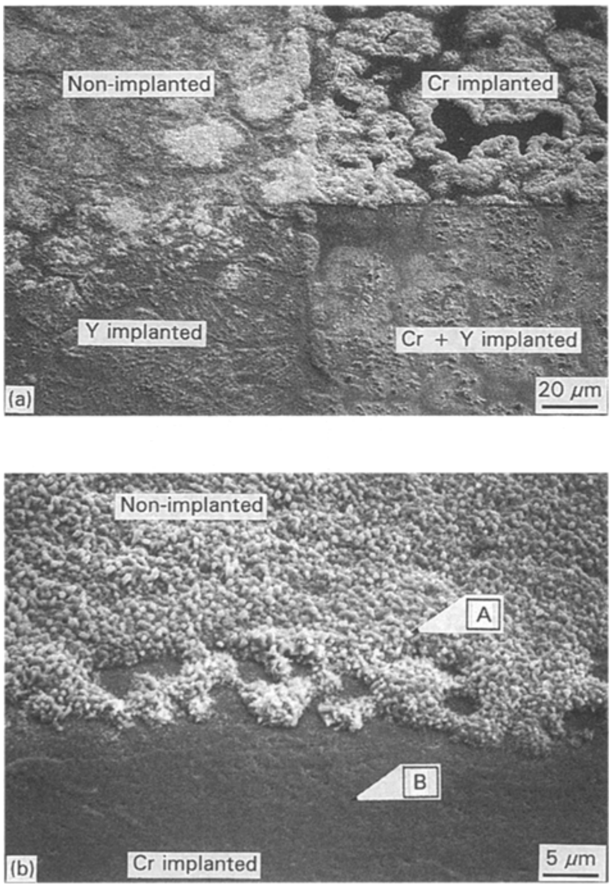

Figure 6 (a) Surface morphology of the oxide scale on a sample implanted with different elements after 24 h exposure in air at 800 °C (areas like in Fig. 4). (b) Boundary between alumina and titania-rich scale.

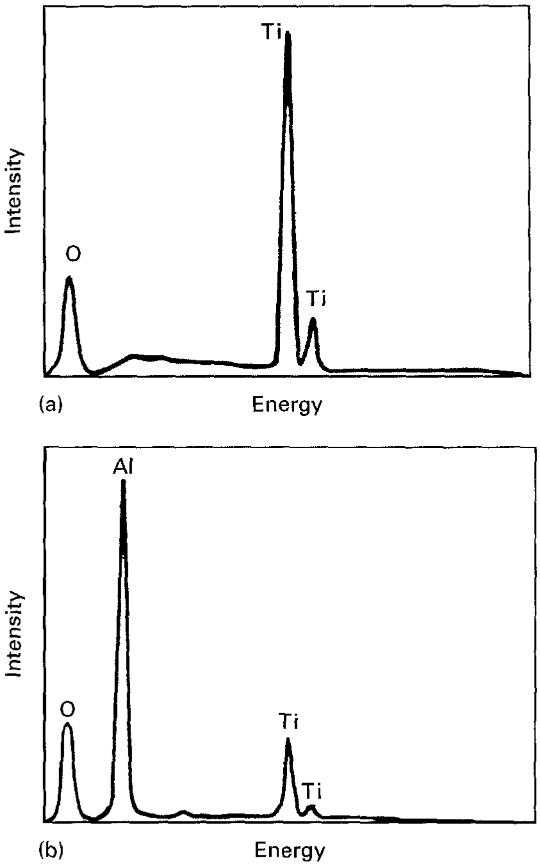

Figure 7 EDX spectra in selected regions of oxide scale shown in Fig. 6b.

previously, that the γ-TiAl, present in the microstructure (Fig. 1) forms an alumina scale on high temperature exposure, whereas the α_2-phase, which is present in the form of an α_2–γ eutectoid structure, forms a rapidly growing titanium oxide [10]. Compared to the non-implanted material a reduction in the formation of fast growing TiO_2 on the two-phase lamellar structure regions was observed after 1 h oxidation on all implanted areas (Fig. 4). Fig. 5 shows the surface morphology of the scale in two selected regions studied using light optical microscopy. A very thin alumina scale, which is transparent to light, formed on the chromium and yttrium implanted regions (bright areas). In contrast, a non-transparent thick titania-based scale (dark areas) formed on the non-implanted region. The thick titania-based scale was formed mainly on the two-phase lamellar α_2/γ structure. The areas in this two-phase region which were initially covered by an alumina layer, gradually disappeared with increasing oxidation time. In spite of this tendency, regions with an alumina scale, which formed on the γ-region, existed even after 24 h oxidation (Figs 6 and 7).

