



Article Oxidation Resistance of γ -TiAl Based Alloys Modified by C, Si and Y₂O₃ Microdopants

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Abstract: This work aimed to study the oxidation resistance of γ -TiAl based alloy, doped with small concentrations of carbon, silicon, and yttrium oxide in air at 800 and 1100 $^\circ$ C for 30 h. The TNM-B1 alloy samples were produced via high-energy ball milling, self-propagating high-temperature synthesis, and hot isostatic pressing techniques. The microstructure, oxidation kinetics at 800-1100 °C, scale structure, and oxidation mechanism were studied. The oxidation of alloys modified with carbon and silicon at 1100 °C was characterized by the formation of a three-layer coating. The Y₂O₃ modified alloy performed the greatest oxidation resistance at 1100 °C and promoted the formation of a dense Al₂O₃ interlayer.

Keywords: Ti-Al based intermetallics; powder metallurgy; oxidation; kinetics; oxide layers; diffusion



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1. Introduction

TiAl alloys have low density and excellent mechanical properties at high temperatures and are considered among the best candidates for turbine blades used in gas turbines and aircraft engines [1,2]. However, poor oxidation resistance at high temperatures (up to 900 °C) impedes further use of these alloys. Many efforts have been made to overcome this challenge such as alloying and nanomodification [3–5]. From the perspective of cost control, alloying is the most extensively used method.

TNM alloys doped with niobium and molybdenum have been created due to the advancement of TiAl-based alloys. Both compounds improve high-temperature oxidation resistance [6,7]. They can enhance oxidation resistance by inhibiting the formation of undesired TiO_2 oxide layers [8] and improve plastic deformation behavior at room temperature by lowering the energy of stacking defects [9–11]. The inclusion of niobium and molybdenum raises the activation energy of diffusion in γ -TiAl and α_2 -Ti₃Al, increasing the creep resistance of the alloys [10,12,13].

The next development step was the creation of TNM-B1 alloys doped with 0.1% B [14,15] and TNM + alloys including C and Si micro concentrations [16–18]. Boron reacts with titanium to form scattered TiB₂ particles, which provide grain refinement to the alloy and, as a result, increase its strength at room and high temperatures. Improving the TNM-B1 group alloys to enhance the performance characteristics of aerospace engines is a considerable challenge. The alloying of these alloys with micro-concentrations of C, Si, and Y_2O_3 is one of the most promising directions in this field. Several studies [19–25] have shown that these additives improve the mechanical characteristics at high temperatures. C and Si additions can be dissolved in the γ -TiAl + α_2 -Ti₃Al matrix, limiting diffusion processes. They can also form the dispersed carbides Ti₃AlC, Ti₂AlC, and Ti₅Si₃ silicide, impeding dislocation migration under load. The TiAl-based alloys containing Y_2O_3 show excellent strength characteristics up to 800 °C [16–18]. Ultrafine Y_2O_3 particles segregate between lamellas along the γ -TiAl and α_2 -Ti₃Al grain boundaries in alloys with a fully

lamellar structure (FL-structure) and serve as nucleation sites, providing grain refinement of the alloy.

TiAl-based alloys, doped with C, Si, and Y_2O_3 , have proven their superior high temperature strength and creep resistance, but some incomplete data on their oxidation resistance can be found. The protection mechanism utilized by the carbon addition consists of impeding either the intracrystalline diffusion by dissolved carbon atoms [26] or the intergranular diffusion of oxygen by the TiC carbide nanoparticles or Ti₂AlC and Ti₃AlC₂ MAX-phases [27,28]. Silicon is considered as the most beneficial element for improving the oxidation resistance of TiAl-based alloys, since it forms SiO₂ oxide with low oxygen solubility, and also suppresses the growth of rutile TiO_2 in the oxide scale. However, it should be noted that the most outstanding results were obtained at sufficiently high Si concentrations (5–13%) [29], which lie far beyond the known limits for effective strength and creep resistance improvement. To achieve a combination of high mechanical properties and oxidation resistance, it is advisable to protect the surface of TiAl-based alloys with coatings of Ti_xSi_y [30,31], TiAlSiN [32,33], Al–Si [34–36], and others, as obtained by magnetron sputtering and ion implantation. The effect of Y/Y_2O_3 additives on the oxidation resistance of TiAl-based alloys is well-covered. In [21,37,38], the positive effect of Y_2O_3 in the oxidized layer was explained by the fact that these particles block the grain boundary migration of oxygen atoms as well as the formation of a stronger oxidized layer due to the pinning of TiO₂ and Al₂O₃ layers with Y-containing phases.

