UDK 669.295:66.094.3
Strokovni članek

ISSN 1580-2949
MTAEC9, 37(6)381(2003)

SILICONIZING AS A METHOD FOR IMPROVING THE RESISTANCE OF TITANIUM TO OXIDATION

SILIKONIZIRANJE KOT METODA POVEČANJA OKSIDACIJSKE SPOSOBNOSTI TITANA

Dalibor Vojtěch, Tomáš Kubatík

Department of Metals and Corrosion Engineering, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
dalibor.vojtech@vscht.cz

Prejem rokopisa - received: 2003-10-01; sprejem za objavo - accepted for publication: 2003-11-11

Titanium alloys are promising materials because of their excellent strength-to-weight ratio and their resistance to corrosion. However, their high-temperature resistance to oxidation is rather poor. One of the methods for improving the oxidation resistance of Ti-based alloys is surface siliconizing. In our investigation we have looked at methods of CVD and powder siliconizing, and the structure, morphology and hardness of the silicon-rich surface layers were investigated. The protection effect of the surface layers was confirmed by measuring the oxidation kinetics.

Key words: titanium, silicon, siliconizing, CVD, oxidation, hardness

Titanove zlitine so obetajoči materiali zaradi dobrega razmerja trdnost/masa in zaradi korozijske odpornosti. Oksidacijska odpornost zlitin je majhna. Od metod za povečanje oksidacijske odpornosti je bilo raziskano silikoniziranje površine. V članku so opisane metode CVD in silikoniziranje v prahu. Določene so bile struktura, morfologija in trdota površine. Oksidacijska odpornost je dokazana z določanjem kinetike oksidacije.

Ključne besede: titan, silicij, silikoniziranje, CVD, oksidacija, trdota

1 INTRODUCTION

Titanium and its alloys are attractive materials because of their superior strength-to-weight ratio and their resistance to corrosion. However, one of the main disadvantages of Ti and Ti-based alloys is their poor resistance to oxidation at high temperatures. The highest operating temperatures for components made of Ti-based alloys are limited to about 550 °C [1,2].

There have been many attempts to improve the high-temperature oxidation resistance of titanium. Among the methods used for this purpose, surface alloying with silicon has been extensively studied. This type of alloying seems to be more suitable than bulk alloying because the silicon significantly modifies the mechanical properties of titanium [3-7]. Besides a reduction in the oxidation rate [7-11], silicon has been shown to improve wear [12,13] and creep [14] resistance.

Although the exact mechanism of the oxidation of titanium alloyed with silicon does not appear to be fully understood, it is generally believed that silicon, which is present both in solid solution in rutile and in small silica particles, plays several roles [8,9]: 1. Si decreases the depth of the oxygen penetration into the alloy substrate, which is in agreement with its β-forming nature, 2. Si dissolved in the TiO_2 surface layer reduces the diffusion rate of oxygen atoms through this layer, and 3. Si modifies the stress relaxation processes in the oxide layer and contributes to the formation of a more compact layer with a lower porosity.

Several methods are used for the surface modification of metals with silicon. Laser surface alloying [10,12], silicon-ion implantation [15-17], vapour-phase siliconizing [18-20] and powder siliconizing [11,21,22] have been the most extensively studied.

The laser surface alloying of titanium with silicon involves rapid melting of a thin surface layer and a simultaneous feeding of silicon powder. As a result, a layer of rapidly solidified (cooling rates of more than 10^4 K/s) Ti–Si alloy with a very fine microstructure is formed [10]. The implantation of accelerated silicon ions into the surface of titanium is also able to improve its oxidation resistance. However, a large dose of ions and/or a high acceleration voltage can lead to the introduction of an excessive number of lattice defects. This enhances the diffusion, and the improvement of the oxidation resistance is not significant. The negative effect of lattice defects can be partially diminished with post-implantation annealing [17]. The wide applicability of both laser surface alloying and ion implantation for the treatment of components from Ti-based alloys seems to be limited, particularly because of their high cost. In addition, the reproducibility of the laser surface alloying appears to be unreliable.

CVD methods have been widely used to produce silicon surface layers, but most of the applications are concentrated in electronics [20]. Despite the fact that this method is relatively simple, there is only little information on CVD applied to titanium with the aim of improving the chemical resistance [18]. In CVD, a number

of compounds have been used as the source of silicon, including $SiCl_4$, $SiCl_2H_2$, SiH_4, and Si_2Cl_6.

The last method, powder siliconizing (or pack cementation), is a very efficient and inexpensive method for modifying the surface of titanium-based alloys. It consists of simply embedding the sample in a powder and then heating to an appropriate temperature. Pure silicon powders or various powder mixtures of silicon, inert fillers and activators can be used as the siliconizing media. Depending on the temperature and the time of the process, as well as on the composition of the substrate, surface layers containing various phases can be formed [21-23].

