# HIGH-TEMPERATURE STRENGTH OF TITANIUM ALLOYS ALLOYED WITH SILICON, ALUMINUM, AND ZIRCONIUM IN AIR

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We study the behavior of VT1-0 titanium alloy alloyed with silicon, aluminum, and zirconium in the process of oxidation in air at 800℃ for 30 h.  It is shown that, as a result of alloying of the alloy with silicon up to 6 wt.%, its high-temperature strength becomes more than two times higher.  This effect is connected with the influence of silicon on the diffusion processes in the metal and scale and changes in the morphology of scale.

Titanium alloys are now extensively used in various branches of engineering due to their relatively small density and high corrosion resistance and strength at room and elevated temperatures.  At present, recently developed Ti–Si refractory titanium alloys draw especial attention of the researchers [1, 2].  Their operating temperatures can be as high as  700–750°C  and even higher.

In the present work, we study the high-temperature strength of alloys of this sort with different contents of alloying elements (silicon, aluminum, and zirconium).

The alloys were prepared by using the procedure of plasma skull melting.  The temperature of a casting mold was equal to  1700°C  and the pressure in the melting chamber varied within the range  0.1–0.6 MPa.  The temperature of the molten metal and its chemical composition were equalized by electromagnetic stirring.  The thermal motion of skull melting was monitored. The mass and temperature of the melt poured into a graphite mold were regulated.  The concentrations of the impurities were as follows (%):  0.02–0.06 $O_2$  and  0.22–0.25 C.  The alloy was additionally alloyed with silicon  (1–6 wt.%),  aluminum  (3 wt.%),  and zirconium  (5 wt.%).  Cast specimens were not subjected to thermal treatment for oxidation.

Specimens  $10 \times 4 \times 3$ mm  in size were oxidized  in a "Derivatograph" device (the changes in the mass were continuously recorded for  6 h) and in a resistance furnace at  800°C  [the mass was periodically measured for the entire period of holding (up to  30 h)].  The accuracy of measurements of the mass was  0.1 mg.  In the course of the tests performed in the "Derivatograph" device, the specimens were heated together with the furnace (at a rate of  20°C/min).  In the electric furnace, they were placed in a chamber preliminarily heated to the required temperature.  Prior to testing, the surfaces of the specimens were ground with emery cloth up to micron purity.  The high-temperature strength of alloys was evaluated according to changes in their mass  $(g/m^2)$.  Their oxidation resistances were compared by analyzing the oxidation rates under identical conditions  $(g/(m^2 \cdot h))$.

The structure of alloys after oxidation was studied by using transverse microsections prepared according to a special procedure capable of preserving brittle scale on the specimen surface.  The microstructure of alloys was studied with a MIM-7 microscope.  Their microhardness was found by using a PMT-3 instrument under loads of  0.196 and  0.49 N  as the average value over  3–5  measurements.  The X-ray phase diffraction analysis of scale was performed in a DRON-3 installation in the  $CuK_\alpha$-radiation.  The microscopic X-ray spectral analysis was carried out with the help of a "Superprobe-733" device.

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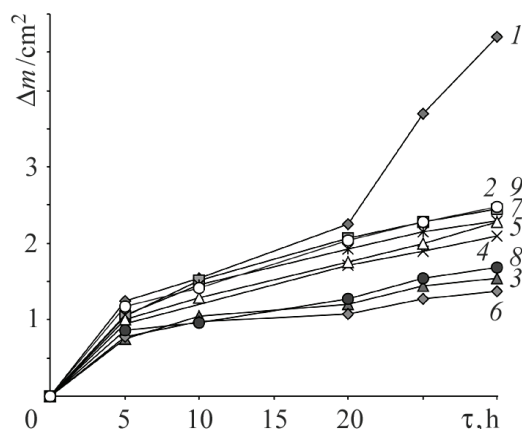
**Fig. 1.** Kinetic oxidation curves plotted at 800°C for 30 h. The numbers of the curves correspond to the numbers in Table 1.