The potential of each of the above-mentioned additives for improving oxidation resistance has been proven by many works. However, there is a lack of data on their comparison with each other, which is possible only when using alloys with an identical chemical composition and microstructure.

This work aimed to study the oxidation resistance of a powder metallurgy manufactured Ti–43Al–4Nb–1Mo–0.1B alloy with an equiaxed microstructure, doped with small (0.2–1.5 wt.%) concentrations of C, Si, and Y_2O_3 . The microstructure, oxidation kinetics at 800–1100 °C, scale structure, spallation resistance, and oxidation mechanism were systematically studied.

2. Materials and Methods

2.1. Initial Powders

Titanium (Polema Co., Tula, Russia, average particle size 15–20 µm), aluminum ("Polema Co.", average particle size 10 µm), niobium (SpecMetallMaster Co., Moscow, Russia, average particle size 40 µm), molybdenum ("Polema Co.", average particle size 5 µm), and boron powders (Ermakchim Co., Moscow, Russia, average particle size 0.2 µm) were used as initial materials for the basic γ -TiAl based TNM-B1 alloy. Carbon black (Ekopol'za, Astrakhan, Russia, P80, specific area 15 m²/g, mass concentration—0.2%), ground silicon single crystals (LLC 'Telekom-STV', Zelenograd, Russia, average particle size 15 µm, mass concentration—1.5%), and Y₂O₃ powder (Plasmatherm, Moscow, Russia, average particle size 0.2 µm, mass concentration—1.5%) were used as the dopants. Hereafter, the corresponding alloys were signed as 0.2C, 1.5Si, and 1.5Y₂O₃.

2.2. Manufacturing and Investigation Methods

The alloys were manufactured according to technological route, described in detail in previous research [39]. It contained three main operations: high energy ball milling (HEBM) and self-propagating high-temperature synthesis (SHS) were used to prepare γ -TiAl based powders followed by hot isostatic pressing (HIP) for powder consolidation.

HEBM was carried out in order to obtain the uniform distribution of components in the powder mixture in an argon atmosphere in an Activator-4M planetary ball mill (Activator, Russia) with steel grinding the media and ball to a powder mass ratio of 15:1. The SHS method was used to obtain the required phase composition of the powder. To start the SHS process in the thermal explosion mode, pre-pressed powders were placed in a tube-type furnace set to 900 °C. A thermocouple placed next to the pressed bars was used to control the temperature. The SHS process was conducted in an inert atmosphere with an argon flow rate of 10 mL/min. Sintered bars were ground to achieve a grain size of less than 65 μ m and distribution quantile value D50 about 32 μ m.

Compact samples were obtained by hot isostatic pressing (HIP) of the powder mixtures in titanium capsules at a temperature of 1250 °C for 2 h. No special heat treatment was carried out after HIP in order to maintain a two-phase near-globular microstructure of the alloys. Oxidation cylindrical specimens of h = 4 and diameter d = 6 mm were cut from the as-HIPed workpieces using wire electrical discharge machining. The oxidation of the specimens' surfaces were polished with abrasive paper 2400 mesh and ultrasonically washed with isopropyl alcohol. Three specimens of each alloy were measured simultaneously to assess the repeatability and scatter of the samples.

Oxidation experiments were carried out in a muffle furnace with an air atmosphere for 30 h at 800 °C and 1100 °C. The first temperature was chosen as it is typical for the operating of TiAl-based turbine units—the main application field of TiAl-based alloys. Oxidation experiments at 1100 °C were meant to demonstrate the potential of the C, Si, and Y_2O_3 modified alloys for use in more extreme conditions and to make the difference in oxidation kinetics more apparent.

