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Effect of Au diffusion in Au-coated ($\gamma + \alpha_2$) titanium aluminides

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Abstract

In order to understand the role of α_2 -Ti₃Al precipitates during the oxidation of Au-coated γ -48-2-2-TiAl alloys, the γ -TiAl and α_2 -Ti₃Al microstructures resulting from Au diffusion at 900°C were investigated. The as-obtained coatings were characterized using scanning electron microscopy (SEM), combined energy and wavelength dispersive X-ray spectroscopies (EDS, WDS), electron backscatter diffraction analysis (EBSD), X-ray diffraction (XRD) and isothermal oxidation tests. Results showed that Au-coated- γ -TiAl alloys presented an upper aluminoferrite TiAlAu₂ layer and a lower non-protective TiAlAu layer, both with narrow homogeneity range, and with thicknesses that could be estimated with the use of the Prasad model. A more complex layer structure is obtained after Au diffusion in α_2 -Ti₃Al alloys, since eight different phases were identified. In the lower layers, two new ternary tetragonal phases (Ti₂AlAu and Ti₃Al₂Au) were found, and a partial diagram for the Al-Au-Ti 900°C isotherm is proposed. Absence or depletion of Al was found in the upper layers and, in addition, a low oxidation resistance of the Au-coated- α_2 -Ti₃Al alloy was reported.

Keywords:

- A. Intermetallics (aluminides)
- B. Oxidation
- C. Coatings

1. Introduction

TiAl-based alloys are continuing to attract attention from the industry as a high-temperature material, due to their exceptional combination of light weight and mechanical properties. Titanium aluminides have been found to exist in three different phases, Ti_3Al (α_2), TiAl (γ), and TiAl_3 . However, most TiAl-based alloys developed for structural applications are essentially two-phase ($\gamma + \alpha_2$) mixtures. According to the Ti-Al diagram, the aluminum content of the Ti_3Al (α_2) phase is between 22% and 39% (at.%), while the TiAl (γ) phase contains 48.5% to 66% (at.%) aluminum.

The attractive features of titanium aluminides are their lower density, higher stiffness, higher strength, improved creep resistance up to moderately high temperatures, lower coefficient of thermal expansion, higher thermal conductivity, and higher melting temperature compared to the conventionally used Ni-based super-alloys, which makes them suitable for potential high-temperature applications in the aerospace, automotive and power generation industries [1-5].

However, the alloys are known to possess a number of limiting properties, such as poor corrosion resistance to chlorine agents and low oxidation resistance above 700°C, which have continued to restrict their wider application. Many studies have already been carried out to successfully improve the oxidation resistance of TiAl, as stated in the review by R. Pflumm et al [6]. To a lesser extent, some corrosion studies are described in the literature [7-10].

Therefore, to enhance the corrosion resistance of TiAl, we modified its surface composition by adding a noble and inert element. Given its high compatibility with titanium, we developed a specific coating based on a gold (Au) electrolytic deposit to protect a γ -48-2-2 alloy (nominal composition Ti-48Al-2Cr-2Nb in at. %) against corrosion by NaCl and oxidation [11]. The coating obtained after diffusion of 20 μm of gold, for 1 hour at 900°C and at 10^{-5} Pa, comprised two layers: an aluminoferrite upper layer TiAlAu_2 and a lower layer TiAlAu . After 1000 hours of cyclic oxidation at 800°C, the formation of a dense but non-homogeneous

protective alumina layer was observed over the entire surface of the sample. Indeed, some more degraded areas appeared locally under the layer of alumina. Since the γ -48-2-2 alloy has a gamma-grain equiaxed microstructure (TiAl) with a few small α_2 -phase precipitates (Ti₃Al) at the grain boundaries, it was assumed that these degradations could be related to the presence of the α_2 precipitates at the grain boundaries of the alloy.

In order to separate the contributions of each phase, so as to be able to validate the latter hypothesis, the present work investigates the microstructures of Au-diffused coatings formed on single-phased samples: a stoichiometric TiAl alloy (called γ -TiAl), i.e., an alloy whose microstructure is a γ -grain microstructure with no α_2 phase precipitates, and a stoichiometric α_2 -Ti₃Al alloy without any γ phase.

To check for destabilization of the upper TiAlAu₂ layer formed over the γ -TiAl alloy after long Au diffusion treatments, the stability of the compositions of the two layers, TiAlAu₂ and TiAlAu, has been studied. For this purpose, the experimental thicknesses of these layers have been compared to those calculated by a typical growth model for layers with a very narrow homogeneity range [12].

