

Influence of different annealing processes under various atmospheres on the oxidation behaviour of γ -TiAl

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ABSTRACT

A detailed study of the oxidation behaviour of bare γ -TiAl based alloy Ti-45Al-8Nb under various conditions, such as different atmospheres, pressures, temperatures (900°C, 1000°C) and times (100–200 h) is presented. Under high vacuum conditions (10^{-6} mbar) a continuous zone of α_2 -Ti₃Al was formed at the surface with an oxygen-enriched phase on top. No oxide scale formation was obvious. During thermal treatment under Ar-atmosphere at low vacuum pressure (approximately 50 mbar) mainly nitrides (TiN, Ti₂AlN) and Al₂O₃ particles were formed at the surface with an α_2 -layer below. Annealing γ -TiAl in hydrogen atmosphere (about 1040 mbar) led to the formation of a thick reaction zone. A TiO₂ layer was formed on top, followed by a mixed oxide scale. Beneath that scale a thick region with alumina, σ -Nb₂Al and α_2 -Ti₃Al was observed.

Moreover, the oxidation behaviour of several thermally pre-treated samples was tested by cyclic oxidation at 900°C in air. The microstructure of the oxide scale formed after testing can be compared with that of non pre-treated material. γ -TiAl annealed under high vacuum conditions exhibits the lowest oxidation rate, while the mass gain of specimens pre-treated under Ar-atmosphere increased rapidly in the first cycles. All pre-treated specimens exceeded a lifetime of 600 cycles at minimum. The reference material failed after 520 cycles.

Keywords: titanium aluminides, vacuum annealing, argon annealing, hydrogen annealing, oxidation behaviour

1. INTRODUCTION

Materials with a low density for high temperature applications are interesting in aerospace and automotive industries. Especially, γ -TiAl based alloys are attractive due to their good mechanical properties, such as low density, high stiffness, high yield strength and good creep resistance in a temperature range from 700°C up to 900°C [1–4]. Titanium aluminides based on γ -TiAl were tested successfully as parts of automotive engines [2,3] as well as components in aeroengines [4], such as low-pressure turbine blades. However, the oxidation rates of titanium aluminides typically increase greatly above temperatures of 750°C due to the formation of fast growing porous titania scales [5–9].

Different thermal treatments can improve the oxidation resistance of titanium aluminides as extensively discussed in the literature [10–14]. It is reported that annealing under various atmospheres and partial pressures of oxygen, nitrogen and hydrogen leads to the formation of different phases as well as the growth of various oxide scales on γ -TiAl, finally affecting the oxidation resistance of the material.

In this study γ -TiAl was thermally pre-treated in high vacuum, Ar-atmosphere as well as hydrogen under various pressures and then tested in air to compare the oxidation behaviour to non pre-treated material.

2. EXPERIMENTAL

2.1 Annealing series of γ -TiAl

The oxidation experiments were performed on γ -TiAl based alloy Ti-45Al-8Nb (in at.%), provided by GKSS (Research Center Geesthacht). The specimens were ground by SiC paper up to 4000 grit, polished and ultrasonically cleaned in ethanol before testing.

In a special high-temperature furnace the annealing experiments were performed under three various atmospheres (high vacuum, Ar-atmosphere and H₂-atmosphere) at two different temperatures (900°C and 1000°C), shown in Table 1.

Before starting each pre-treatment process of the furnace was evacuated to 10^{-6} mbar. During high vacuum annealing the specimens were heated to set point temperature, held for the according time and subsequently cooled down. In the

Table 1 Pre-treatment annealing conditions

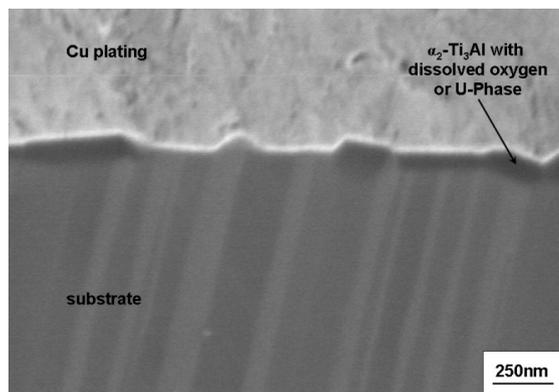
	High vacuum	Ar-atmosphere	H ₂ -atmosphere
900°C	100 h	100 h	–
1000°C	100 h, 200 h	100 h, 200 h	10 h

second pre-treatment process, the chamber was flooded by Ar (purity: 99,996%) up to a pressure of 10 mbar before heating. At exposure temperature a pressure of 50 mbar was reached. At annealing in hydrogen atmosphere (purity: 99,993%) it was necessary to work with an absolute pressure of 1040 mbar. The furnace chamber was filled with hydrogen until the pressure was reached by operating at a gas flow of 5 L/h. The heating rate for all thermal treatments was 4 K/min.

