

NANOCRYSTALLINE γ -TiAl BASED MICROALLOYED COATINGS AS GAS CORROSION BARRIERS

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Abstract. γ -titanium aluminide is a promising structural material for use in automotive and aircraft applications due to its low density and creep and a relatively high strength even at the temperature as high as 1200K, however its resistance to gas corrosion at high temperatures still needs to be improved. It has been proved in the work by means of SEM, EDS, EBSD, X-Ray and microthermogravimetric analyses at 1173K that a great improvement of this resistance has been achieved due to Ag or Cr or Nb or Mo or Si or Ta microalloyed γ -TiAl based magnetron sputtered nanocrystalline coatings.

1. INTRODUCTION

γ -titanium aluminide is a promising structural material for use in automotive and aircraft applications due to its low density and a relatively high strength and low creep even at the temperature as high as 1200K [1-4]. Nevertheless, some of its properties (as, for example, poor oxidation resistance at high temperatures over 1000K or poor toughness at ambient temperature) still need to be improved. Numerous research groups try to improve the high-temperature oxidation resistance of the γ -TiAl aluminide by alloying it in the bulk with single or multiple elements or by means of various surface treatments including surface coatings. On the other hand, alloying of the γ -TiAl in the bulk may have a deleterious effect on the mechanical properties of the material [5-7]. As opposed to the last method, alloying of thin γ -TiAl aluminide coating on non-alloyed γ -TiAl substrate does not aggravate so much the mechanical properties of the former due to important influence of the surface/coating interface. Moreover, the protective properties of the γ -TiAl coating against oxidation can be increased to

a great extent due to nanocrystallinity of the coatings [8-10]. In numerous papers deposition of the coatings is being executed by means of magnetron sputtering [11-14].

It was the aim of the present work to investigate first the morphology of the oxide scale formed on the bare γ -Ti40%at.Al substrate and next the effect of ternary elements additions (Ag, Cr, Mo, Nb, Si, Ta or W) or quaternary ones (Cr + Nb, Ta + Nb, W + Cr or Ag + Si) to the magnetron sputtered γ -TiAl based coatings onto the protective properties of the coatings against oxidation.

2. EXPERIMENTAL

γ -Ti40at.%Al alloy has been used as the substrate. At first 15 mm diameter disks 0.5 mm thick have been cut off from the primary ingots. In the next step the both flat surfaces of the disks have been ground up to a 1500 grit finish with SiC paper, then ultrasonically cleaned in acetone and used as specimens. The micro-alloyed γ -TiAl aluminide coatings with different ternary or quaternary elements have been co-deposited by magnetron sputtering on all