This paper deals with the properties of silicon-rich surface layers on pure titanium prepared with powder siliconizing.

2 EXPERIMENTAL

Titanium of technical purity (99.6 %) in the form of annealed bars (10 mm in diameter) was used as the substrate for siliconizing. The cylindrical samples of 2 mm in height for powder siliconizing and 10 mm in height for CVD were cut directly from these bars. Before siliconizing, the substrate surface was given a final polish with 1-micron diamond paste, then washed and dried.

In the case of powder siliconizing, the sample together with the silicon powder (purity 99.99 %, powder fraction less than 45 µm, irregular particles) were placed into a silica glass tube, which was then evacuated and sealed. The tubes were heated at temperatures of (800, 900, 1000 and 1100) °C for 3 h. Silane SiH_4 (mixture with Ar of purity 99.999 %) was used as the precursor for the CVD. This compound undergoes a thermal decomposition above approximately 600 °C to form solid silicon, which is deposited on the substrate and then diffuses into the substrate. The apparatus used for the CVD consisted of a silica glass tube, as a reaction zone, placed in the resistance furnace. The depositions took place at (900, 1000 and 1100) °C for 3 h. Optical microscopy, SEM, EDS, XRD and hardness measurements were used for the characterization of the siliconized samples.

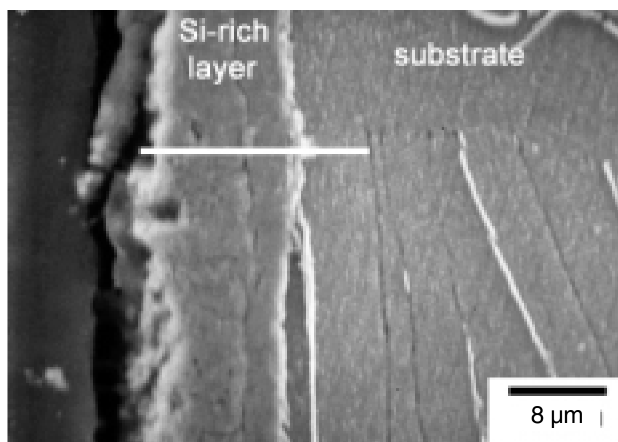

Figure 1: Cross-section of the sample which was powder siliconized at 1100 °C for 3 h
Slika 1: Prerez vzorca, ki je bil silikoniziran 3 h pri 1100 °C

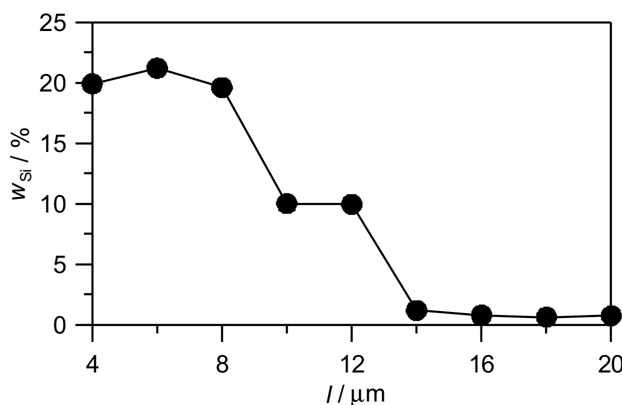

Figure 2: Silicon concentration profile along the line in **Figure 1**
Slika 2: Profil koncentracije silicija na črti na **sliki 1**

The cyclic oxidation of the siliconized samples was conducted at 850 °C for 300 h in air. One cycle consisted of heating at 850 °C for 50 h and then cooling to room temperature for about 10 min. The oxidation kinetics was monitored by measuring the weight gain as a function of oxidation time.

3 RESULTS

The microstructure of the Si-rich layers is shown in **Figure 1**, where a cross-section of the powder-siliconized sample is shown. We can see a dense, compact layer with a thickness of about 10 µm. The layer consists of two sharply separated sub-layers. A chemical microanalysis was performed along the line in **Figure 1**, and the results are plotted in **Figure 2**. The Si-distribution curve shows that the outer sub-layer contains a mass fraction of approximately 20 % Si and the inner only approximately 10 % Si. At the boundaries