Post-oxidation investigations of the microstructure were performed using a LEO Gemini field emission gun scanning electron microscope (SEM) equipped with an Oxford energy-dispersive X-ray spectrometry (EDS) detector attached. Chemical compositions were determined using semi-quantitative analysis for spot and line scan measurements.

2.2 Cyclic oxidation test of annealed γ -TiAl

After pre-treatment the material was tested under cyclic conditions in air at 900°C. One cycle consisted of 1 h heating and 10 min cooling down to 60°C. During cyclic testing the mass gain was measured at certain intervals. Oxide scale spallation was considered as sample failure. For comparison a non pre-treated γ -TiAl specimen was tested. After testing the specimens were investigated by means of SEM and EDS analysis.


Figure 1 SEM micrograph of TiAl samples after high-vacuum annealing at 900°C for 100 h.

3. RESULTS AND DISCUSSION

3.1 Annealing pre-treatment of γ -TiAl

The oxidation behaviour of γ -TiAl varies under different oxygen and nitrogen partial pressures [15–20]. In Table 2 the values of partial pressures used in the experiments are listed. Since the oxygen partial pressures were much higher than the decomposition pressure of the oxides [21], oxidation processes were expected during each pre-treatment.

High vacuum annealing

During high-vacuum annealing at 900°C for 100 h phase changes took place at the surface (Figure 1). On top of the γ -TiAl based alloy consisting of γ -TiAl- and α_2 -Ti₃Al lamellae [3,22], a thin (few hundreds of nanometers) subsurface zone

Table 2 Oxygen, nitrogen and water partial pressures during different heat treatments (a) high vacuum annealing, (b) argon annealing, and (c) hydrogen annealing

(a)			
Elements in atmosphere	Ratio n_i [%]	Experimental pressure p [mbar]	Partial pressure p_i [mbar]
Oxygen (O ₂)	21	1.00E-06	2.10E-07
Nitrogen (N ₂)	78	1.00E-06	2.80E-07
(b)			
Elements in argon 4.6	Ratio n_i [ppm] ^a	Experimental pressure p [mbar]	Partial pressure p_i [mbar]
Oxygen (O ₂)	6	50	3.00E-04
Nitrogen (N ₂)	20	50	1.00E-03
(c)			
Elements in hydrogen 4.3	Ratio n_i [ppm] ^a	Experimental pressure p [mbar]	Partial pressure p_i [mbar]
Oxygen (O ₂)	2	1040	2.08E-03
Nitrogen (N ₂)	50	1040	5.20E-02
Water (H ₂ O)	20	1040	2.08E-02

n_i – content of the element/molecule.

^aAccording to gas supplier specifications.