To avoid the spalled oxide scale from leaving the crucible and to ensure proper interaction between the specimens and air, the specimens were kept in alundum crucibles protected by a corundum slip with small gaps. A schematic illustration of the oxidation test is shown in Figure 1.



Figure 1. A schematic illustration of the equipment for the oxidation test.

The crucibles were placed in the center of the furnace to ensure a constant temperature. The weights of the specimens were measured every 15 min during the first 1 h of the oxidation experiments using a high-precision (0.1 mg) electronic balance (A&D, Tokyo, Japan), after which the measuring period was 1 h. The measurement period was 5 h after completing 5 h of exposure. At each measure, the crucibles with the specimens were removed from the furnace and air cooled for around 0.5 h to room temperature before being weighed. After the measurement, the samples in the crucibles were again put back into the working furnace.

An additional experiment on the oxidation annealing of samples, consisting of Y_2O_3 particles and the main oxide components (Al₂O₃ and TiO₂), was carried out at a temperature 1100 °C. This allowed us to reveal the Y_2O_3 phase stability under oxidation conditions and the interaction direction in the presence of Al₂O₃ and TiO₂.

After the oxidation tests, the phase composition of the oxide scale was studied by X-ray diffraction analysis (XRD) on a D2 PHASER diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) using Cu radiation in the scattering angle $2\theta = 20^{\circ}-110^{\circ}$ range, step 0.02° , and an exposition time of 0.6 s. The structure of the as-HIPed and oxidized specimens

was investigated in cross-section polished samples using an S-3400 N scanning electron microscope (Hitachi, Tokyo, Japan) fitted with a NORAN energy dispersive spectrometer.

The fine structure of the oxide scale after annealing was analyzed by transmission electron microscopy (TEM) using a JEM 2100 microscope (Jeol, Tokyo, Japan), equipped with an X-MAX 80 EDX detector (Oxford Instruments, Abingdon, UK). A lamella with dimensions of $5 \times 3 \mu m$ was produced using a focused ion beam technique using a Scios dual-beam microscope (Field Electron and Ion Company, Hillsboro, OR, USA).

3. Results and Discussion

3.1. The Structure and Phase Composition of as-HIPed Samples

The investigated TiAl alloys had an irregular two-phase structure and consisted of grains of γ -TiAl and α_2 -Ti₃Al. Figure 2 shows the images of typical structures of the samples with each dopant after HIP. The microstructure of the studied alloys is not typical for common TiAl-based alloys produced by casting (leading to the formation of a duplex or lamellar structure). They inherited the microstructure of the powder particles after HEBM and SHS [39]. This was preserved due to consolidation at low temperature, below the β -Ti field in the Al–Ti phase diagram, and the lack of special heat treatment.





(b)



(c)

Figure 2. The SEM images of the as-HIPed alloys: 0.2C (a), 1.5Si (b), and 1.5Y₂O₃ (c).

The average grain size of γ -TiAl was 12.5 µm and that of α_2 -Ti₃Al was 5 µm. The major alloying components—niobium and molybdenum—were dissolved in the matrix during the HEBM process of preparing the powder mixture. Nevertheless, there was a limited number of grains in the structure of all alloys with a higher proportion of these components, which was indicated by the XRD method as a solid solution of molybdenum in niobium (Nb) (Figure 3). As carbon and silicon were dissolved in the γ -TiAl and α_2 -Ti₃Al

phases, no carbides or silicides were found in the 0.2C and 1.5Si alloys (Figure 3). At the HIP temperature, yttrium oxide Y_2O_3 had little interaction with TiAl and took the form of submicron particles that were uniformly dispersed throughout the matrix (Figure 2c).



Figure 3. The XRD patterns of the as-HIP-ed alloys 0.2C, 1.5Si, and 1.5Y₂O₃.