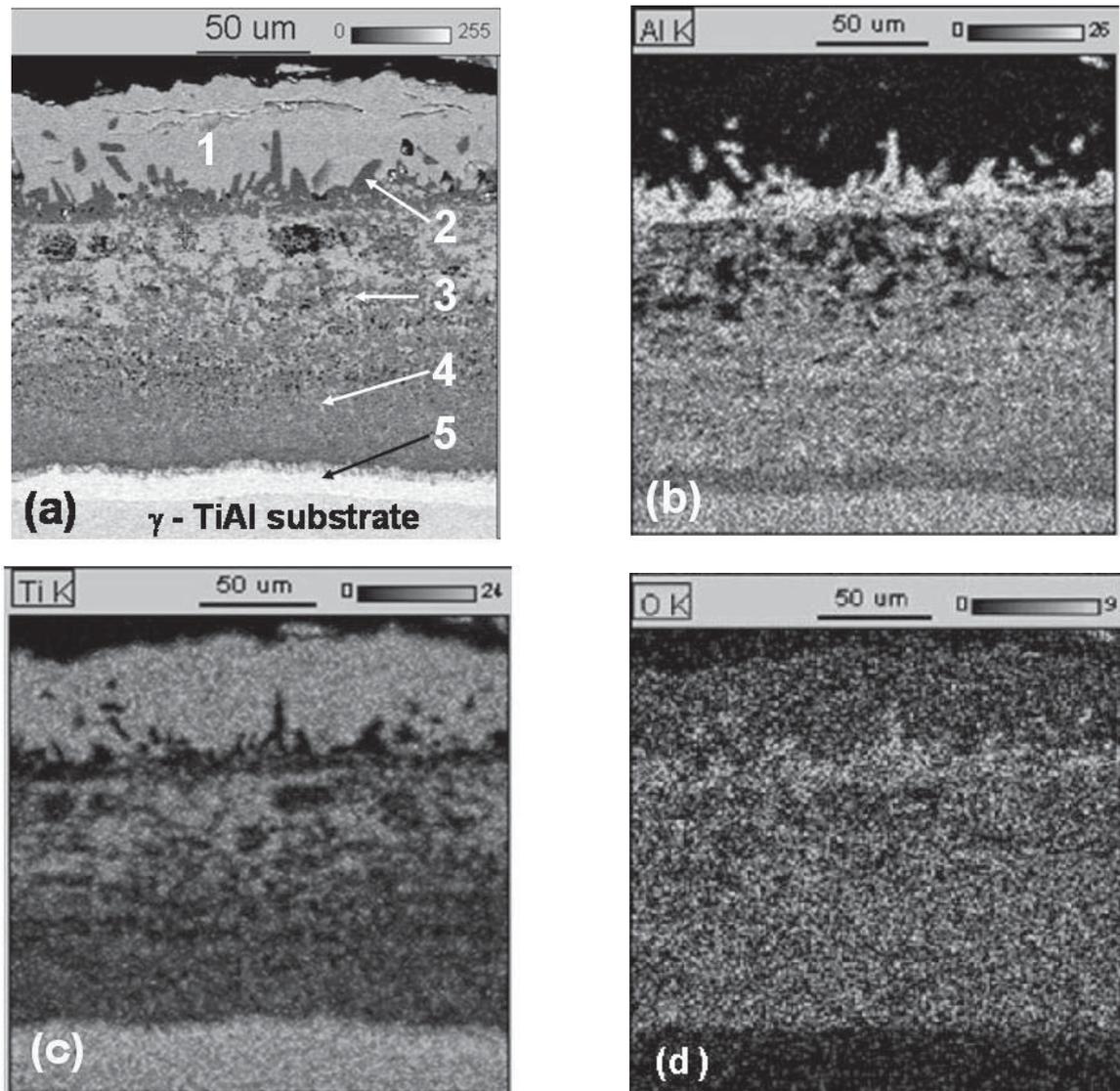


Fig. 1. BSE image of cross-section of the oxide scale on bare γ -TiAl substrate after isothermal oxidation in static air at the temperature of 1173K during the period of 120 hours (a) and the surface distribution of aluminum (b), titanium (c), and oxygen atoms (d), respectively.

sides of the rotating γ -TiAl specimens in a vacuum chamber equipped with four independent magnetrons [15]. High purity silver, titanium, aluminium, chromium, niobium, molybdenum, silicon, or tantalum discs were used. The deposition has been conducted in Ar atmosphere at the pressure 0.02 Pa at the substrate temperature approximately 400K. Isothermal oxidation tests have been performed at 1173K in static air under atmospheric pressure. The weight gain of the specimens was measured in an intermittent way with use of an analytical balance with accuracy of $1 \cdot 10^{-4}$ g. The results of the high-temperature oxidation have been analysed and com-

pared with the relevant characteristics of bare γ -TiAl substrate. The accompanying changes in the morphology, microstructure, chemical and phase composition of the amorphous primary deposits have been investigated by means of SEM, X-Ray, EBSD and EDS methods.

3. RESULTS AND DISCUSSION

3.1. Oxidation of bare substrate

Scale structure on bare γ -Ti40%at.Al substrate after isothermal oxidation in static air during 120 hours at 1173K is presented in Fig. 1a. Five different