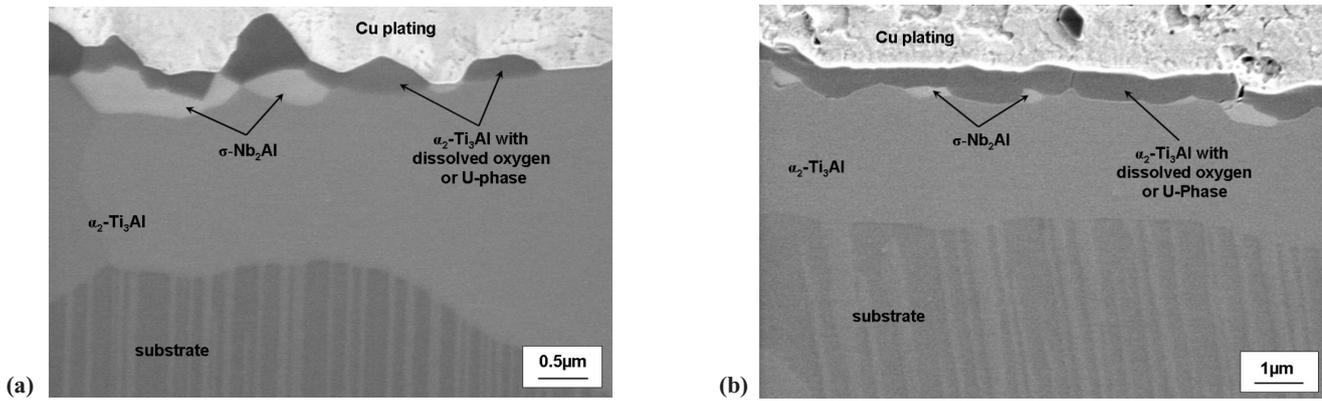


Figure 2 Cross-section of TiAl samples after high-vacuum annealing at 1000°C for (a) 100 h; (b) 200 h.

formed. Due to the marginal dimensions the nature of this zone could not be identified by EDS analysis.

At 1000°C the subsurface zone thickened substantially, forming a continuous layer after 200 h (Figure 2). According to the measured composition (Table 3) this zone could be concluded to contain α_2 -Ti₃Al phase with 15 at.% oxygen in solution. Earlier studies by Dettenwanger and Schütze on the oxidation behaviour of α_2 -Ti₃Al showed the formation of a Ti–21Al–15O (at.%) layer [23] with an unknown crystallographic structure. The composition of the phase observed at the surface of the vacuum pre-treated specimens (Ti–4.6Nb–23.2Al–15O) is close to that phase found by the above mentioned authors. According to Dettenwanger and Schütze the nature of this phase is still unknown; therefore, the phase will be denoted as “U-phase” in the following. Below the U-phase precipitations of a Nb-rich phase, presumably σ -Nb₂Al phase [24–27], and a thick α_2 -Ti₃Al zone were formed at 1000°C after 100 h (Figure 2a). Within the latter phase no oxygen could be measured (Table 3). Upon extended exposure, the U-phase formed a continuous layer on top of the α_2 -Ti₃Al phase (Figure 2b). Due to the high niobium content of 10.5 at.% in the α_2 -Ti₃Al phase region compared to its concentration in the outer phase (4.6 at.%) it could be assumed that formation of the U-

phase led to enrichment of Nb at the interface between U-phase and α_2 -phase resulting in the growth of σ -Nb₂Al.

The reason for the formation of continuous α_2 -Ti₃Al zone at the surface is not clear yet. It could be induced by the presence of oxygen, in this case probably by attendance of the U-phase. Another reason could be that α_2 -Ti₃Al is more thermodynamically stable. Kattner *et al.* determined the temperature-dependent Gibbs-energy ΔG^f of the α_2 -Ti₃Al and γ -TiAl [28]:

$$\Delta G_{\alpha_2}^f = (-29,633.6 + 6.70801 \cdot T) \frac{J}{\text{mol atom}}$$

$$\Delta G_{\gamma}^f = (-37,445.1 + 16.79376 \cdot T) \frac{J}{\text{mol atom}}$$

These equations indicate that the Gibbs-energy of the α_2 -phase is lower than that of the γ -phase above approximately 775 K. That means, the α_2 -phase is more thermodynamically stable especially at the surface, where no local equilibrium between both phases exists.

Unexpectedly, neither oxides nor nitrides were formed under the high vacuum conditions at 900 and/or 1000°C.

Table 3 Composition of phases of differently pre-treated TiAl-material measured by EDX; concentration in at.%

System	Phases	Composition c [at.%]				
		N	O	Al	Ti	Nb
High vacuum annealing (Figure 2)	α_2 -Ti ₃ Al + O or U-phase	–	15.0	23.2	57.2	4.6
	presumably σ -Nb ₂ Al	–	–	31.8	51.4	16.8
	α_2 -Ti ₃ Al	–	–	33.6	55.9	10.5
Annealing under Ar- atmosphere (Figure 3)	TiN	45.0	–	0.7	53.4	0.9
	Ti ₂ AlN	35.2	–	7.8	56.3	0.7
	Al ₂ O ₃	–	63.8	34.4	1.7	0.2
	α_2 -Ti ₃ Al	–	–	31.2	64.6	4.2
	σ -Nb ₂ Al	–	–	34.7	28.8	36.5
Annealing under H ₂ -atmosphere (Figure 4)	TiO ₂	–	67.5	–	32.5	–
	mixed oxides	–	65–75	10–20	7–15	1–6
	Al ₂ O ₃	–	61.8	27.1	9.3	1.8
	σ -Nb ₂ Al	–	–	29.6	41.0	29.4
	α_2 -Ti ₃ Al	–	–	30.2	57.9	11.9