Figure 3 shows the X-ray diffraction patterns of the 0.2C, 1.5Si, and 1.5Y₂O₃ alloys. Each X-ray diffraction pattern had a set of peaks typical of γ -TiAl and α_2 -Ti₃Al. The ratio of these phases remained constant, regardless of the type of alloying addition (5:1 by weight). A solid solution based on niobium (Nb) and the intermetallic compound AlMo₃ was also found in all alloys in a range of 1–3 % (Table 1).

	Phase Concentration, wt. %					
Sample	γ-TiAl P4/mmm	α ₂ -Ti ₃ Al P63/mmc	(Nb) Im-3m	AlMo ₃ Pm-3n		
0.2C	78	17	3	2		
1.5Si	80	15	3	2		
1.5Y ₂ O ₃	80	17	2	1		

Table 1. The phase composition of the HIP-ed alloys 0.2C, 1.5Si, and 1.5Y₂O₃.

3.2. Oxidation Kinetics at 800 °C; of TiAl-Based Alloys

The oxidation kinetic curves of the alloys 0.2C, 1.5Si, and $1.5Y_2O_3$ after isothermal annealing in an oxidizing environment at 800 °C are shown in Figure 4. The experimentally obtained curves were approximated using the power–law dependence:

$$\Delta M^n = k \cdot t \tag{1}$$

where ΔM is the weight gain ($\mu g/cm^2$); *n* is the power law exponent; *k* is the oxidation rate constant; *t* is the duration of the process.

For all alloys, the specific weight gain after 30 h of annealing was negligible $-3.5-4.1 \text{ ug/cm}^2$ (Table 2). The oxidation of the samples was intense during the first 2 h of annealing. After 5 h of annealing, the weight gain of the samples was modest and did not surpass $0.5 \mu \text{g/cm}^2$.



Figure 4. The oxidation kinetic curves after isothermal annealing at 800 °C.

Table 2. The oxidation kinetics characteristics of the 0.2C, 1.5Si, and $1.5Y_2O$ alloys at 800 °C and the values of the oxide layer thickness (h) after 30 h of isothermal holding.

Alloy	ΔM , $\mu g/cm^2$	k	n	h, µm
0.2C	3.9	1368	5498	2.06
1.5Si	4.1	87.5	5580	2.28
$1.5Y_2O_3$	3.5	1446	5461	1.89

XRD and SEM were used to analyze the phase composition and the microstructure of the oxidized layer. Figure 5 shows the X-ray diffraction patterns of the alloys 0.2C, 1.5Si, and 1.5Y₂O₃ after oxidation resistance tests at 800 °C. All X-ray diffraction patterns revealed peaks corresponding to the γ -TiAl, α_2 -Ti₃Al, (Nb), and AlMo₃ phases in the original samples. Notably, the concentration of the α_2 -Ti₃Al phase after annealing was considerably reduced in all of the studied samples—6–8 wt. % (compared to 17–20 wt. % before annealing). The content of the oxide phases in the surface layer was low (i.e., roughly around 5% (Table 3)). The rutile TiO₂ peaks (110) at 27.2° and (101) at 2 θ = 35.7° as well as the Al₂O₃ phase (104) peaks at 2 θ = 35.1° indicate their presence.



Figure 5. The XRD patterns of the 0.2C, 1.5Si, and $1.5Y_2O_3$ alloys' oxidized layers after annealing at 800 °C.

	Phase Concentration, wt. %							
Sample	γ-TiAl P4/mmm	α ₂ -Ti ₃ Al P63/mmc	(Nb) Im-3m	AlMo ₃ Pm-3n	TiO ₂ P42/mnm	Al ₂ O ₃ P63mc		
0.2C	74	8	3	2	9	4		
1.5Si	76	8	3	2	7	4		
1.5Y ₂ O ₃	77	6	3	1	10	3		

Table 3. The phase composition of the 0.2C, 1.5Si, and $1.5Y_2O_3$ alloys after oxidation annealing at 800 °C.