**Table 1. Oxidation Rates $(g/(m^2 \cdot h))$ of VT1-0 Alloy at 800°C for Different Contents of Silicon and Times of Holding**

| No. | Si, % | Holding for 5 h with continuous recording of the mass | Holding in the furnace, h | | | |
|-----|-------|-------------------------------------------------------|---|---|---|---|
| | | | 5 | 10 | 20 | 30 |
| 1. | 0 | 0.28 | 2.5 | 1.6 | 1.1 | 1.6 |
| 2. | 1 | 0.20 | 2.1 | 1.5 | 1.0 | 0.8 |
| 3. | 2 | 0.14 | 1.5 | 1.0 | 0.6 | 0.5 |
| 4. | 4 | 0.12 | 1.9 | 1.3 | 0.9 | 0.7 |
| 5. | 6 | 0.1 | 2.1 | 1.5 | 0.9 | 0.7 |
| 6. | 2 + 3% Al | 0.095 | 1.6 | 0.9 | 0.5 | 0.5 |
| 7. | 4 + 3% Al | 0.11 | 2.0 | 1.3 | 0.9 | 0.8 |
| 8. | 6 + 3% Al | 0.105 | 1.7 | 1.0 | 0.6 | 0.6 |
| 9. | 4 + 3% Al + 5% Zr | 0.2 | 2.3 | 1.4 | 1.0 | 0.8 |

As a result of introducing silicon, the oxidation rate of VT1-0 alloy decreases and the best results are obtained for a silicon content of 2% (Table 1).

For higher contents of silicon, its oxidation rate remains almost constant. The data of tests performed by using different procedures for 5 h practically coincide. The procedure of subsequent holding for up to 30 h confirms these results. The alloys containing 2% of silicon and additionally alloyed with aluminum exhibit the lowest oxidation rates. Note that, in short-term tests, the oxidation rate insignificantly depends on the concentrations of silicon (up to 6%) and aluminum (3%). At the same time, the oxidation resistance decreases as a result of long-term holding. The negative role of zirconium (weakening the influence of silicon and aluminum) is also corroborated. However, the oxidation rate of high alloy remains two times lower than for the unalloyed titanium (Table 1).
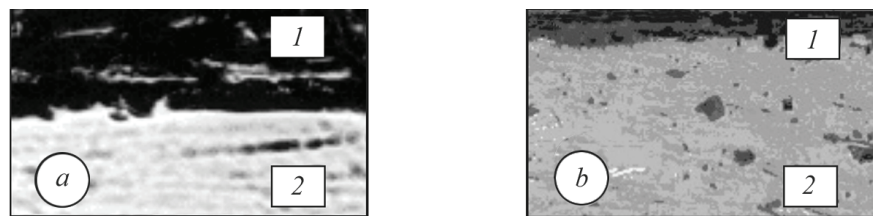
**Fig. 2.** Microstructure of alloys after oxidation at 800°C: (a) VT1-0 alloy, holding for 6 h, ×400; (b) alloy with 4% Si, holding for 30 h, ×250: (1) scale, (2) base metal.

**Table 2. Parameters of Oxidation**

| Alloy | $n$ | $K_p$ |
|---|---|---|
| VT1-0 | 2.05 | 70.0 |
| VT1-0 + 2% Si | 2.16 | 26.2 |
| VT1-0 + 4% Si | 2.2 | 18.0 |
| VT1-0 + 4% Si + 3% Al | 2.3 | 19.5 |
| VT1-0 + 4% Si + 3% Al + 5% Zr | 2.12 | 37 |

The kinetics of oxidation can be described by a power dependence $q^n = K_p\tau$, where $q$ is the relative increment of mass, $\tau$ is the time of oxidation, $K_p$ is the constant of oxidation (Fig. 1).

For given $\tau_1$ and $\tau_2$, we determine the corresponding increments of mass. Then the exponent $n$ and constant $K_p$ can be found for each alloy by the graphic-analytic method (Table 2).

