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## Oxidation resistance of nanocrystalline microalloyed $\gamma$ -TiAl coatings

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**Abstract:**  $\gamma$ -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 1200 K, 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 1173 K that a great improvement of this resistance can be achieved due to Ag, Cr, Mo, Nb, Si, Ta or W micro-alloyed  $\gamma$ -TiAl based magnetron sputtered nanocrystalline coatings: the parabolic rate constant of the oxidation of some coatings is four orders of magnitude less than that of the bare  $\gamma$ -TiAl substrate.

**Keywords:** Titanium aluminides, Nanocrystalline coatings, Gas corrosion barriers, Microalloying

### 1. INTRODUCTION

$\gamma$ -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 1200 K [1-4]. Nevertheless, some of its properties (as, for example, poor oxidation resistance at high temperatures over 1000 K or poor toughness at ambient temperature) still need to be improved. Numerous research groups try to improve the oxidation resistance of the  $\gamma$ -TiAl aluminide by alloying it in the bulk with single or multiple elements or by means of various surface treatments including surface coatings. It is obvious that alloying of the  $\gamma$ -TiAl in the bulk may have a deleterious effect on some mechanical properties of the material [5-7]. As opposed to that, deposition of thin micro-alloyed  $\gamma$ -TiAl aluminide coating on the non-alloyed  $\gamma$ -TiAl substrate does not aggravate the mechanical properties of the latter. Moreover, the protective properties of the  $\gamma$ -TiAl coating against oxidation can be increased to a great extent due to nanocrystallinity of the coatings [8-10]. Coatings deposition is being executed mostly by means of magnetron sputtering [11-14]. It was the aim of the present work to investigate the effect of ternary (Ag, Cr, Mo, Nb, Si, Ta or W) or quaternary elements additions (Ag and Si or Cr and Nb or Ta and Nb or W and Cr, respectively) to the magnetron sputtered  $\gamma$ -TiAl based coatings onto the protective properties of the coatings against oxidation.

### 2. EXPERIMENTAL

$\gamma$ -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  $\gamma$ -TiAluminide coatings with different ternary or quaternary elements have been co-deposited by magnetron sputtering on all sides of the rotating  $\gamma$ -TiAl specimens in a vacuum chamber equipped with four independent magnetrons [15] with high purity Ag, Al, Cr, Mo, Nb, Ta, Ti or W targets. Coatings deposition has been conducted in Ar atmosphere at the pressure 0,2 Pa at the substrate temperature approximatively 400 K. Isothermal oxidation tests have been performed at 1173 K in static air under atmospheric pressure. The weight gain of the specimens was measured with use of an analytical balance with accuracy of  $1 \cdot 10^{-4}$  g. The results of the high-temperature oxidation of the coated specimens have been analysed and compared with the relevant characteristics of bare  $\gamma$ -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

It has been shown in the former paper [16] that about 200  $\mu\text{m}$  thick graded multilayer oxide scale composed of corundum and rutile phases is being formed on bare  $\gamma$ -Ti40at.% Al substrate after isothermal oxidation in static air during 120 hours at 1173 K with about 50  $\mu\text{m}$  thick rutile layer on the top of the scale succeeded by 20  $\mu\text{m}$  thick corundum layer and next by a graded composite  $\text{Al}_2\text{O}_3 + \text{TiO}_2$  layer. The parabolic rate constant of the growth of the scale calculated from the weight gain of the specimens was as great as  $2,6 \cdot 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ .

#### 3.2 Oxidation of coated substrate

The chemical compositions of different coatings deposited onto the  $\gamma$ -Ti40at.% Al substrate and their oxidation rate constants  $k_p$  as well as designations of the samples are given in Table 1.

Table 1.

Designation of the deposition process, coatings composition, oxidation conditions and parabolic rate constants of oxidation for different coatings on  $\gamma$ -Ti40at.% Al substrate.

Process No.	Substrate	Coating	Oxidation conditions	Parabolic rate constants $k_p$ [ $\text{g}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$ ]
		Without coating		2,61E-09
1	$\gamma$ -Ti40at.% Al	$\gamma$ -Ti50at.% Al	In static air at the temperature of 1173 K during the period of 120 hours	8,62E-11
2		$\gamma$ -TiAl(0,88 at.% Nb)		1,81E-11
3		$\gamma$ -TiAl(4,14 at.% Nb)		5,79E-13
4		$\gamma$ -TiAl(4,72 at.% Cr+5,89 at.% Nb)		8,33E-13
5		$\gamma$ -TiAl(1,06 at.% Ta)		5,27E-11
6		$\gamma$ -TiAl(4,05 at.% Ta)		6,31E-13
7		$\gamma$ -TiAl(5,7 at.% Ta+5,89 at.% Nb)		3,75E-11
8		$\gamma$ -TiAl(4,17 at.% W+3,79 at.% Cr)		8,33E-13
9		$\gamma$ -TiAl(1,9 at.% Si)		4,54E-12
10		$\gamma$ -TiAl(3,97 at.% Si)		5,79E-13
11		$\gamma$ -TiAl(1,88 at.% Ag)		4,69E-11
12		$\gamma$ -TiAl(3,36 at.% Ag)		3,7E-11
13		$\gamma$ -TiAl(2,86 at.% Ag+6,33 at.% Si)		2,05E-12
14		$\gamma$ -TiAl(1,29 at.% Mo)		9,26E-12
15		$\gamma$ -TiAl(7,56 at.% Mo)		8,33E-13
16		$\gamma$ -TiAl(1,41 at.% Ag+5,49 at.% Si)		4,6E-13