The cross-sections of the specimens after oxidation resistance testing were investigated to determine the thickness and structure of the oxidized layer. In all cases, the oxidized layer, which had an average thickness of 2–3 μ m, was mainly composed of rutile TiO₂ (Figure 6). The surface of the 0.2C and 1.5Y₂O₃ samples had the densest oxide coatings. Long longitudinal fractures were observed at the interface between the oxide layer and the matrix in the 1.5Y₂O₃ alloy, resulting in partial spallation of the coating and the formation of routes for oxygen transport into the sample (Figure 6b). Al₂O₃ granules were found in the structure where partial spallation of the oxide layer was observed.





(c)

Figure 6. A cross-sectional oxidized layer image of the alloys 0.2C (a), 1.5Si (b), and $1.5Y_2O_3$ (c) after isothermal annealing at 800 °C.

3.3. Oxidation Kinetics at 1100 °C of TiAl-Based Alloys

Figure 7 shows the appearance of the TiAl-based alloy specimens after annealing at 1100 °C. Apparently, the oxides covered a large section of the sample surface (light gray).

The $1.5Y_2O_3$ sample had the smoothest surface and no signs of the oxide layer spallation. The degradation of the coating was seen locally on the surface of the 0.2C sample. At the same time, the covering of the 1.5Si sample was nearly totally damaged, indicating its poor strength.



Figure 7. The sample images after annealing at 1100 °C.

The oxidation kinetic curves of the alloys 0.2C, 1.5Si, and $1.5Y_2O_3$ after isothermal annealing in an oxidizing atmosphere at 1100 °C are shown in Figure 8. The power–law dependency was used to approximate the experimental curves (1). Table 4 displays the parameters produced by approximating the experimental data, the specific weight increase of the samples after testing (M), and the average coating thickness value (h).



Figure 8. The oxidation kinetic curves after isothermal annealing at 1100 °C.

Table 4. The oxidation kinetics characteristics of the 0.2C, 1.5Si, and 1.5Y₂O alloys at 1100 $^{\circ}$ C and the values of the oxide layer thickness (h) after 30 h of isothermal holding.

Alloy	ΔM , ug/cm ²	k	n	h, µm
0.2C	61	1911	2704	2086
1.5Si	37	8862	2921	1744
1.5Y ₂ O ₃	17		5641	1342

The behavior and oxidation tendency of the 0.2C, 1.5Si, and $1.5Y_2O_3$ alloys changed significantly when the annealing temperature was raised. The 0.2C sample had the largest specific weight increase (61 ug/cm²), which was 1.6 times higher than the 1.5Si sample and nearly four times higher than the $1.5Y_2O_3$ sample (Figure 8). The oxidation process was most intense during the first 3 h of annealing when a thick oxide layer developed on the surfaces of the samples. The oxidation rate was then reduced due to a delay in the diffusion processes in the sample's near-surface layers.

During annealing at 1100 °C, the alloy $1.5Y_2O_3$ had the lowest total specific weight growth. Its oxidation resistance was characterized by a high n-value of 5.641. The weight gain of the sample was negligible despite the annealing time of longer than 5 h. At the same time, a gradual rise in mass was seen in this area for the 0.2C and 1.5Si alloys.

The X-ray diffraction patterns of the 0.2C, 1.5Si, and 1.5Y₂O₃ alloys after annealing at 1100 °C are shown in Figure 9. According to the intensity of the peaks, the main phases in the surface layer were Al₂O₃ (approximately 50%) and TiO₂ (35%). The α_2 -Ti₃Al phase was found in all samples, although its concentration did not surpass 10% (Table 5). The presence of two different oxides with crystal structures similar to those of rutile TiO₂ but with different lattice parameters *a* and *c* distinguished the 0.2C and 1.5Si alloys from the 1.5Y₂O₃ alloy. This was demonstrated by the splitting of all peaks related to TiO₂ (Figure 9, angles of 27–28°).



Figure 9. The XRD patterns of the oxidized layers of 0.2C, 1.5Si, and $1.5Y_2O_3$ alloys after annealing at 1100 °C.