In the process of oxidation, the masses of alloys vary according to a power law whose exponent $n$ is almost equal for all analyzed alloys. At the same time, the constants of oxidation are noticeably different. Thus, the maximum value of the constant corresponds to the oxidation of VT1-0 alloy and the smallest constants are observed for the alloys with 4% Si and 4% Si + 3% Al. These regularities show that the process of oxidation is controlled by the diffusion processes.

In the course of oxidation of titanium, the principal role is played either by the diffusion of titanium cations or by the diffusion of oxygen (in this case, the points of view of the researchers are contradictory [4, 5]). Therefore, despite the existence of satisfactory agreement between the experimental data on the rate of the process and the phase composition of scale, different authors have different opinions concerning the mechanism of this process.

The data of metallographic analysis and X-ray phase diffraction analysis reveal the following picture: In the process of oxidation, a layer of scale is formed on the surface with satisfactory adhesion for all alloys, except the alloy without silicon. In the unalloyed material, the multilayer scale begins to crumble after testing for 10 h (Fig. 2a). Its structure is fine-grained and homogeneous (Fig. 3a). The cracks are located in the outer layer (Fig. 3b). On the surface of alloys with concentrations of silicon of 2% and higher, the layer of scale does not suffer crumbling after oxidation for 6 h and holding for 30 h, although the level of adhesion insignificantly decreases. In alloys with 2–6% of silicon, the layer of scale contains elongated crystals whose number increases if we introduce 3% of aluminum.
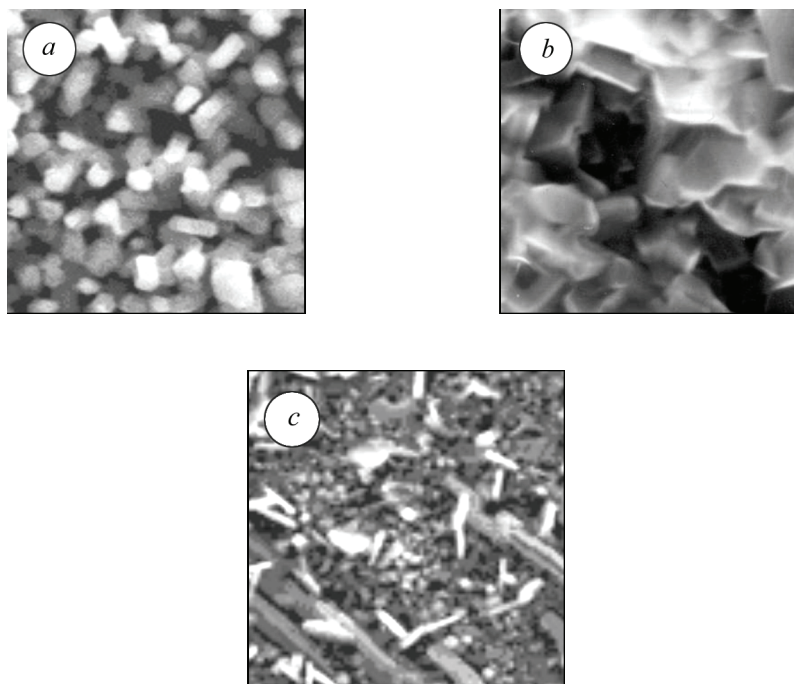
**Fig. 3.** Morphology of scale formed on alloys as a result of oxidation at $800°C$: (a, b) VT1-0 alloy (outer layer), (c) alloy with 2% Si + 3% Al; (a) $\times 3000$, (b) $\times 10{,}000$, (c) $\times 1000$.

The oxide film contains numerous defects and, hence, the process of oxidation should not obey a parabolic law. However, under the influence of alloying, the structural morphology changes and the level of adhesion increases, which significantly decreases the rate of oxidation.