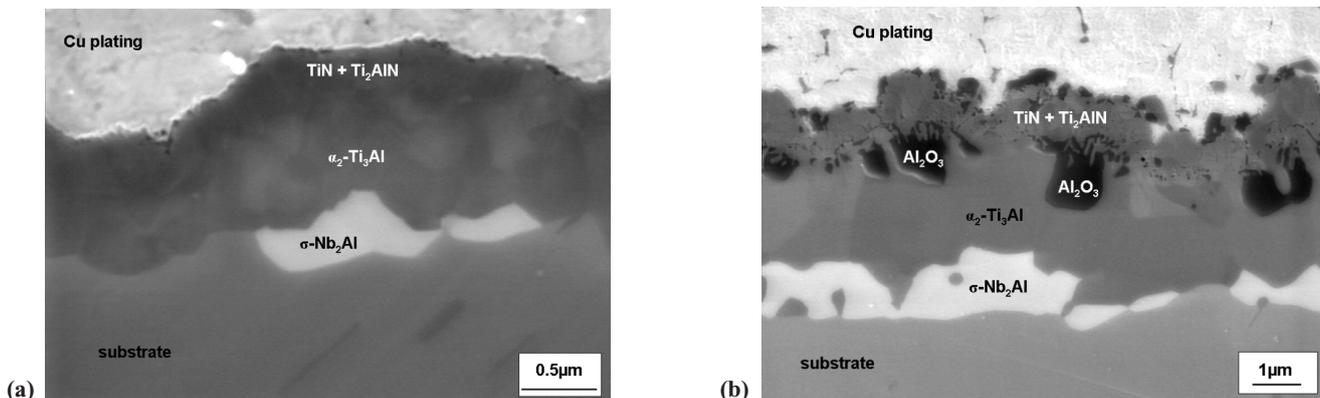


Figure 3 Cross-section of TiAl samples after annealing under Ar-atmosphere for 100 h (a) at 900°C; (b) at 1000°C.

Annealing under Ar-atmosphere

During the annealing processes under Ar-atmosphere the partial pressures of oxygen and nitrogen were much higher compared to the vacuum pre-treatment (Table 2).

As shown in Figure 3 mainly nitrides TiN and Ti_2AlN were formed at the surface as founded in the transition region during usual oxidation processes of γ -TiAl in air [29,30]. The nitrides were seen at both annealing temperatures (900°C and 1000°C). Below this nitride layer different intermetallic phases were formed. α_2 - Ti_3Al grew continuously beneath the nitrides. Niobium enriched precipitates, presumably σ - Nb_2Al , were formed at the α_2 - Ti_3Al/γ -TiAl interface. It can be assumed that the formation of this phase is caused by titanium consumption as a result of α_2 - Ti_3Al growth. The composition of phases is shown in Table 3.

In spite of the relatively high oxygen partial pressure (3×10^{-4} mbar) no oxidation took place at 900°C. However, the nitrogen partial pressure (10^{-3} mbar) was obviously sufficient to form a continuous nitride layer at the surface.

After 100 h at 1000°C additionally precipitates of alumina were formed at the nitride/ α_2 - Ti_3Al interface. According to the results of the high vacuum annealing experiments, presumably the α_2 -phase should be formed first. Subsequently the growth of the nitrides and alumina could take place simultaneously. The oxygen partial pressure was too low for the formation of titania [21].

With longer exposure times up to 200 h at 1000°C all phases grew substantially. The thickness of the reaction zone increases from 4.5 up to 7.5 μ m. The σ - Nb_2Al formed a nearly continuous layer below the α_2 - Ti_3Al phase.

Annealing under H_2 -atmosphere

SEM analysis shows the formation of a reaction zone, approximately 20 μ m in thickness, after 10 h at 1000°C under hydrogen atmosphere at 1040 mbar (Figure 4). A mixed oxide scale mainly consisting of titania and alumina was formed, accompanied by a dense titania layer on top (Table 3). Beneath that scale a huge mixed zone consisting of alumina, α_2 - Ti_3Al and σ - Nb_2Al precipitates could be observed.