Table 5. The phase composition of the 0.2C, 1.5Si, and $1.5Y_2O_3$ alloys after oxidation annealing at 1100 °C.

	Phase Concentration, wt. %							
Sample	TiO ₂ P42/mnm	(Ti,Nb)O ₂ P42/mnm	Al ₂ O ₃ P63mc	(Nb) Im-3m	α ₂ -Ti ₃ Al P63/mmc	NbO Pm-3n		
0.2C	25	17	52	2	6	2		
1.5Si	27	19	42	3	7	2		
1.5Y ₂ O ₃	38	-	51	1	10	-		

The lattice parameters of the phase close to stoichiometric TiO₂ are a = 4.5903 Å and c = 2.9593 Å. The lattice parameters of the second oxide were slightly increased—a = 4.6263 Å and c = 2.9903 Å. According to the results presented in several publications [40,41], this lattice expansion results from a certain titanium atom's replacement in the TiO₂ lattice with niobium atoms. Therefore, this phase was labeled as (Ti, Nb) O₂.

Figure 10 shows the cross-sectional microstructures of the oxidized layer of the alloys 0.2C, 1.5Si, and $1.5Y_2O_3$. The thickness ranged from 13.42 microns (alloy $1.5Y_2O_3$) to 20.86 microns on average (alloy 0.2C). In the oxidized layer, three separate areas could be identified. The first (upper) was made up of large TiO₂ granules with a porous and loose structure. The second (intermediate) was mainly made of Al₂O₃. The bottom layer was a TiO₂ and Al₂O₃ grain combination that was particularly noticeable in alloys 0.2C and 1.5Si (Figure 10a,b). The bottom layer was a mixture of the TiO₂ and Al₂O₃ grains, particularly

noticeable in alloys 0.2C and 1.5Si (Figure 10a,b). There was a thin layer (2–3 μ m) with an increased niobium concentration at the interface between the matrix and the oxidized layer in all of the studied alloys.



Figure 10. The cross-sectional oxidized layer image of alloys 0.2C (**a**), 1.5Si (**b**), and $1.5Y_2O_3$ (**c**) after isothermal annealing at 1100 °C and a magnified image of the area highlighted by a white dotted line (**d**).

The oxidized layer on the surface of the 0.2C and 1.5Si samples had poor adhesion to the base, contained pores and wide fractures that passed between the $Al_2O_3/TiO_2 + Al_2O_3$ layer and the $TiO_2 + Al_2O_3$ /base layer. Due to its loose structure, the bottom layer offered poor oxidation protection for the substrate and less inhibited the oxygen penetration into the material, as evidenced by a significant number of oxide grains at the distance of 10–20 µm from the oxidized layer. The Al_2O_3 oxide grains were mainly localized in an intermediate layer enriched with niobium and molybdenum (Figure 10a). This layer limits oxygen diffusion into the material's structure as well as titanium and aluminum diffusion toward the surface and so performs a protective function more efficiently than an oxide coating with a high number of fractures and holes.

The oxidized layer on the surface of the $1.5Y_2O_3$ sample was much denser and devoid of serious defects (Figure 10b). Its distinguishing feature was the lack of a layer of $TiO_2 + Al_2O_3$ oxides. A layer of Al_2O_3 in evenly dispersed Y_2O_3 nanoparticles was also a thin layer with a higher concentration of Nb and Mo at the interface, acting as a reliable diffusion barrier and halting the oxidation process.

4. Discussion

The oxidation kinetic curves, phase composition, and the oxidized layer microstructures of alloys 0.2C, 1.5Si, and $1.5Y_2O_3$, air-annealed at 800 and 1100 °C, yielded the following important results. Oxidation is accompanied by forming an oxide coating based on rutile TiO₂ (800 °C) or a two/three-layer coating TiO₂/Al₂O₃/TiO₂ + Al₂O₃ (1100 °C). This process is described by power law equations with an exponent >2, indicating that the oxide layer formation is limited diffusion. Indeed, factors such as density and strength of the oxide layer, and the existence of fractures and other defects that function as routes for oxygen atom diffusion, have a significant impact on alloy oxidation resistance.