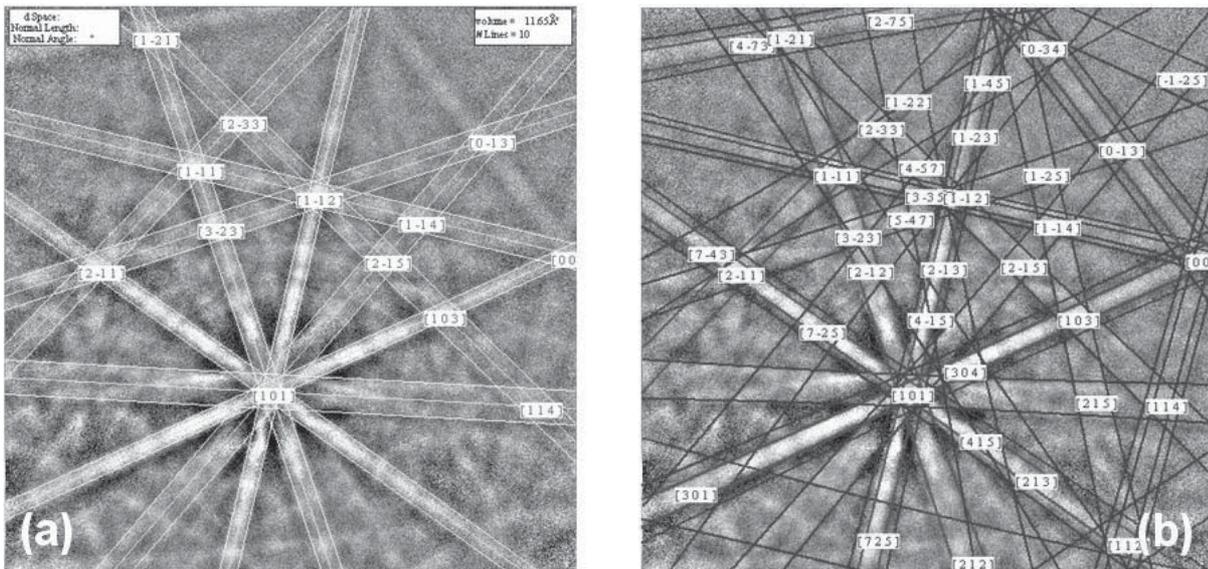


Fig. 2. (a) EBSD diffraction pattern from the area marked 1 in Fig. 1a with indexed planes; (b) diffraction pattern simulation performed for the TiO_2 phase from card Nr. 77-0441 of the ICDD data base.

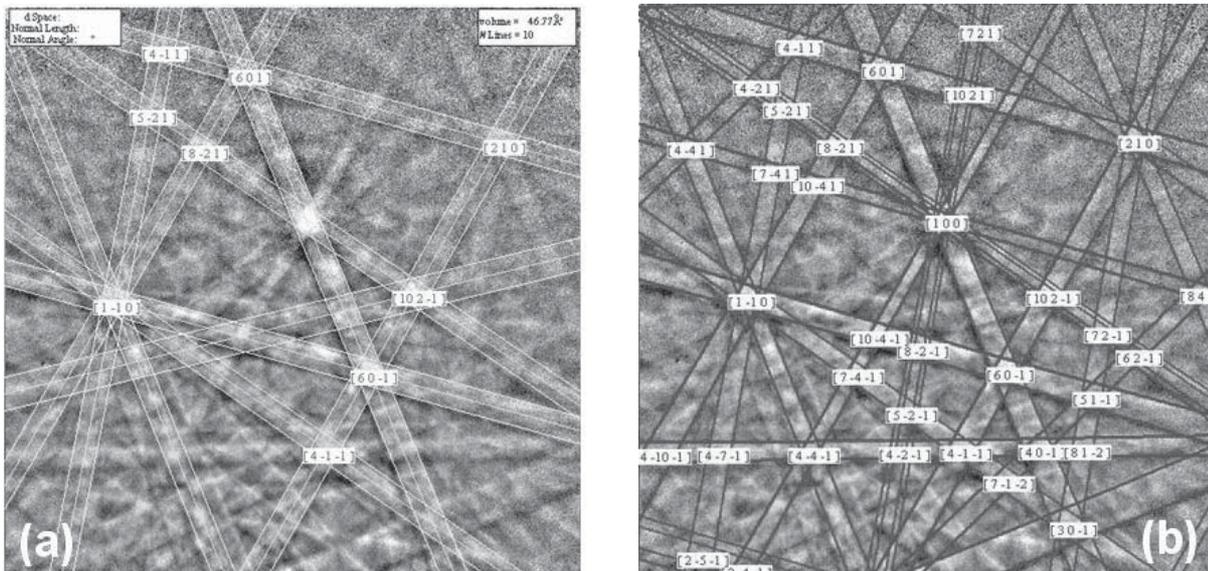


Fig. 3. (a) EBSD diffraction pattern from the area marked 2 in Fig. 1a with indexed planes; (b) diffraction pattern simulation performed for the Al_2O_3 phase from card Nr. 46-12-12 of the ICDD data base.