The oxygen and nitrogen partial pressures were much higher in hydrogen than in the other atmospheres (Table 2). However, in the H_2 -atmosphere the oxygen partial pressure could be reduced by the formation of H_2O :



Therefore the oxide formation should be suppressed. However, investigations of Kremer and Auer revealed poor oxidation behaviour of γ -TiAl in water vapour containing atmosphere caused by enhanced Al_2O_3 growth [20]. These results are in good agreement with the present findings on enhanced oxidation in hydrogen containing atmosphere. The massive growth of alumina can be explained concerning the following reaction [19]:



According to Zeller *et al.* water molecules are dissociated on rutile by forming H and OH^- [31]. The dissolution of H atoms or OH^- groups could lead to a change in the defect chemistry of TiO_2 and therefore in the transport mechanisms through titania, finally resulting in enhanced oxidation of γ -TiAl.

The primary inward growth of Al_2O_3 induced the depletion of aluminum in the γ -TiAl phase leading to the formation of α_2 - Ti_3Al and σ - Nb_2Al . Nitrides could not be observed.

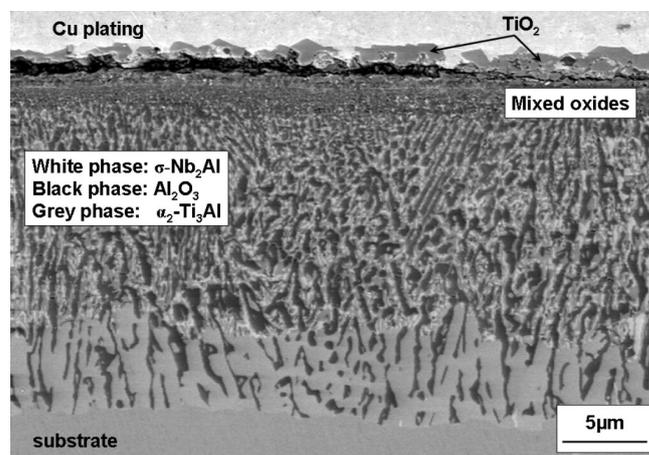


Figure 4 SEM micrograph of TiAl samples after annealing under H_2 -atmosphere at 1000°C for 10 h.

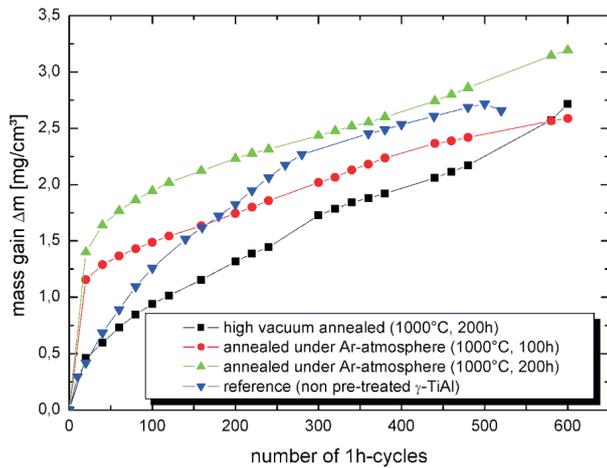


Figure 5 Oxidation kinetics of pre-treated and non pre-treated γ -TiAl thermally cycled at 900°C in air.

Due to the enhanced oxide formation, exposure under hydrogen atmosphere is not appropriate to increase the oxidation resistance of γ -TiAl. Therefore, hydrogen pre-treatments were not considered further for sample exposure to air.

3.2 Cyclic oxidation test of pre-treated γ -TiAl

The oxidation behaviour of the differently pre-treated γ -TiAl alloy was compared with that of non pre-treated samples by

cyclic testing in air at 900°C. The measurements show that the high vacuum annealed specimen has the lowest oxidation rate, followed by non pre-treated material with a slightly higher mass gain (Figure 5). The material pre-treated in Ar-atmosphere exhibited the highest mass gain, especially within the first 20 cycles. Therefore the nitrides on top of the samples grown during the annealing process under Ar, seem to oxidize much faster than the intermetallic α_2 - and γ -phases at 900°C. This effect is also described by Rakowski *et al.* and Zheng *et al.* [18,32]. But after the high mass gain in the first cycles the oxidation kinetics of γ -TiAl annealed under Ar-atmosphere reveal a lower slope compared to the sample pre-treated under high vacuum conditions as well as to the reference material.