In all cases, the X-ray phase diffraction analysis shows that scale is mainly formed by the $TiO_2$ phase (rutile). Moreover, the traces of silicon dioxide ($\alpha$-$SiO_2$) and aluminum oxide ($\gamma$-$Al_2O_3$) are also detected in alloys. The intensities of the lines corresponding to these phases depend on the time of holding. The intensity of the $TiO_2$ line increases with the time of holding. This can be explained by the increase in the thickness of scale. At the same time, the intensity of the $\alpha$-$SiO_2$ lines becomes lower, which can be regarded as an indirect indication of the formation of $\alpha$-$SiO_2$ under the layer of $TiO_2$ [4]. Moreover, as a result of thickening of the layer of $TiO_2$, the fraction of this oxide in scale decreases. The amounts of formed aluminum and zirconium oxides are very small but the dissolution of these elements in the $TiO_2$ lattice promotes its loosening and, hence, the process of diffusion of oxygen through titanium dioxide is accelerated [5]. The results of X-ray phase diffraction analysis agree with the kinetic curves and reveal the deceleration of the process of oxidation on alloys alloyed with silicon and aluminum, which may happen as a consequence of changes in the structure and phase composition of scale.

The data of metallographic analysis, together with the data on microhardness, show that, in the process of oxidation of titanium, oxygen dissolves in the surface layer of the metal parallel with the formation of an oxide film. This is explained by its high solubility in titanium and predominant diffusion in the oxide films [7]. The microhardness of the surface layers and the base metal of alloys and the depth of saturation show that the metal layer neighboring with the layer of scale is characterized by elevated hardness (Table 3, Fig. 2b), which gradually decreases with depth (Fig. 2b). Note that the hardness of alloys alloyed with silicon is lower and the depth of gas saturation in these alloys is smaller. After alloying with aluminum (3%), these characteristics of the surface layer do not undergo any significant changes. As the time of holding increases to 30 h, the depth of gas saturation suffers more pronounced changes than the hardness of the surface layer.

**Table 3. Microhardness $H_\mu$ of the Base Metal (Numerator) and Surface Layer (Denominator) and the Depths of Gas Saturation $h$ in Alloys Oxidized at 800°C for Different Times of Holding**

| Alloy | $H_\mu$, GPa | $h$, μm |
|-------|:---:|:---:|
| Holding for 5 h | | |
| VT1-0 | 2.11/5.43 | 50 |
| VT + 4% Si | 2.32/3.99 | 40 |
| VT + 6% Si | 2.37/4.07 | 40 |
| VT + 4% Si + 3% Al | 2.98/4.16 | 30 |
| VT + 6% Si + 3% Al | 3.07/4.34 | 30 |
| Holding for 30 h | | |
| VT1-0 | 2.31/5.69 | 210 |
| VT + 4% Si | 3.14/6.79 | 180 |
| VT + 6% Si | 3.67/6.47 | 160 |
| VT + 4% Si + 3% Al | 3.78/6.08 | 140 |
| VT + 6% Si + 3% Al | 4.02/6.43 | 140 |

As in the case of commercially pure titanium, the process of oxidation of Ti–Si -system alloys at 800°C obeys a parabolic law. First, the oxidation of titanium is characterized by the diffusion of its ions accompanied by the formation of an outer layer of scale formed by rutile [5]. After a certain period of time, we observe the formation of cavities on the scale–metal interface, which turn into barriers for the transition of ions into scale as the temperature and duration of holding increase. As a result, the contact of scale with the base is deteriorated. After this, scale is formed mainly as a result of the diffusion of oxygen, its dissolution in the metal, and the formation of laminated rutile scale guaranteeing a certain level of high-temperature strength.

Thus, despite the well-pronounced improvement of high-temperature strength of VT1-0 alloy after alloying with silicon, the mechanism of formation of scale depends on the competing processes of diffusion of titanium and oxygen (as in the case of unalloyed metal). As a result of alloying of titanium with silicon, the rate of transition of titanium ions into the layer of scale decreases. This is reflected in the improvement of the adhesion of scale. Moreover, the rate of diffusion of oxygen ions also decreases, which promotes the decrease in the depth of gas saturation.