sublayers (marked 1 to 5) have been observed on the cross-sections of the specimen. Surface distribution of elements obtained by means of electron energy dispersive spectroscopy (EDS) is given in Figs. 1b - 1d and the phases identified on the section by means of the electron back-scattered diffraction (EBSD) are given in Figs. 2 and 3. It follows from these figures that the outer layer in the scale marked 1 in Fig. 1a was composed mostly of rutile. The best fit was attained for the TiO_2 lattice described

in the card number 77-0441 of the ICDD data base. The inner sublayer of the scale marked 2 in Fig. 1a was composed of $\alpha\text{-Al}_2\text{O}_3$ grains (see Fig. 3) and the best fit was attained for the Al_2O_3 lattice described in the card number 46-12-12 of the ICDD data base. The next sublayer of the scale marked 3 in Fig. 1a was composed of a mixture of TiO_2 and Al_2O_3 grains. Phase composition of the next layer marked 4 in Fig 1a was similar to the previous one with the distinction that the grains of TiO_2 and Al_2O_3

Table 1. Oxidation conditions, samples' designations and parabolic rate constants of oxidation of different coatings on γ -Ti40at.%Al substrate.

Sample No.	Substrate	Coatings	Oxidation conditions	Parabolic rate constants k_p [g·cm ⁻⁴ ·s ⁻¹]
1		Without coating	In static air at the temperature of 1173K during the period of 120 hours	$2,61 \cdot 10^{-9}$
2		γ -Ti50%at.Al		$8,62 \cdot 10^{-11}$
3		γ -TiAl(0.88 at. %Nb)		$1,81 \cdot 10^{-11}$
4		γ -TiAl(4.14 at. %Nb)		$5,79 \cdot 10^{-13}$
5		γ -TiAl(4.72 at. %Cr+5.89 at. %Nb)		$8,33 \cdot 10^{-13}$
6		γ -TiAl(1,06 at. %Ta)		$5,27 \cdot 10^{-11}$
7		γ -TiAl(4,05 at. %Ta)		$6,31 \cdot 10^{-13}$
8	γ -Ti40	γ -TiAl(5,7 at. %Ta+5,89 at. %Nb)		$3,75 \cdot 10^{-11}$
9	at.%Al	γ -TiAl(4,17at.%W+3,79 at.% Cr)		$8,33 \cdot 10^{-13}$
10		γ -TiAl(1,9 at.%Si)		$4,54 \cdot 10^{-12}$
11		γ -TiAl(3,97 at.%Si)		$5,79 \cdot 10^{-13}$
12		γ -TiAl(1,88 at.%Ag)		$4,69 \cdot 10^{-11}$
13		γ -TiAl(3,36 at.%Ag)		$3,7 \cdot 10^{-11}$
14		γ -TiAl(2,86 at.%Ag+6,33 at.%Si)		$2,05 \cdot 10^{-12}$
15		γ -TiAl(1,29 at.%Mo)		$9,26 \cdot 10^{-12}$
16		γ -TiAl(7,56 at.%Mo)		$8,33 \cdot 10^{-13}$

phases are smaller than in the case of the sublayer No. 3. Lower down there was an intermediate layer marked 5 in Fig. 1a which was more rich in titanium than the substrate due to upward diffusion of Al atoms. These results suggest that bare γ -TiAl substrate has poor oxidation resistance at the temperature of the investigation due to complex structure of the oxide scale and different thermal expansion coefficients of the constituent phases [15]. To improve this resistance different microalloyed γ -TiAl based coatings have been deposited onto the γ -TiAl substrate.