In order to characterize the phases formed on the α_2 -Ti₃Al alloy after Au diffusion, different analysis techniques were combined. Finally, isothermal oxidation tests at 800°C were conducted to determine the ability of the Au-diffused α_2 -Ti₃Al alloy to form dense and protective alumina.

2. Experimental procedure

γ -TiAl and α_2 -Ti₃Al alloys prepared by double vacuum arc melting, re-melted seven times and annealed, were used as substrates for the coating experiments. Their bulk composition (at.%) was measured to be Ti50Al50 and Ti75Al25 for the γ and α_2 alloys, respectively

(induction coupled plasma technique). The alloy microstructures were checked by means of scanning electron microscopy.

Specimens were cut into 10*15*2.5 mm parallelepiped blocks by electro-discharge machining. After being ground down to an 800-grid finish using SiC paper, the specimens were sandblasted and then ultrasonically cleaned using alcohol. The Au deposition experiments are described in Reference [11].

After Au deposition, the specimens were heat-treated in a vacuum furnace (10^{-5} Pa, heating rate of $10^{\circ}\text{C}/\text{minute}$ up to 900°C with a threshold from 1 to 113 hours). The cooling rate was $15^{\circ}\text{C}/\text{minute}$. Specimens coated according to these steps (Au deposit and vacuum heat treatment) are called Au-coated specimens throughout the remainder of this article.

Surface and cross-sectional examinations were performed using a high-resolution field emission gun scanning electron microscope (FEG-SEM Zeiss Merlin and Gemini). Secondary (SE) and back-scattered electron (BSE) imaging modes were used. Energy dispersive X-ray spectroscopy (EDS-SDD with SAMx microanalysis software [13]) was used to determine the elemental composition and mapping of the regions of interest. In order to ensure state-of-the-art quantitative composition measurements, long-time acquisition and metallic standards (Al, Ti, Au, and Ti-50Al) were used.

X-ray diffraction (PANalytical Empyrean diffractometer, Cu-K α radiation) was also used in the Bragg-Brentano reflection geometry. To identify the crystallized phases of the inner layers of the coating, mechanical grinding down to grid 4000 was performed, followed by surface SEM examinations.

Electron backscatter diffraction (EBSD) is used in this study to locate crystallized phases previously identified by X-ray diffraction. Indeed, EBSD has been proven to be a powerful tool for phase identification in multiphase materials, by analyzing Kikuchi patterns or electron backscattered diffraction patterns (EBSPs) [14]. At each pixel, an EDS spectrum is acquired

while the EBSD pattern is collected. The EDS peaks are identified to determine the chemical element present and databases are searched for all crystals that match the chemistry. These tables are compared sequentially with the interplanar angles and lattice parameters measured from the EBSD pattern. The phases having provided the best match and fit are selected and compared with those determined by surface XRD analysis. All of these experiments were performed on a FEG-SEM ZEISS Merlin with an EBSD system (TSL instrumentation software and NORDIFF detector) and EDS system (SAMx software and SDD detector). Moreover, a dedicated EDS mapping experiment at 8kV provided not only spectral imaging to qualitatively differentiate intermetallic phases presenting a similar composition, but also – through a special quantification procedure available in the SAMx software – chemical quantitative imaging, as reported in a previous article [15].

800°C isothermal tests were carried out in an open, horizontal furnace.

All of the compositions are given in at.%.

3. Experimental results

3.1. Characterizations of Au-coated γ -TiAl and α_2 -Ti₃Al specimens

3.1.1. Influence of the heat treatment duration on Au-coated- γ -TiAl specimens

The characteristics of the Au-coated γ -TiAl specimens analyzed in this section are given in Table 1.

	Vacuum	TiAlAu ₂	TiAlAu
γ -TiAl	diffusion	thickness* (μm)	thickness* (μm)
	duration (h)	$\pm 2 \mu\text{m}$	$\pm 2 \mu\text{m}$
Specimen A	1	48	21
Specimen B	2	43	32
Specimen C	3	37	35
Specimen D	7	24	40
Specimen E	13	15	60
Specimen F	113	0	74

Table 1: Characteristics of the 29 μm Au-coated γ -TiAl specimens. Temperature of the vacuum diffusion treatment: 900°C. *Thicknesses measured from SEM micrographs.