4. Discussion

The studied Ti–50Al (at %) alloy is a two phase material. The microstructure of the alloy consists of two types of grains: oval-like grains, consisting of an eutectoid structure of α_2-Ti_3Al and γ-TiAl as well as path-like Al-rich grains consisting of γ-phase (Fig. 1). This structure is a result of the applied casting procedure. The solidification process of the liquid alloy begins with formation of α-Ti crystals (solid solution of Al in Ti) in which the concentration of aluminium is smaller than the average aluminium concentration in the alloy (Fig. 8, point A). With decreasing temperature, the

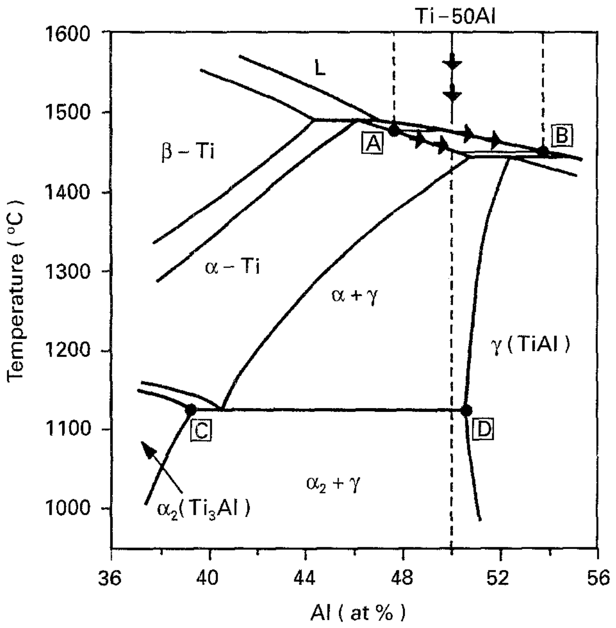

Figure 8 Part of the Ti–Al phase diagram [11], illustrating precipitation of various phases during cooling of Ti–50Al from the melt.

amount of solid α-Ti increases whereas the remaining liquid part of the alloy becomes more and more enriched with aluminium until its concentration reaches point B. Consequently, the remaining liquid part of the alloy after solidification forms aluminium-enriched γ-TiAl path-like grains between the primary formed α-Ti oval grains. At 1125 °C, the α-Ti grains transform into a two-phase lamellar structure (polysynthetically twinned crystals, PST) due to eutectoid reaction ($\alpha \rightarrow \alpha_2 + \gamma$). The average concentration of aluminium in these two-phase grains is the same as that of the primary formed α-Ti crystals.

After 1 h exposure the non-implanted material showed mainly a titania scale, except in those areas of the alloy where very large γ-TiAl grains were present. Implantation of chromium and/or yttrium led to the formation of a continuous alumina layer on practically the whole surface of the alloy. Also the thermogravimetric results showed a significant smaller mass gain of the material implanted with Cr and/or Y than for the non-implanted material.

All these results indicate that chromium and yttrium alloying additions can have a similar positive effect on the oxidation behaviour of TiAl intermetallic based materials as on the oxidation behaviour of conventional alumina forming Fe-, Ni- or Co-based high-temperature alloys: both elements tend to enhance the selective oxidation of aluminium. Comparison with literature data [7, 8] indicates that this positive effect requires a sufficiently high concentration of chromium and/or yttrium which can be achieved in the surface regions of the alloy by ion implantation. This result confirms studies in which it was found that an addition of 2 at % Cr to Ti–48Al enhanced the growth rate of the mixed titania/alumina scale [7, 8] whereas an addition of 5 at % tended to promote the formation of a protective alumina scale [11]. After longer oxidation time the positive effect of the implanted yttrium and/or chromium vanishes as the yttrium and/or chromium content is extremely low in respect to the total specimen size. If after longer times, the concentration of the implanted elements is too low to stabilize an alumina scale, the two elements can affect the oxidation behaviour in a different manner, e.g. by doping of the titania by three-valent Y and Cr ions which then could even lead to an enhancement of the scale growth rate [7, 8]. In the case of yttrium an additional factor can play a role: if yttrium is added to the titanium aluminide as an alloying element, it tends to be tied up in the form of an intermetallic compound which is precipitated at the alloy grain boundaries [7]. Upon high temperature exposure of the alloy the yttrium tends to severely oxidize internally because of the higher thermodynamic stability of yttria compared to titania or alumina [7]. This internal oxidation leads to an additional oxygen uptake, indicating a higher corrosion rate during thermogravimetric analysis.

5. Conclusion

Implantation of chromium and/or yttrium to the intermetallic compound Ti–50Al (at %) in sufficiently high doses favours the formation of an alumina scale thereby suppressing the formation of rapidly growing titania. This indicates that the alloying additions of both elements can act similarly on the oxidation behaviour of TiAl-based materials as on that of conventional Fe-, Ni- or Co-based alumina-forming high temperature alloys. The amount of implanted yttrium and/or chromium is, however, too small to sustain this positive effect over longer times. Comparison with literature data indicates that after breakdown of the alumina scale and subsequent formation of rapidly growing titania, both yttrium and chromium can then even be detrimental, perhaps due to doping of the titania and/or formation of internal oxides.

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