3.2 Scale investigation on coated substrate

The chemical compositions of different coatings deposited onto the γ -Ti40at.%Al substrate and their oxidation rate constants k_p as well as designations of the samples are given in Table 1. The thickness of the coatings was about 4 μ m (Fig. 4). An example of the fracture of the sample No. 14 before and after 120 hours oxidation in static air is given in Fig. 5. One can see from Fig. 4 that the micro-al-

loyed γ -TiAl coatings have a uniform, dense, small grain structure as opposed to the coarse-grained γ -TiAl substrate. Moreover, no cracks have been observed neither in the coating nor at the interface coating/substrate (Fig. 4). The very good adhesion between the substrate and the coatings is evidently due to perfect compatibility of the coatings and the substrate under consideration: all of them are based on the γ -TiAl phase. The characteristic feature of the micro-alloyed coatings under investigation was that their structure after oxidation was non-uniform: a thin and dense Al_2O_3 oxide layer of the thickness about 1 μ m has been created on the coating's surface (Fig. 4; see also [16,17]). The X-Ray diffraction profile of the α - Al_2O_3 phase has been performed with use of X'Pert PHILIPS powder diffractometer working in continuous mode with use of a strip detector of monochromatic CuK_α radiation and Bragg-Brentano geometry. The identification of this phase has been performed with use of the ICDD data base. This important finding – formation of only α - Al_2O_3 scale without TiO_2 phase in the present study should be attributed to the small grain, dense structure of the magnetron sputtered coatings and, to some

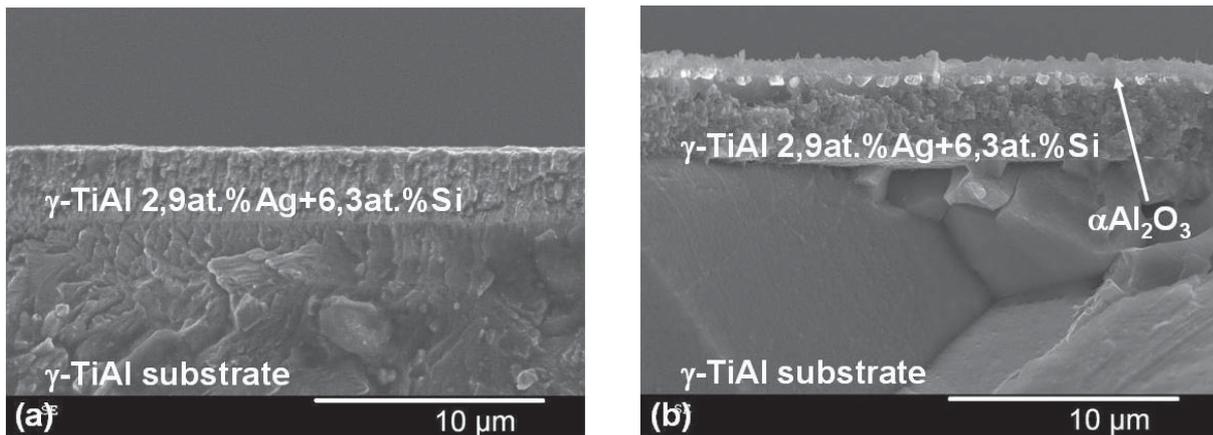


Fig. 4. SEM morphology of the fracture of the sample No. 14 coated with $\gamma\text{-TiAl}$ (2.9 at.%Ag, 6.3 at.%Si) before (a) and after (b) oxidation in static air during the period of 120 hours at 1173K.

extent, to the effect of the ‘third element’ (as Ag or Cr or Mo or Nb or Si or Ta): both of them are conducive to the increase of the Al diffusivity in the coating and, subsequently, to preferential nucleation and growth of the $\alpha\text{-Al}_2\text{O}_3$ phase [18]. It is well known that the α -corundum is thermodynamically very stable and that the diffusion coefficient of the oxygen atoms in this phase is the smallest one among the materials known nowadays [19]. The morphology of the oxide scale is changing to a great extent as well: the mean grain size of the $\alpha\text{-Al}_2\text{O}_3$ crystallites on the surface of the non-alloyed $\gamma\text{-TiAl}$ coating is about one order of magnitude less than that of the TiO_2 crystallites on the surface of bare $\gamma\text{-TiAl}$ substrate (Fig. 5). With increase of concentration of the alloying elements (Ag or Cr or Mo or Nb or Si or Ta) in the coating the grain size of the $\alpha\text{-Al}_2\text{O}_3$ crystallites is decreasing further up to a value less than 1 μm which is about two orders of magnitude