As already published [11], when vacuum heat treating (900°C, 1 hour) a 29 μm Au coating that was deposited on a γ -TiAl alloy, the initial Au layer was consumed completely and the formed coating was composed of TiAlAu₂ and TiAlAu layers from the surface to the bulk alloy (Fig. 1, Spots 1 and 2, respectively). A zone enriched in Au is present (Fig. 1, Spot 3) at the interface between the lower TiAlAu layer and the γ -TiAl alloy. Semi-quantitative EDS measurements of the layers are given in Table 2. Previous work [11] showed that the upper TiAlAu₂ layer, which contains around 25% at. of Al, transformed into an adequately dense and protective alumina layer during oxidation at 800°C, but the TiAlAu layer did not effectively provide good resistance to oxidation.

Fig. 1: Typical SEM micrograph of a 29 μm Au-coated γ -TiAl alloy -Specimen A.

Spot	Al (at.%)	Ti (at.%)	Au (at.%)	Corresponding phases of the ternary Al-Au-Ti diagram [16]
1	26.1	23.6	50.4	TiAlAu_2
2	33.8	32.1	34.0	TiAlAu
3	41.2	48.0	10.8	TiAl enriched in Au
4	49.5	50.5		TiAl

Table 2: Semi-quantitative EDS analysis of a 29 μm Au-coated γ -TiAl alloy (Specimen A, spots in Fig. 1).

The thicknesses of the TiAlAu layer and of the diffusion zone enriched in Au increased according to the duration of the diffusion dwell period, while that of the TiAlAu_2 layer decreased (Fig. 2). The duration of the diffusion treatment leading to the total consumption of the TiAlAu_2 layer was estimated at 20 hours (Fig. 3). Even after long diffusion treatments, no additional phase was identified.

Fig. 2: SEM micrographs (BSE) of 29 μm Au-coated $\gamma\text{-TiAl}$ specimens according to the duration of the diffusion treatment: a) Specimen A - diffused for 1 hour; b) Specimen E - diffused for 13 hours; c) Specimen F - diffused for 113 hours.

Fig. 3: Experimental and theoretical curve thicknesses of the TiAlAu_2 and TiAlAu layers versus the diffusion dwell duration (900°C , 29 μm Au deposit, Specimens A to F). Vertical lines represent the uncertainties in the measured thicknesses. (*Color should be used for this figure in print*).

It should be noted that although the layer thicknesses vary, their chemical composition remain constant over a long diffusion dwell time. As shown in Fig. 4 with the example of Specimen D, the EDS profiles from the substrate $\gamma\text{-TiAl}$ to the surface indicated that the TiAlAu_2 and TiAlAu formed phases have a very narrow homogeneity range, the variation of composition in these phases being less than a few percent of the molar fraction.

Fig. 4: EDS profiles of the 29 μm Au-coated γ -TiAl Specimen D (diffused for 7 hours). (*Color should be used for this figure in print*).

3.1.2. Characterization of Au-coated α_2 -Ti₃Al specimens

Fig. 5 shows the BSE images of 25 μm Au-coated α_2 -Ti₃Al specimens diffused at 900°C (diffusion dwell times 1, 7 and 24 hours, Specimens G, H and I, respectively) and the corresponding EDS profiles (from the substrate to the surface).

Fig. 5: SEM micrographs (BSE) and corresponding EDS profiles along the red lines of a 25 μm Au- α_2 -Ti₃Al-coated specimen, according to the duration of the diffusion treatment; a) and d) Specimen G - diffused for 1 hour; b) and e) Specimen H - diffused for 7 hours; c) and f) Specimen I - diffused for 24 hours. (*Color should be used for this figure in print*).

For the 1-hour Au-coated Specimen G, the mean composition of the outer phase is $\text{Ti}_{24}\text{Al}_{13}\text{Au}_{63}$ (overall composition %at., Spot 1 in Fig. 6). In its lower part, there are some islands of a phase with a composition close to TiAlAu_2 , which gathered into a continuous layer (Spot 2 in Fig. 6) resting on a very thin layer ($\sim 1 \mu\text{m}$) that has a composition similar to that of TiAlAu (Spot 3 in Fig. 6). Just below, there is another layer composed of $\text{Ti}_{50}\text{Al}_{26}\text{Au}_{24}$ (Spot 4 in Fig. 6). Finally, in contact with the substrate there is a two-phase layer composed of elongated and alternating phases (Spots 5 and 6 in Fig. 6).

Fig.6: SEM micrographs of a 25 μm Au-coated α_2 - Ti_3Al specimen, diffused for 1 hour at 900°C (Specimen G).

Spot	Al (at.%)	Ti(at.%)	Au(at.%)	XRD corresponding phase of Fig. 7a
1	13.1	24	62.9	$(\text{TiAl})\text{Au}_2$ tetragonal phase
2	22.2	28.8	49	TiAlAu_2 cubic
3	28.7	38.0	33.3	
4	26.2	50	23.8	
5	38.2	47.6	14.1	
6	10.3	66.3	23.3	

Table 3: EDS analysis results of a 25 μm Au-coated- α_2 - Ti_3Al specimen (1 hour diffusion, Specimen G, spots in Fig. 6).