The non pre-treated material failed after 520 cycles while the other specimens showed no spallation up to 600 cycles when the test was terminated for microstructures investigations of the oxide scale.

Although on top of the high vacuum annealed specimen Ti-rich α_2 -phase was present before cyclic testing, the material showed the lowest mass gain accompanied with the thinnest oxide scale of all samples tested (Figure 6). Compared to the reference material a higher oxidation rate was expected due to the high Ti-content as described by Dettenwanger and Schütze [23]. Presumably the presence of a continuous layer of the oxygen-containing U-phase on the surface affected the oxidation behaviour beneficially. This effect is not yet fully clear and will be investigated in more detail in further experiments.

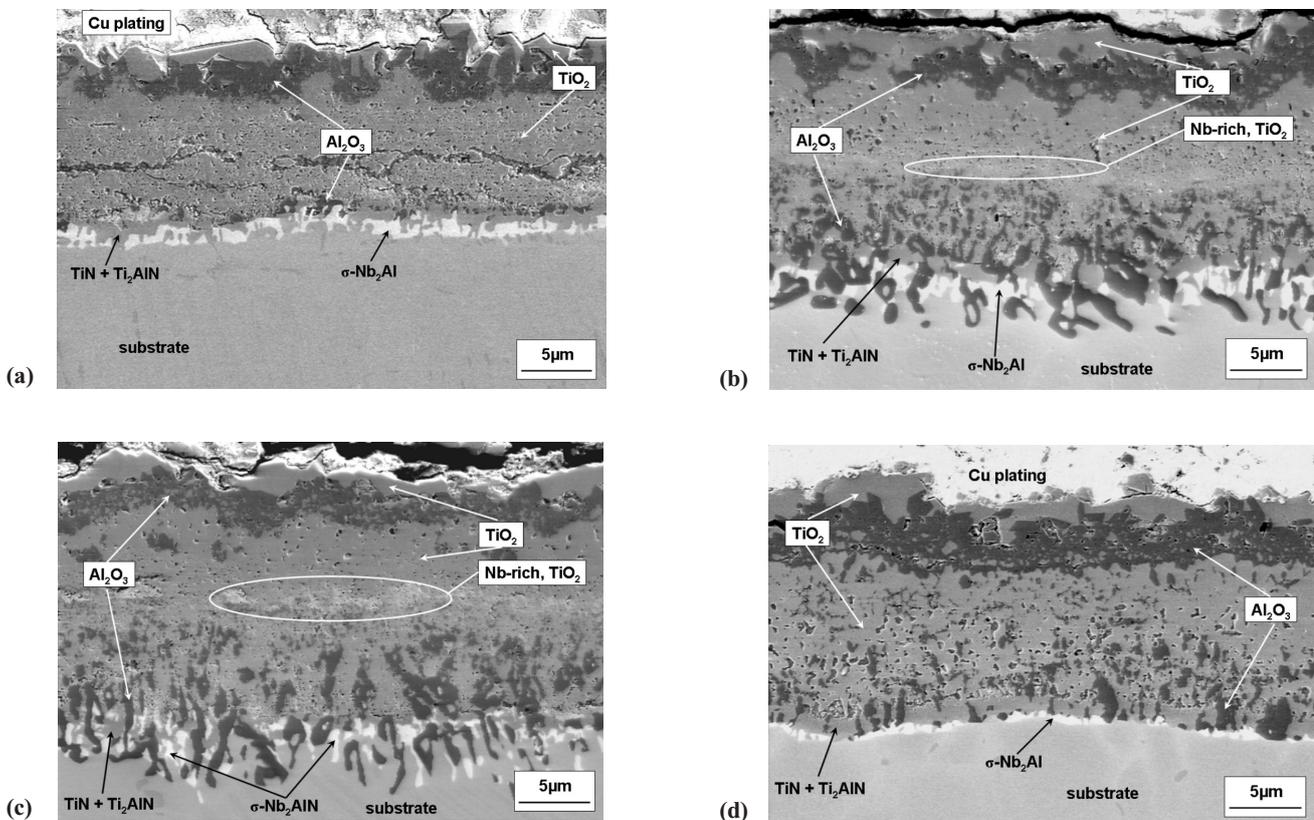


Figure 6 Cross-section of variously pre-treated specimens, cyclic tested at 900°C in air for (a) 600 cycles; high vacuum annealing at 1000°C for 200 h; (b) 600 cycles; annealing under Ar-atmosphere at 1000°C for 100 h; (c) 600 cycles; annealing under Ar-atmosphere at 1000°C for 200 h; (d) 520 cycles; non pre-treated γ -TiAl.