As a rule, the researchers tried to explain the influence of alloying elements on the initial stage of the process of oxidation of titanium by using the Wagner theory. Indeed, titanium dioxide is an $n$-type semiconductor, i.e., is characterized by the deficiency of oxygen. Therefore, the high-temperature strength of titanium can be affected by the metals whose valency is lower or higher than the valency of titanium $(4^+)$ provided that their oxides are soluble in titanium dioxide. If the valencies of alloying elements are lower than $4^+$, then the indicated elements must decrease the high-temperature strength of titanium. At the same time, if their valencies are higher than $4^+$, then the high-temperature strength of titanium must increase and, finally, if the valency of alloying ele-

ments is equal to $4^+$, then their influence should be practically absent. According to the Wagner theory, silicon and zirconium do not affect the high-temperature strength of titanium and aluminum decreases this parameter. Actually, this is not true, as follows, in particular, from the results of our investigations. Thus, the influence of alloying elements on the high-temperature strength of titanium is most often explained by the formation of protective films with the same structure and phase composition as on unalloyed titanium [4, 11]. In our investigations, the phase compositions of scale for all alloys [this is mainly the $TiO_2$-phase (rutile)] weakly varies as a result of alloying in the course of both short- and long-term holding. Thus, the increase in the high-temperature strength of the investigated alloys can, most likely, be explained by the influence of the structure and morphology of scale but not by the influence of its phase composition. In the alloys containing silicon, the dissolution of this element in titanium (the maximum solubility of silicon in $\alpha$-titanium is $0.45$ wt.% at a temperature of the eutectoid transformation equal to $860°C$) decreases the lattice constant of the latter and inhibits diffusion. The process of oxidation is sharply decelerated as a result of introduction of $0.43$ wt.% of silicon [6]. As the concentration of is silicon increases further, the high-temperature strength of titanium insignificantly increases. As a result of alloying of VT1-0 alloy with silicon in amounts greater than $0.45$ wt.%, we observe the formation of silicides in its structure. These silicides precipitate on grain boundaries and inside the grains decelerating the diffusion of titanium and oxygen ions and, hence, the formation of titanium dioxide.

Moreover, the process of oxidation of titanium silicides in contact with oxygen is much slower (Fig. 3e) than in titanium [12], which also promotes the increase in the high-temperature strength of alloys. In the alloys additionally alloyed with aluminum, we observe the formation of complex-alloy silicides $(Ti, Zr)_5 (Al, Si)_3$. However, the effect of these silicides on the high-temperature strength of titanium is insignificant. This means that, in the solid solution, silicon promotes the increase in high-temperature strength. At the same time, aluminum and zirconium worsen the diffusion characteristic of the lattice. Thus, it is possible to assume that the pronounced positive influence of aluminum on the high-temperature strength of titanium can be expected after longer periods of holding characterized by the accumulation of substantial amounts of titanium dioxide in the scale.

## CONCLUSIONS

The procedure of alloying of commercially pure VT1-0 titanium with $1–6$ wt.% of silicon leads to a significant decrease in the rate of oxidation and the depth of gas saturation of the metal. The optimal content of silicon characterized by a more than twofold increase in high-temperature strength at $800°C$ is equal to $1–2\%$.

Silicon and aluminum affect the rate of diffusion of titanium and oxygen ions and, hence, the structure and morphology of scale and the depth of saturation of titanium with oxygen. As a rule, the high-temperature strength of titanium increases when silicon is in the $\alpha$-Ti solid solution, which decreases the lattice constants. The increase in the content of silicon up to the formation of the $Ti_5 Si_3$ intermetallic compound also somewhat increases the high-temperature strength of the alloy because the process of oxidation of titanium silicides in contact with oxygen is much slower than for titanium.

As a result of additional alloying of Ti–Si-system binary alloys with aluminum and zirconium, their high-temperature strength insignificantly decreases because the ionic radii of these elements are larger than for titanium and, as constituents of the solid solution, they worsen the diffusion characteristic of the lattice. Moreover, we observe the formation of more complex silicides $[(Ti, Zr)_5 (Al, Si)_3]$ whose chemical resistance is somewhat lower than the resistance of simple silicide $[Ti_5 Si_3]$.

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