The top surface X-ray diffraction pattern (Specimen G, 1h-Au-coated α_2 alloy, Fig. 7) indicates that the upper layer is mainly composed of two phases: a (TiAl)Au₂ (refined) tetragonal phase and a TiAlAu₂ cubic phase. For the (TiAl)Au₂ tetragonal phase, calculation using the Fullprof software, with the deduced parameters $a = b = 3.40 \text{ \AA}$ and $c = 8.55 \text{ \AA}$, gives a good fit to the positions of all of the intense lines (Table 4). The two parameters “a” and “c” are close to those of the TiAu₂ tetragonal phase ($a = 3.429 \text{ \AA}$ - $c = 8.538 \text{ \AA}$), suggesting that the phase is significantly richer in Ti than in Al, as confirmed by the EDS analysis of Table 3 (Spot 1). This (TiAl)Au₂ tetragonal phase presents a preferential orientation (110). The phases of the lower layers could not be identified due to the low intensity of the peaks.

<i>hkl</i>	<i>d(obs)</i> $\text{\AA}$	<i>d(cal)</i> $\text{\AA}$
002	4.2667	4.275
101	3.1596	3.16
110	2.4070	2.405
103	2.1836	2.184
112	2.0972	2.096
200	1.6984	1.7005
114	1.5976	1.5976
202	1.5793	1.5801

Table 4: X-Ray diffraction pattern of (TiAl)Au₂ (I4/m m; $a=b= 3.401 \text{ \AA}$, $c=8.550 \text{ \AA}$).

Fig. 7: XRD pattern of the top surface of Specimen G, 1h-Au-coated α_2 alloy

Since longer diffusion dwell times permit layer growth, EDS/EBSD and XRD analyses were conducted on a 24h-Au-coated α_2 alloy for a better identification of the different phases of the coating (Fig. 8 and Fig. 9). The 24h-Au-coated Specimen I presents a quite unchanged overall morphology of the layers, compared to the 1h-Au-coated Specimen G, but another “lamellar phase” located under the TiAlAu₂ phase was identified (Spot 3 in Fig. 8 and Table 5).

Fig. 8: EDS and EBSD combined analysis of Specimen I, EBSD diffraction patterns and chemical compositions (measurements with standard, % at.) of the different layers of the coating. (*Color should be used for this figure in print*).

Spot	Al	Ti	Au	XRD corresponding phases of Fig 7
1	1.4	35.5	63.3	TiAu ₂ tetragonal
2	19.5	32.5	48	TiAlAu ₂ cubic
3	9.9	41.4	48.6	TiAu orthorhombic
4	31.7	33.5	34.8	TiAlAu hexagonal
5	25.2	50.1	24.8	Ti ₂ AlAu tetragonal
6	7.1	71.1	21.8	Ti ₃ Au cubic
7	33.2	52.6	14.2	Ti ₃ Al ₂ Au tetragonal

Table 5: EDS analysis results for a 25 μm Au-coated- α_2 -Ti₃Al alloy (24h diffusion, Specimen I, spots in Fig. 8) - Analysis with standards.

The top surface X-ray diffraction pattern of Specimen I (24h-Au-coated, Fig. 9a- α line) indicates that the (Ti,Al)Au₂ (refined) tetragonal peaks that were visible after 1 hour of diffusion have disappeared. The outer layer was only composed of TiAu₂ tetragonal and TiAlAu₂ cubic phases. Concerning the TiAlAu₂ cubic phase, it is worth noting that the peaks are slightly shifted with respect to those given in the 00-041-0937 sheet. Parameter “a” of the TiAlAu₂ cubic phase was found to be equal to 3.215 Å (instead of 3.198 Å). Given that a TiAu similar cubic phase (Pm-3m) exists (with a = 3.254 Å), it suggests, in agreement with the previous EDS analysis of Table5 (Spot 2), that the stoichiometry of the TiAlAu₂ cubic phase is depleted in Al.