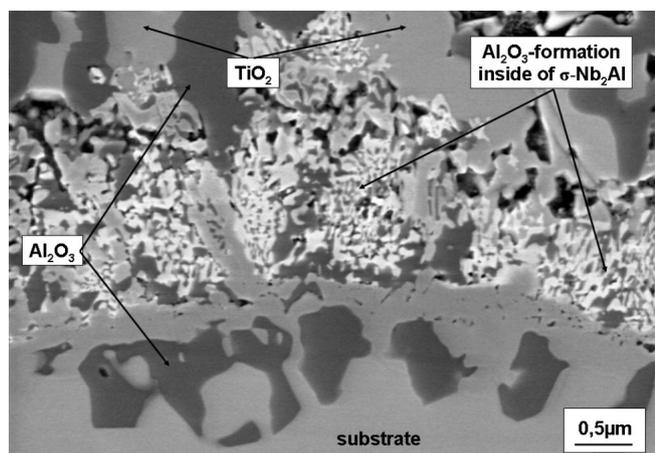


Figure 7 SEM micrograph of σ -Nb₂Al with an enhanced alumina formation.

The scale microstructure of the Ar annealed specimens differs slightly. In the bottom part of the oxide scale the concentration of Al₂O₃ particles is higher compared to the reference sample. Furthermore, a zone of Nb-enriched TiO₂ (composition: (64–74)O–(4–12)Al–(10–14)Ti–(7–15)Nb) was present directly above the region with alumina precipitates (Figure 6b,c). Due to the formation of a distinct σ -Nb₂Al zone after pre-treatment in argon it can be assumed that an enhanced alumina formation occurred in air according to oxidation of the σ -phase (composition: (37–47)O–(15–18)Al–(11–16)Ti–(22–30)Nb), shown in Figure 7. In addition to the Al₂O₃ growth, Nb enriched in the growing TiO₂ scale during oxidation of Nb₂Al. The distinct alumina region at the scale bottom could have led to the noticeably lower mass gain after approximately 20 h-cycles (Figure 5).

4. CONCLUSIONS

High-temperature annealing experiments under various atmospheres exhibit no oxidation processes under high vacuum conditions ($p = 10^{-6}$ mbar) at 1000°C. Mainly α_2 -Ti₃Al-phase was formed underneath the surface. In the outer part, a zone was formed in which 15 at.% oxygen was measured; either oxygen was dissolved in α_2 -Ti₃Al or formed a new phase (unknown “U-phase”).

Under Ar-atmosphere at 900°C nitrides (TiN + Ti₂AlN) were formed at the surface. Below this layer a zone of α_2 -Ti₃Al was observed. At an annealing temperature of 1000°C precipitations of alumina formed additionally at the nitride/ α_2 -Ti₃Al interface.

Much stronger oxidation occurred during exposure in hydrogen. A 20 μ m thick oxide scale was formed already after 10 h, mainly consisting of a mixture of alumina, α_2 -Ti₃Al and σ -Nb₂Al. At the surface a mixed oxide scale was grown with a dense TiO₂ layer on top.

Oxidation tests in air at 900°C exhibited different results of the differently pre-treated samples. The high vacuum annealed material showed the lowest oxidation rate presumably caused by the presence of the U-phase. The mass gain of the Ar-atmosphere pre-treated material increased much

faster in the first test cycles because of the high amount of nitrogen contained in the nitride layer leading to enhanced formation of titania. Upon extended exposure the mass gain increased rapidly, presumably due to the formation of Al₂O₃ caused by oxidation of σ -Nb₂Al in the transition region. Although no continuous alumina scale was formed at the surface all pre-treated samples obtained a longer lifetime at 900°C than the reference material.

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