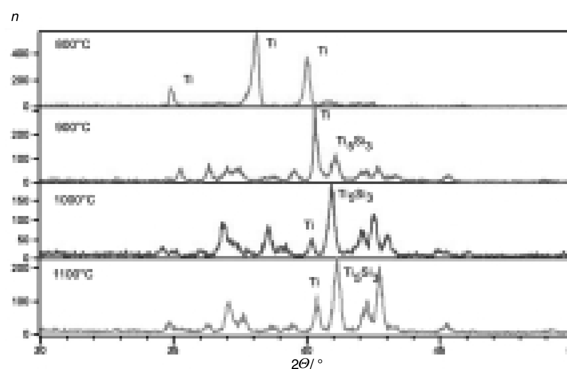

Figure 3: XRD patterns of the samples powder siliconized at different temperatures
Slika 3: XRD-spektri vzorcev, ki so bili silikonizirani pri različnih temperaturah

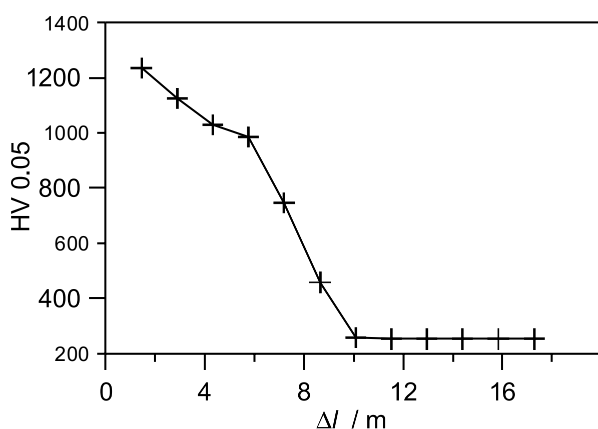

Figure 4: Microhardness profile in the cross-section of the sample which was powder siliconized at 1100 °C for 3 h (Δ*l* – distance from the surface)

Slika 4: Profil mikrotrdote na prerezu vzorca, ki je bil silikoniziran 3 h pri 1100 °C

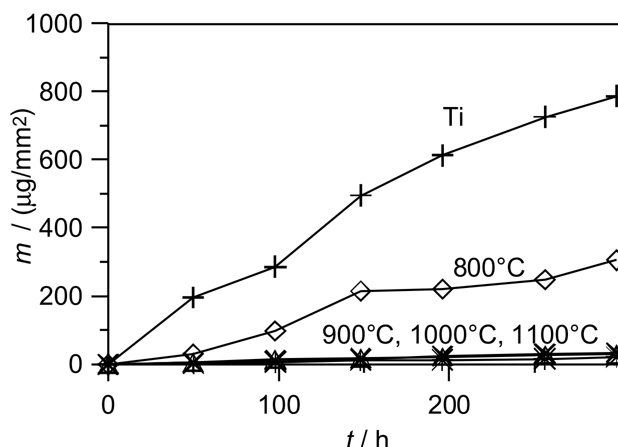

Figure 5: Kinetics of cyclic oxidation at 850 °C of the samples powder siliconized at different temperatures

Slika 5: Kinetika ciklične oksidacije vzorcev, ki so bili silikonizirani pri različnih temperaturah

between both sub-layers and between the inner sub-layer and the metallic substrate, the silicon concentration decreases steeply. The Si-concentration in the metallic substrate is very small. The surface concentrations of silicon in the powder-siliconized samples are listed in **Table 1**. After siliconizing at 900–1100 °C, the surface concentration remains nearly constant and practically independent of the siliconizing temperature. However, the siliconizing at 800 °C produces a layer containing less silicon. The results of XRD on the powder-siliconized samples, see **Figure 3**, revealed the presence of only Ti and Ti_5Si_3 phases. The total volume fraction of silicide in the layers is observed to increase with the siliconizing temperature. Moreover, a temperature of 800°C seems to be too low to form a sufficient amount of silicide. In **Figure 4**, a microhardness profile in the cross-section of a siliconized sample is plotted. We can clearly see that a surface hardness above 1200 HV can be easily achieved by surface siliconizing.

Table 1: Surface concentrations of silicon in the samples which were powder siliconized at different temperatures.

Tabela 1: Površinska koncentracija silicija pri vzorcih, ki so bili silikonizirani pri različni temperaturi

siliconizing temperature (°C)	800	900	1000	1100
Si concentration (%)	13.5	21.9	25.4	21.5

The kinetics of cyclic oxidation at 850 °C is shown in **Figure 5** for the samples siliconized in powder at different temperatures. The rate of mass growth due to oxidation is the highest for pure titanium. In this case, the plot of mass gain versus oxidation time seems to be almost linear, which corresponds to a weak protection effect of the scale against oxidation. **Figure 5** also shows that all Si-rich layers slow down the oxidation and that the protecting effect of the layer prepared at 800 °C is insufficient. The oxidation kinetics of samples prepared at 900–1100 °C is very similar and approaches the parabolic kinetic law. This implies a strong protecting effect of the scales in which the diffusion of oxygen is the process controlling the oxidation.