XRD analysis of Specimen I performed after grinding (removal of matter down to a depth of around 25 μm , Fig. 9b- β line) identifies the underlying phases as a TiAu orthorhombic (martensitic) phase with a = 4.61 Å, b = 3.00 Å, c = 4.81 Å, and a TiAlAu hexagonal phase. After another sequential grinding (Fig. 9c, χ line), new peaks are visible. They can be assigned to a Ti₃Au cubic phase and to a tetragonal phase, close to the γ -TiAl phase, but with

the following parameters: $a = b = 3.97 \text{ \AA}$ and $c = 4.15 \text{ \AA}$, $c/a = 1.045$, Table 6, i.e., a more elongated phase than the γ -TiAl phase. On the large diffraction angle ($2\theta \sim 55^\circ$ - 80°), it is worth noting that two peaks coexist at a significantly close range (e.g., $d = 1.6677 \text{ \AA}$ and $d = 1.6636 \text{ \AA}$; $d = 1.4352 \text{ \AA}$ and $d = 1.4312 \text{ \AA}$; $d = 1.2418 \text{ \AA}$ and $d = 1.2369 \text{ \AA}$; Table 6). These duplicate peaks may be attributed either to one phase whose composition varies, or to two different phases whose crystallographic parameters are very close.

hkl	$d(obs) \text{ \AA}$	$d(cal) \text{ \AA}$
001	4.1533	4.15
110	2.8048	2.807
111	2.319	2.325
002	2.0788	2.075
200	1.9857	1.9850
201	1.7904	1.7907
112	1.6677	1.6686
	1.6636	
202	1.4352	1.4344
	1.4312	
113	1.2418	1.2409
	1.2369	

Table 6: X-Ray diffraction pattern of the refined tetragonal phase ($P4/mmm$; $a=b= 3.97 \text{ \AA}$, $c= 4.15 \text{ \AA}$; $c/a = 1.045$).

Fig. 9: XRD patterns; α) top surface of Specimen I - α line; b) and c) surfaces of Specimen I after sequential grindings - β and χ lines respectively; d) SEM image of specimen I: the α, β and χ lines correspond to the surface analyzed by XRD after grinding.

Combined EBSD analysis and chemical EDS mapping performed on Specimen I (Fig. 8, Table 5) allows the XRD results (Fig. 9) to be refined, since it gives the topological distribution of the phases over the entire coating. Indeed, as shown in Fig. 10 with the example of Spot 7, the tetragonal phase with parameters as determined by XRD analysis ($c/a = 1.045$) provided the best match and fit for the two phases in Spots 5 and 7 of Fig. 8.

Fig 10: a) EBSD pattern (Spot 7) and b) overlay of the best solution (Tetragonal)[P4/mmm], $c/a = 1.045$). (*Color should be used for this figure in print*).

By the way, from the outer layer to the substrate, the layer sequence can be described as TiAu₂ tetragonal/ TiAlAu₂ cubic /TiAu orthorhombic/TiAlAu hexagonal/tetragonal phase [P4/mmm] /Ti₃Au cubic+ tetragonal phase [P4/mmm]. The image quality (IQ) map constructed from electron backscatter diffraction data shows a typical martensitic microstructure of the TiAu phase (herringbone morphology [17]) (Fig. 11).

Fig. 11: upper) EBSD phase distribution map of Specimen I and color coded map; lower) corresponding image quality map (*Color should be used for this figure in print*).

The EBSD phase distribution map (Fig. 11) shows a crystallographic continuity between the single-phased layer (Phase 5 of Fig. 8), which is just beneath TiAlAu, and the elongated dark phase (Phase 7 of Fig. 8) of the two-phase layer that is in contact with the substrate. It

suggests that these two phases, although they have different compositions according to the EDS analysis, have similar tetragonal crystallographic structures.

EDS quantitative imaging of the Au-coated α_2 -Ti₃Al alloy (Specimen I) was used to differentiate these two phases appearing after interdiffusion of Au, Ti and Al at 900°C, allowing us to propose a partial diagram for the Al-Au-Ti corresponding isotherm section (Fig. 12, Table 7). This mapping was performed over a zone covering the interdiffusion layers from α_2 -Ti₃Al (substrate) to TiAu, bringing out two unknown ternary intermetallics: Ti₂AlAu (Phase 5 of Fig. 8) and Ti₃Al₂Au (Phase 7 of Fig. 8), compatible with these two intermetallics, which are undifferentiated in the EBSD map of Fig. 11. The tie-lines and tie-triangles were measured through a manual postprocessing procedure of the quantitative 2D-data. For each tie-line between two particular phases, 1D-composition profiles across the interface between these two phases are being plotted, so that the near-interface compositions of the coexisting phases can be measured. Every profile is chosen perpendicular to the interface. The tie-triangles are deduced by three different tie-lines evaluated near a trijunction point. The TiAu compound seems to show a quite high solubility in Al in Fig. 12a, but it has been difficult to analyze this properly near the edge zone of the EDS map. It is worth noting that Au was never found in the α_2 -Ti₃Al substrate.