During annealing at 800 °C, all of the analyzed alloys exhibited excellent oxidation resistance. The significant decrease in the concentration of the α -Ti₃Al phase after annealing may indicate that the oxidation process is selective. The α -Ti₃Al phase is more actively involved in oxidation during the initial stage due to a higher solubility of oxygen (45% vs. 5% for γ -TiAl) [42], which is attributed to the structural features of this compound. One unit cell of α -Ti₃Al contains two octahedral pores through which oxygen atoms diffuse [43].

We supposed that doping the TiAl-based alloys with carbon at concentrations lower than the solubility limit of the γ -TiAl and α -Ti₃Al phases would block oxygen diffusion since carbon atoms will also occupy the octahedral pores and form an interstitial solid solution. However, at 1100 °C, the alloy 0.2C was characterized by the lowest hightemperature oxidation resistance, attributed to the presence of cracks and pores in the coating. A plausible reason for this is the interaction between the carbon and oxygen yielding gaseous CO and its accumulation in pores, which increases the internal stresses in the coating and causes its partial degradation.

The silicon-doped alloy (alloy 1.5Si) exhibited a greater high-temperature oxidation resistance despite numerous spallations of the oxide layer (Figure 7). A possible explanation of the effect of silicon as a dopant is provided below. A SiO₂ layer impeding oxygen diffusion through the coating can potentially be formed during oxidation. In this case, this mechanism is unlikely to occur since the structure and phase composition investigation revealed no traces of crystalline SiO₂. However, it is highly likely that γ -Ti(Al,Si) and α -Ti₃(Al,Si) interstitial solid solutions contained silicon atoms. Being a component of the compounds, silicon binds titanium and prevents the formation of TiO₂ [44].

Doping with Y_2O_3 nanoparticles had a dramatic impact on the oxidation resistance of the TiAl-based alloy. The structure of a thin lamella cut by the FIB method from an oxidized layer was examined to provide a detailed explanation of oxidative processes (Figure 11). The main phases were Al_2O_3 and TiO_2 , which was established by analyzing the EDX elemental maps.



Figure 11. The STEM image of a lamella cut from the oxide layer of a $1.5Y_2O_3$ sample (**a**), HRTEM image of a $Y_2Ti_2O_7$ particle (**b**), and electron diffraction from this grain (**c**); EDS elemental maps of titanium (**d**), aluminum (**e**), yttrium (**f**), and oxygen (**g**).

Yttrium was found only in a few grains, the composition of which contained 18 at.% Y, 18 at.% Ti, and 64 at.% O, equivalent to a $Y_2Ti_2O_7$ compound. The presence of this phase, with space group Fd-3m and a lattice period of 0.9934 nm, was also confirmed by the electron diffraction analysis.

Thus, at a temperature of 1100 °C, the introduced Y₂O₃ nanoparticles interacted with TiO_2 to form the Y₂Ti₂O₇ compound. In order to study the possibility of the formation of double oxides in the Y-Ti-O and Y-Al-O systems, mixtures of Y₂O₃-TiO₂, Y₂O₃-Al₂O₃, and Y_2O_3 -Al₂ O_3 -TiO₂ powders with an equimolar ratio of components were annealed. Annealing conditions were similar to the oxidation resistance tests ($1100 \degree C$, in air). Y₂Ti₂O₇ oxide was the prevailing phase in the annealed Y_2O_3 -TiO₂ composition. There were no TiO_2 peaks on the radiograph, indicating that it was completely oxidized (Figure 12). Table 6 shows that the sintered sample includes 25% of Y_2O_3 , which did not participate in the reaction:

$$Y_2O_3 + 2 TiO_2 = Y_2Ti_2O_7$$



Figure 12. The X-ray patterns of the Y₂O₃-TiO₂, Y₂O₃-Al₂O₃, and Y₂O₃-Al₂O₃-TiO₂ powder mixtures sintered at 1100 °C.