4 DISCUSSION

It was shown that siliconizing produces surface layers that are rich in silicon. It can be assumed from **Figures 1 and 2**, **Table 1** and from the Ti–Si equilibrium phase diagram [24], that the outer sub-layer contains a significant share of silicide Ti_5Si_3. This assumption was also confirmed by XRD (**Figure 3**).

The protecting effect of such layers was clearly proved. It was also shown that the properties and phase composition of the surface layers strongly depend on the temperature of siliconizing. The powder-siliconizing temperature of 800 °C is insufficient to produce a layer that provides enough protection. This was also confirmed by XRD, which did not reveal any significant volume fraction of silicide in the surface layer, although approximately 13 % of Si was found on the surface of this sample with EDS, see **Table 1**. This discrepancy may be due to a distribution inhomogeneity of the silicide particles.

From the practical point of view, powder siliconizing at 900 °C or more for 3 h seems to be sufficient to produce protection against oxidation. Such a process can significantly increase the hardness and improve the wear resistance.

5 CONCLUSIONS

The results presented in this work show that surface siliconizing is a prospective method for improving the high-temperature oxidation resistance and wear resistance of titanium. In particular, powder siliconizing appears to be an inexpensive and very efficient method. However, it is very important to pay attention to the

adhesion of such layers, particularly under conditions of sudden temperature changes.

ACKNOWLEDGEMENTS

The research on surface modification of Ti-based alloys is financially supported by the research project MSM223100002.

6 REFERENCES

[1] Materials Science and Technology, Volume 8 – Structure and Properties of Nonferrous Alloys, VCH Verlagsgesellschaft mbH, Weinheim, 1996

[2] ASM Handbook, Volume 2 – Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, ASM International, 1990

[3] Zhu J., Kamiya A., Yamada T., Watazu A., Shi W., Naganuma K.: Mat. Trans. 42 (**2001**), 336

[4] Lavelle B., Dabosi F.: in Proc. Titanium 80, Eds. Kimura H., Izumi O, The Met. Soc. AIME, Warrendale, 1980, 2275

[5] Saha R. L., Nandy T. K., Misra R. D. K.: Scripta metall. 23 (**1989**), 81

[6] Mazur V. I., Sukhikh L. L., Firstov S. A., Kulak L. D.: in Proc. The Processing, Properties and Application of Metallic and Ceramic Materials, 1 (**1992**), 141

[7] Lee D. B., Park K. B., Jeong H. W., Kim S. E.: Mat. Sci. Engng. A328 (**2002**), 161

[8] Chaze A. M., Coddet C.: J. Mat. Sci. 22 (**1987**), 1206

[9] Chaze A. M., Coddet C.: Oxid. Met. 27 (**1987**), 1

[10] Majumdar J. D., Weisheit A., Mordike B. L., Manna I.: Mat. Sci. Engng.A 266 (**1999**), 123

[11] Liang W., Zhao X. G.: Scripta mater. 44 (**2001**), 1049

[12] Majumdar J. D., Mordike B.L., Manna I.: Wear 242 (**2000**), 18

[13] Dong H., Bloyce A., Morton P. H., Bell T.: in Proc. Titanium 95: Science and Technology, IOM, London, (**1996**), 2007

[14] Winstone M. R., Rawlings R. D., West D. R. F.: J. Less Common Met. 39 (**1975**), 205

[15] Tomaschov N. D., Ziltschova O. A., Zalavutdynov R. C., Gorodeckij A. E., Guseva M. I., Vladimirov B. G.: Zaschtita Metallov 27 (**1991**), 1014 (in Russian)

[16] Baszkiewicz J., Kaminski M., Kozubovski J., Krupa D., Gosiewska K., Barcz A., Gavlik G., Jagielski J.: J. Mat. Sci. 35 (**2000**), 767

[17] Taniguchi S., Kuwayama T., Zhu Y. C., Matsumoto Y., Shibata T.: Mat. Sci. Engng. A277 (**2000**), 229

[18] Motojima S., Kohno M., Hattori T.: J. Mat. Sci. 22 (**1987**), 770

[19] Kharatyan S. L., Chatilyan A. A., Voskerchan G. A., Manasaryan Z. A.: Chemical Physics Reports 16 (**1997**), 1217

[20] Choy K. L.: Progress in Materials Science 48 (**2003**), 57

[21] Li X. Y., Taniguchi S., Matsunaga Y., Nakagawa K., Fujita K.: Intermetallics 11 (**2003**), 143

[22] Koo C. H., Yu T. H.: Surface and Coatings Technology 126 (**2000**), 171

[23] Cockeram B., Wang G.: Thin Solid Films 269 (**1995**), 57

[24] Hansen M.: Constitution of Binary Alloys, McGraw-Hill Book Company, 1958