The analyses performed on the 24h-Au-diffused Specimen I enables the completion of Table 3 by identification of the phases of the 1h-Au-diffused Specimen G as per: (TiAl)Au₂ tetragonal/ TiAlAu₂ cubic /TiAlAu hexagonal / Ti₂AlAu tetragonal /Ti₃Au cubic + Ti₃Al₂Au tetragonal.

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Fig. 12: a) Automatic retrieval of the compositions obtained by quantitative EDS imaging; b) Measurements of tie-lines (black) and tie-triangles (in yellow) after data analysis; the red points correspond to theoretical stoichiometric compositions; the single-phased regions in purple serve the purpose of guiding the eye only. (*Color should be used for this figure in print*).

Three-phase equilibrium	Phase 1			Phase 2			Phase 3		
	Al (at. %)	Au (at. %)	Ti (at. %)	Al (at. %)	Au (at. %)	Ti (at. %)	Al (at. %)	Au (at. %)	Ti (at. %)
Ti ₃ Al, Ti ₃ Al ₂ Au, Ti ₃ Au	26.2	0.0	73.8	32.3	14.7	52.9	6.4	22.5	71.1
Ti ₂ AlAu, Ti ₃ Al ₂ Au, Ti ₃ Au	26.9	22.6	50.5	33.7	15.8	50.6	5.2	24.9	69.9
Ti ₂ AlAu, TiAlAu, TiAu	23.6	25.8	50.5	29.9	34.9	35.3	2.6	46.3	51.1

Two-phase equilibrium	Phase 1			Phase 2		
	Al (at. %)	Au (at. %)	Ti (at. %)	Al (at. %)	Au (at. %)	Ti (at. %)
TiAlAu, TiAu	30.4	35.7	34.0	4.4	49.8	45.8

Table 7: Measurements associated with the proposed Al-Au-Ti diagram (Fig. 12).

3.2. Characterizations of oxidized coated α_2 -Ti₃Al specimens

A few coupons of 1-hour Au-coated α_2 Ti₃Al were oxidized at 800°C in isothermal tests that were carried out in an open, horizontal furnace. For comparison with a previous study [11], the same isothermal oxidation test was also conducted on an Au-coated γ -48-2-2 TiAl alloy, which contains α_2 precipitates, as described in [11].

As shown in Fig. 13, Au-coated γ -48-2-2 TiAl possesses a quite good oxidation resistance. Formation of a thin alumina covers over much of the TiAlAu₂ upper layer surface, but some highly oxidized areas appear locally (around 2 μ m in depth).

Fig 13: SEM micrograph of a 29 μ m Au-coated γ -48-2-2-TiAl specimen (1 hour diffusion) after isothermal oxidation (100 h, 800°C, atmospheric pressure)

Fig 14: SEM micrograph of a 25 μm Au-coated $\alpha_2\text{-Ti}_3\text{Al}$ specimen (1 hour diffusion) after isothermal oxidation (100 h, 800°C, atmospheric pressure)

In contrast, the 1-hour Au-coated $\alpha_2\text{Ti}_3\text{Al}$ does not resist oxidation at 800°C. Pitting oxidation appears as of 100 hours of oxidation at 800°C, and more than a quarter of the thickness of the coating is attacked in the highly altered areas (Fig. 14).

4. Discussion

During the vacuum heat treatment of a 29 μm Au coating deposited on a $\gamma\text{-TiAl}$ alloy, the Au diffused and formed, from the surface to the bulk, the TiAlAu_2 and TiAlAu phases in agreement with the work of Jorda [18]. The EDS profiles measured through the Au-diffused coatings show that these phases have a very narrow homogeneity range and that their thicknesses vary according to the duration of the diffusion treatment. EDS analyses did not permit any additional phase to be identified during long diffusion dwell times, suggesting a good stability of the formed layers in terms of chemical composition and aluminum content. To assess this stability, a comparison between the experimental thicknesses of the layers and those calculated from a growth model of layers with narrow homogeneity range (or line compounds) is discussed. In a binary distribution system A/B, A being a coating with a finite thickness and B being the semi-infinite substrate, Prasad [12] developed a model, based on the integrated diffusion coefficient, as published by Wagner [19], to calculate the consumption rate of the end-member A and the growth rates of the product phases A_2B and AB . This model can be applied to our case, with A corresponding to Au, B to TiAl , A_2B to TiAlAu_2 and AB to TiAlAu , with the following assumptions: (a) the species Ti and Al diffuse at the same speed; (b) the influence of one species on the diffusion of the other two is negligible; (c) the variations of composition in the TiAlAu and TiAlAu_2 phases are neglected; and (d) Au and TiAl do not diffuse in a solid solution in the TiAl and Au phases respectively.