Table 6. The phase composition of the Y_2O_3 -Ti O_2 , Y_2O_3 -Al₂ O_3 , and Y_2O_3 -Al₂ O_3 -Ti O_2 powder mixtures sintered at 1100 °C.

		Pl	hase Concent	ration, wt.	%	
Sample	Y ₂ O ₃ Ia-3	Al ₂ O ₃ R-3c	Y ₂ Ti ₂ O ₇ Fd-3m	YAlO ₃ Pbnm	Y ₄ Al ₂ O ₉ P21/c	Y ₃ Al ₅ O ₁₂ Ia-3d
Y ₂ O ₃ -TiO ₂	25	-	75	-	-	-
Y ₂ O ₃ -Al ₂ O ₃	6	5	-	80	11	-
Y ₂ O ₃ -Al ₂ O ₃ -TiO ₂	-	-	70	10	-	20

The phase composition of the Y₂O₃-Al₂O₃ sample is represented by the double oxides YAlO₃ and Y₄Al₂O₉, indicating the presence of the following reactions:

$$Y_2O_3 + Al_2O_3 = 2YAlO_3$$

01/110

$$2Y_2O_3 + Al_2O_3 = Y_4Al_2O_9$$

Furthermore, only around 5% of the original components of the Y_2O_3 and Al_2O_3 mixture did not react.

Thus, the fundamental possibility of the formation of double oxides at 1100 °C was established based on studies of the phase composition of the sintered mixtures Y₂O₃-TiO₂ and Y_2O_3 -Al₂O₃. An annealing of a powder mixture of three oxides, Y_2O_3 -Al₂O₃-TiO₂, was carried to determine the predominant direction of the Y_2O_3 reaction. The X-ray diffraction pattern showed three phases: $Y_2Ti_2O_7$ (70%), $Y_3Al_5O_{12}$ (20%), and YAlO₃ (10%). The findings showed that $Y_2Ti_2O_7$ is more likely to form during the interaction of three oxides, and that unreacted yttrium oxide Y_2O_3 generates yttrium aluminum garnet $Y_3Al_5O_{12}$ with an Al:Y = 5:3 ratio.

The $Y_2Ti_2O_7$ phase, which forms during the oxidation of TiAl-based alloys, promotes an increase in oxidation resistance by decreasing the proportion of TiO₂. Due to strong chemical interactions with simple oxides, $Y_2Ti_2O_7$ oxide has great thermal stability, corrosion resistance, and boosts the strength of the oxidized layer [45–48]. The oxidation resistance of the alloy also arises in the case of the formation of the $Y_3Al_5O_{12}$ phase [49].

5. Conclusions

The oxidation behavior of the γ -TiAl-based alloy doped with carbon, silicon, and yttrium oxide at low concentrations, during isothermal oxidation tests in laboratory air at 800 and 1100 °C for 30 h was studied. The following conclusions can be drawn based on the obtained results:

- 1. All of the alloys exhibited a high oxidation resistance at 800 °C. The oxidation kinetics can be described by a power–law with a power–law exponent of 5.461–5.580. A coating based on rutile TiO₂ (~2 μ m thick) was formed on the surface;
- Oxidation of the 0.2C and 1.5Si alloys at 1100 °C caused the formation of three-layer TiO₂/Al₂O₃/(TiO₂ + Al₂O₃) coatings with a porous structure and a large number of cracks, resulting in spallation;
- 3. The alloy modified with $1.5Y_2O_3$ had the best oxidation resistance at $1100 \,^{\circ}$ C. During annealing, the oxide layer formed the $Y_2Ti_2O_7$ phase, which has low oxygen permeability and high temperature stability. The formation of $Y_2Ti_2O_7$ was accompanied by a decrease in the concentration of undesirable TiO₂ oxide;
- 4. An interlayer rich in niobium and molybdenum was formed at the oxide layer/matrix interface. This interlayer ensures thermal stability of the alloy by preventing oxygen diffusion into the material bulk as well as titanium and aluminum diffusion toward the surface.

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