less than that of the grains of the rutile scale on the bare substrate. This effect is obviously due to small grain, dense structure of the magnetron sputtered $\gamma\text{-TiAl}$ based coatings which is advantageous to more uniform nucleation of the oxide phases and to increased defect density on the coatings’ surface due to increasing concentration of the atoms of the micro-alloying elements in the relevant ternary coatings. Nevertheless, any synergistic effect of two different alloying elements in the quaternary $\text{TiAl}(\text{Cr},\text{Nb})$, $\text{TiAl}(\text{Ta},\text{Nb})$, $\text{TiAl}(\text{W},\text{Cr})$ and $\text{TiAl}(\text{Ag},\text{Si})$ γ -aluminide coatings has not been observed.

4. CONCLUSIONS

The following conclusions have been drawn from the observations made in the work:

1. Magnetron sputtered Cr or Nb or Ta or Mo or Ag or Si-alloyed $\gamma\text{-TiAl}$ coatings are well adhering

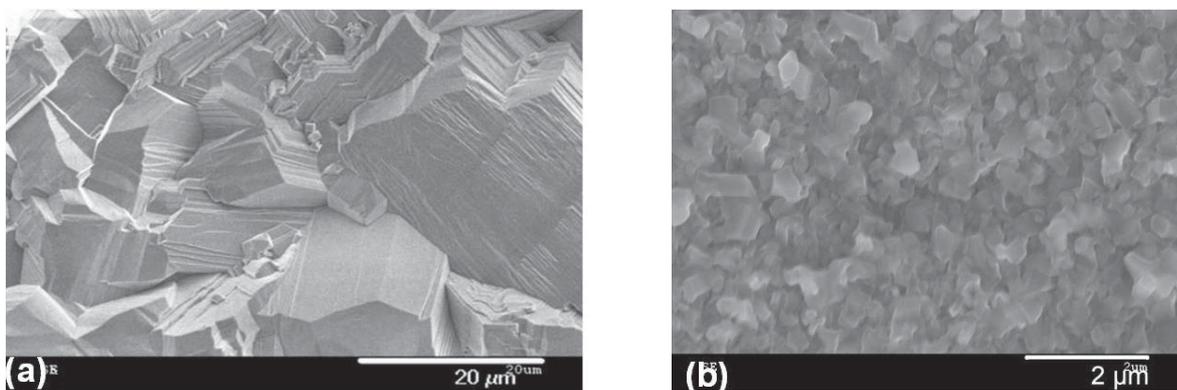


Fig. 5. The morphology of the oxide scale on the surface of two different samples after 120 hours oxidation in static air at 1173K: a) sample No. 1; b) sample No. 14.

and show a uniform, dense structure as opposed to the coarse-grained γ -TiAl substrate and protect well the latter against oxidation at the temperature as high as 1173K.

2. The resistance of the γ -TiAl-based coatings to oxidation is due to formation of thin, tight α -Al₂O₃ layer on the surface of the primary deposits which turns down the oxidation rate of the latter several orders of magnitude.
3. Both the dense structure as well as the effect of the 'third element' (Cr or Nb or Ta or Mo or Ag or Si) in the ternary γ -TiAl based coatings are conducive to the increase of the diffusivity of the Al atoms in the coatings and, subsequently, to preferential nucleation of the α -Al₂O₃ phase on the coatings' surface and, simultaneously, to the grain refinement of the oxide scale.
4. Any synergistic effect of two alloying elements in the coatings (Cr and Nb, Ta and Nb, W and Nb, Ag and Si) in the quaternary TiAl(Cr,Nb), TiAl(Ta,Nb), TiAl(W,Cr) and TiAl(Ag,Si) coatings has not been observed in the work.
5. Magnetron sputtered Cr or Nb or Ta or Mo or Ag or Si-alloyed γ -TiAl based ternary coatings are promising materials for protection of elements made of titanium alloys against oxidation in aviation, automotive or other applications at the temperature as high as 1173K.

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