Given that the Au finite layer is consumed completely after the 1h diffusion dwell period, the system can be reduced to the growth of a single-phased TiAlAu between the end-member TiAlAu₂ and the semi-finite substrate (TiAl).

$\Delta x_{tc}^{A_2B}$ and Δx_{tc}^{AB} are the thicknesses of the product phases A₂B and AB respectively, after the 1h (t_c) diffusion dwell period (Specimen A).

The integrated diffusion coefficient of the product phase TiAlAu can be written as:

$$\check{D}_{int}^{AB} = ((a^{AB}b^{AB})(\Delta x'^{AB})^2) / ((a^{AB}+b^{AB}) 2t) \quad (\text{Eq.1})$$

With

$$a^{AB} = N_{B}^{AB} - N_{B}^{-}$$

$$b^{AB} = N_{B}^{+} - N_{B}^{AB}$$

N_{B}^{+} and N_{B}^{-} being the initial molar fraction of Species B, in B and A respectively;

N_{B}^{AB} being the initial molar fraction of Species B in AB;

$\Delta x'^{AB}$ is the total thickness of the product layer AB formed during the diffusion dwell period.

$$\Delta x'^{AB} = ((a^{AB}+b^{AB}) 2 \check{D}_{int}^{AB} t) / (a^{AB}b^{AB})^{1/2} \quad (\text{Eq.2})$$

$$\Delta x'^{AB} = k (t^{1/2}) = k (t_d + t_c)^{1/2} \quad (\text{Eq.3})$$

With t_d = duration of the diffusion dwell period (hour), t_c equal to 1h and total time t = t_d+t_c.

$$k = ((a^{AB}+b^{AB}) 2 \check{D}_{int}^{AB} / (a^{AB}b^{AB}))^{1/2} \quad (\text{Eq.4})$$

By equating the number of atoms A consumed from the A₂B (A_{2/3}B_{1/3}) with the amount of atoms A present in $\Delta x'^{AB}$ (A_{1/2} B_{1/2}), and knowing the molar volumes V_m of the phases, we can write:

$$(2/3)(\Delta x^{A_2B}/V_m^{A_2B}) = (1/2)(\Delta x'^{AB}/V_m^{AB}) \quad (\text{Eq. 5})$$

$$(\Delta x^{A_2B}/V_m^{A_2B}) = (3\Delta x'^{AB}/4V_m^{AB})$$

$$\text{with } \Delta x'^{A_2B} = \Delta x_{tc}^{A_2B} - \Delta x^{A_2B}$$

$$\text{and } \Delta x'^{AB} = \Delta x_{tc}^{AB} + \Delta x^{AB}$$

Then, the thickness of the product phase A_2B at the end of the diffusion dwell period can be written as:

$$\Delta x'^{A_2B} = \Delta x_{tc}^{A_2B} - (3V_m^{A_2B}/4 V_m^{AB})(\Delta x'^{AB} - \Delta x_{tc}^{AB}) \quad (\text{Eq. 6})$$

The relation between the thicknesses of the $TiAlAu_2$ and $TiAlAu$ layers is then described by Eq.7.

$$\Delta x'^{A_2B} = \Delta x_{tc}^{A_2B} - (3V_m^{A_2B}/4 V_m^{AB}) (k (t_d + t_c)^{1/2} - \Delta x_{tc}^{AB}) \quad (\text{Eq.7})$$

A good general match between the experimental thicknesses of the $TiAlAu_2$ and $TiAl$ layers and the theoretical ones is obtained (Fig. 3), with an estimated integrated diffusion coefficient of the product phase $TiAlAu$ equal to $10^{-14} \text{ m}^2/\text{s}$ and the numerical values of Table 8.

N_B^+	1	$\Delta x_{tc}^{A_2B}$	48 μm
N_B^-	0	Δx_{tc}^{AB}	21 μm
N_B^{AB}	1/3	$\check{D}_{TiAlAu}^{int}$	$10^{-14} \text{ m}^2/\text{s}$
a^{AB}	1/3		
b^{AB}	2/3		

Table 8: Numerical values used to solve Eq.7.