The thickness of the coatings was about 4  $\mu\text{m}$  (Figure 1). An example of the fracture of a sample from the process No. 16 before and after 120 hours oxidation in static air is given in

the figure as well. One can see that the primary uniform amorphous micro-alloyed  $\gamma$ -TiAl coating transformed during high-temperature oxidation into a dense, nanocrystalline structure as opposed to the coarse-grained  $\gamma$ -TiAl substrate. At the same time a thin and dense  $\text{Al}_2\text{O}_3$

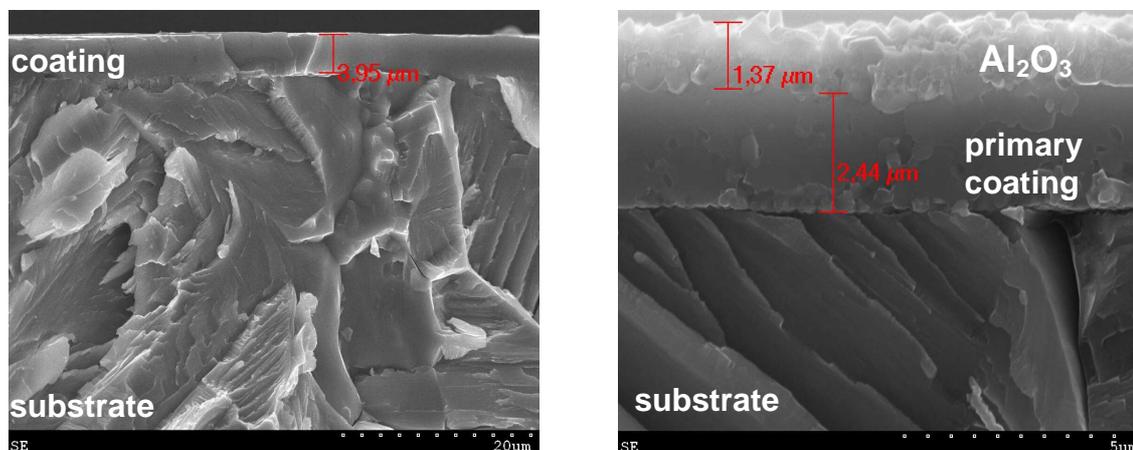


Figure 1. SEI image of the fracture of a  $\gamma$ -TiAl substrate with  $\gamma$ -TiAl coating alloyed with 2,9at.%Ag and 6,3at.%Si deposited in the process No. 16 before (left) and after (right) oxidation in static air during the period of 120 hours at 1173 K.

oxide layer of the thickness about 1  $\mu\text{m}$  has been created on the coating's surface (Figure 1; see also [17,18]). Moreover, no cracks have been observed neither in the coating nor at the coating/substrate interface (Fig. 1). This good adhesion between the substrate and the coatings is evidently due to perfect compatibility of the coating and the substrate: both of them are based on the  $\gamma$ -TiAl phase. The important finding – formation of single  $\alpha$ - $\text{Al}_2\text{O}_3$  scale in the present study (without rutile) – should be attributed to the nanocrystallinity of the magnetron sputtered coatings and, to some extent, to the effect of the “third element” (as Ag, Cr, Mo, Nb, Si, Ta or W): 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 [19]. It is well known that the  $\alpha$ -corundum is thermodynamically very stable and that the coefficient of the heterodiffusion of the oxygen atoms in this phase is the smallest one among the materials known to-day [20]. 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  $\gamma$ -TiAl coating is about one order of magnitude less than that of the  $\text{TiO}_2$  crystallites on the surface of bare  $\gamma$ -TiAl substrate [16]. With increase of concentration of the alloying elements 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  $\mu\text{m}$  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 nanocrystallinity of the magnetron sputtered  $\gamma$ -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 TiAl(Cr,Nb), TiAl(Ta,Nb), TiAl(W,Cr) and TiAl(Ag,Si)  $\gamma$ -aluminide coatings has not been observed.

#### 4. CONCLUSIONS

The following conclusions can be made from the observations made in the work:

1. After deposition the magnetron sputtered  $\gamma$ -TiAl coatings alloyed with Ag, Cr, Mo, Nb, Si, Ta or W ternary elements are amorphous and well adhering to the  $\gamma$ -TiAl substrate.

2. During subsequent high-temperature tests the coatings transform into a uniform, dense, nanocrystalline structure (as opposed to the coarse-grained  $\gamma$ -TiAl substrate) well protecting the latter against oxidation at the temperature as high as 1173 K.
3. The resistance of the coatings to oxidation is due to formation of thin, tight  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer on the surface of the primary deposits which turns down the oxidation rate of the latter several orders of magnitude.
4. Both the nanocrystallinity as well as the effect of the “third element” (as Ag, Cr, Mo, Nb, Si, Ta or W) in the ternary  $\gamma$ -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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase on the coatings’ surface and to the grain refinement of the oxide scale.
5. Any synergistic effect of two alloying elements in the quaternary TiAl(Cr,Nb), TiAl(Ta,Nb), TiAl(W,Cr) and TiAl(Ag,Si) coatings has not been observed in the work.
6. Magnetron sputtered  $\gamma$ -TiAl based ternary or quaternary coatings with Ag, Cr, Mo, Nb, Si, Ta or W alloying elements are promising materials for protection of products made of titanium alloys against oxidation in aviation, automotive or other applications at the temperatures as high as 1173 K.

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