After the heat treatment (900°C for 1 hour) of a 25 μm Au coating deposited on an α_2 - Ti_3Al specimen, the following successive product phases were identified: $(TiAl)Au_2$ tetragonal/ $TiAlAu_2$ cubic / $TiAlAu$ hexagonal/ Ti_2AlAu tetragonal/ Ti_3Au cubic + Ti_3Al_2Au tetragonal phase. The two ternary compounds $TiAlAu$ and $TiAlAu_2$ were clearly identified by Jorda et al. [18] when investigating the phase equilibria of the ternary Ti-Au-Al at 500°C. Two new ternary compounds, Ti_2AlAu and Ti_3Al_2Au , not reported in the Jorda 500°C ternary diagram, were found to exist after Au diffusion at 900°C. The Ti_2AlAu participates in a three-

phase equilibrium with Ti_3Au and another ternary compound ($\text{Ti}_3\text{Al}_2\text{Au}$), and in a three-phase equilibrium with TiAlAu and TiAu . In the EBSD mapping the Ti_2AlAu and $\text{Ti}_3\text{Al}_2\text{Au}$ are associated with the same tetragonal structure as that determined by XRD analysis ($P4/mmm$, $c/a = 1.045$). However, the existence of duplicate peaks on the large diffraction angle at close inter-reticular distance suggests close but slightly different cell parameters for these two phases. Additional experiments and analyses would be necessary to properly assess their structures.

For longer diffusion (24 h), the upper $(\text{TiAl})\text{Au}_2$ tetragonal phase that was found to be depleted in Al transformed into a TiAu_2 tetragonal phase, and the TiAu orthorhombic phase clearly appeared between the TiAlAu_2 cubic phase, which was depleted in Al, and the TiAlAu hexagonal phases. Comparison of the 7 h and 24 h EDS profile points shows that the TiAlAu layer grows from the aluminum consumption of the TiAlAu_2 layer, leading to the formation of the TiAu layer between them. Since the TiAlAu phase has a very narrow homogeneity range and has a greater aluminum content (33% at. Al) than the semi-infinite substrate (Ti_3Al , 25% at. Al), the system quickly freezes. The upper layer of the $\alpha_2\text{Au}$ -diffused coating consists of a non-protective TiAu_2 layer [20] and a TiAlAu_2 layer that is too depleted in Al to be effective against oxidation. The first oxidation isothermal tests of a 25 μm Au-coated $\alpha_2\text{-Ti}_3\text{Al}$ substrate (1-h Au diffusion treatment) confirmed this poor resistance to oxidation (Fig. 14)

5. Conclusion

In this study, the microstructures of Au-diffused coatings on $\alpha_2\text{-Ti}_3\text{Al}$ alloys, compared to those on $\gamma\text{-TiAl}$ alloys, were investigated in order to understand the role of α_2 precipitates in the resistance to oxidation of Au-coated $\gamma\text{-48-2-2-TiAl}$ specimens.

When vacuum heat treating (900°C, 1 hour) a 29 μm Au coating that was deposited on a $\gamma\text{-TiAl}$ alloy, the Au diffused and formed, from the surface to the bulk, an upper aluminoferrite TiAlAu_2 layer and a lower non-protective TiAlAu layer. The thicknesses of the TiAlAu_2 and

TiAlAu layers could be estimated using the Prasad model and an estimated integrated diffusion coefficient of the product phase TiAlAu equal to 10^{-14} m²/s.

After the vacuum heat treatment (900°C, 1 hour) of a 25µm Au coating deposited on α_2 -Ti₃Al alloy, the following successive product phases were identified: (TiAl)Au₂ tetragonal/TiAlAu₂ cubic /TiAlAu hexagonal/Ti₂AlAu tetragonal/Ti₃Au cubic + Ti₃Al₂Au tetragonal. For longer diffusion (24 h) the upper (TiAl)Au₂ tetragonal phase transformed into a TiAu₂ tetragonal phase and the TiAu orthorhombic phase appeared between the TiAlAu₂ cubic, which was depleted in Al, and the TiAlAu hexagonal phases.

Two new ternary compounds, Ti₂AlAu and Ti₃Al₂Au, were found in this study. The Ti₂AlAu participates in three-phase equilibria with Ti₃Au and Ti₃Al₂Au, and also in three-phase equilibria with TiAlAu and TiAu. A partial diagram for the Al-Au-Ti 900°C isotherm is proposed.

Absence or depletion of Al in the upper layers (TiAu₂ and TiAlAu₂) of an Au-coated α_2 -Ti₃Al substrate is probably the cause of its low resistance to oxidation.

This may also explain why some pitting oxidation appears locally during the oxidation of the Au-coated γ -48-2-2-TiAl. After Au diffusion, if the surface of each TiAl gamma grain transformed into an upper aluminoferrite TiAlAu₂, the Ti₃Al precipitates present at the boundary grains would have transformed into a non-protective alloy that is highly oxidized.

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