

EFFECT OF VACUUM DIFFUSED OVERLAYERS ON THE PROPERTIES OF NIOBIUM AND ITS ALLOYS (E)

L. M. Petrovskaya and E. P. Ponomarenko

UDC 621.793.083.4

The use of niobium alloys in engineering is rather limited due to their strong oxidation at high temperatures. To use such alloys at working temperatures up to and above 1200°C therefore, it is necessary to cover them with protective layers.

Chromium-aluminum-silicon and chromium-titanium-silicon complexes thermally stable for 100 h even above 1100-1370°C are well known, as are coverings of the TRW and "Pfaudler"-type, thermally stable above 1100°C for 300-400 h [1, 2]. Data is also available on the deposition onto niobium and its alloys VN-2, VN-4 of diffusion chromium-titanium-silicon and chromium-aluminum-silicon layers, stable for up to 100 h at 1100°C [3, 4].

Thermally stable layers can be deposited onto niobium and its alloys VN-2, VN-4 by metallization in an MPV-3 vacuum furnace at 1200-1400°C with residual gas pressure $1 \cdot 10^{-4} - 5 \cdot 10^{-5}$ torr. The specimens were $10 \times 10 \times 20$ mm in size with surface purity $\nabla 7 - \nabla 8$. The thermal stability experiments were carried out at 600-1200°C for periods up to 200 h. The heat resistant properties of the VN-2 alloy with vacuum-diffused coverings were determined at 1000°C for 100 h.

During the vacuum-diffused chrome plating of niobium and its alloy VN-4 (Fig. 1a), approximately the same dependence of layer thickness growth on holding time (Fig. 2) was obtained (the layer thickness is taken to be the microscopically visible zone after etching). A thicker layer forms on VN-4, apparently due to the favorable influence of molybdenum on the chromium diffusion into the niobium matrix, since molybdenum forms directly with chromium a series of solid solutions [5]. The chromium content in the niobium and VN-4 alloy diffused layer was approximately 55%, and according to x-ray data, the layer composition is intermetallic NbCr₂. The microhardness of the layers was 570 and 650 kg/mm² on niobium and VN-4 alloy, respectively. The higher layer microhardness on VN-4 alloy is due to the presence of alloying elements (molybdenum, carbon). Residual shear stresses which gradually decrease within the substrate arise during the chrome plating of niobium (Fig. 3).

During the 1300°C vacuum diffused silicon plating, a similar thickness layer forms (Fig. 2) consisting of niobium silicide NbSi₂ with microhardness 1100-1200 kg/cm² (see Fig. 1b upper layer) and a silicide Nb₅Si₃ with microhardness ~1000 kg/mm² (lower layer). Residual tensile stresses form in the layer which gradually decrease towards the surface from the basal layer (Fig. 3).

TABLE 1. Thermal Stability of Protected Niobium Alloy VN-4

Type of covering	600 °C		1000 °C		1200 °C	
	time, h	wt. increase	time, h	wt. increase	time, h	wt. increase
Titanium plated	100	1.5	—	—	—	—
Chrome plated	—	—	60	50	—	—
Silicon plated	—	—	—	—	100	16
Chrome-titanium-silicon plated	—	—	—	—	100	5

The possibility of using a deep titanium-plated substrate to intensify the chromium diffusion was studied, since chromium dissolves well in titanium over a narrow temperature interval (1350-1400°C) and forms a continuous series of solid solutions [5]. In the ternary system titanium-chromium-niobium, the titanium at 1250°C forms a solid solution with the chromium, based on the intermetallic TiCr₂, but at higher temperatures (1350°C and above) the TiCr₂ does not form [6]; the titanium in solid

UkrNIIspestal', Zaporozh'e. Translated from Fiziko-Khimicheskaya Mekhanika Materialov, Vol. 7, No. 5, pp. 82-84, September-October, 1971. Original article submitted March 12, 1970.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

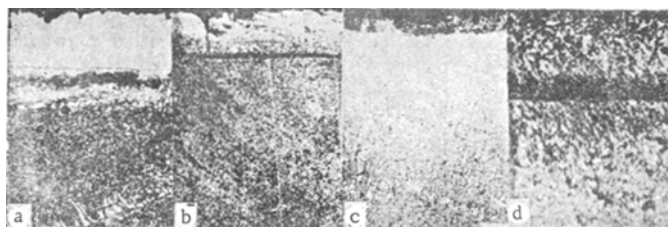


Fig. 1. Structure of a VN-4 alloy after a vacuum-diffused chrome plating (a), silicon plating (b), titanium plating (c), and chromium-titanium-silicon plating (d). Etching in mixture of hydrofluoric and nitric acid.

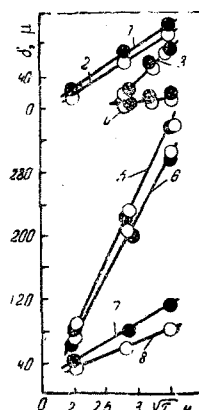


Fig. 2

Fig. 2. Diffused layer thickness on niobium (light points) and a VN-4 alloy (dark points) as a function of the isothermal treatment period. 1,2) Chrome plating at 1300°C; 3) silicon plating at 1300°C; 4) silicon plating at 1200°C; 5) titanium plating at 1400°C; 6) titanium plating at 1350°C; 7,8) titanium plating at 1300°C.

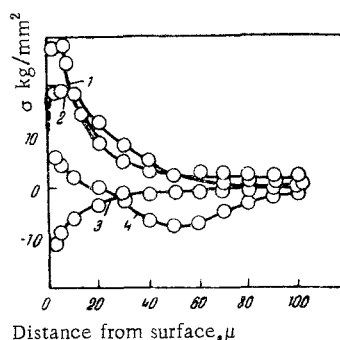


Fig. 3

Fig. 3. Variation in residual internal stress in niobium after vacuum-diffused silicon plating (1), chrome-titanium plating (2), chrome plating (3), and titanium plating (4).

solution, for example, facilitates the saturation of the niobium matrix with chromium and the formation at 1380-1400°C of 1.5-1.8 times deeper layers during chromium plating.

The existing means of diffused titanium plating do not allow deep coverings to be obtained on refractory metals because of the finite saturation temperature and the tendency for the substrate to oxidize. A vacuum method is therefore used [7] which obviates niobium oxidation and allows saturation to occur at a temperature of 1400°C (Fig. 1).

The layer thickness change during titanium plating in a powder (sponge) at 1300-1400°C for 12 h was calculated to have an approximate parabolic dependence (Fig. 2). As for chromium plating, titanium saturation of a VN-4 alloy is more intensive than for pure niobium (Fig. 2). The microhardnesses of the titanium layer on niobium and VN-4 are 280 and 370 kg/mm² respectively. During the formation of a titanium film with up to a 10-μ-thick condensed surface layer, tensile stresses occur which decrease with depth in the layer and become compressional at 50 μ depth (Fig. 3).

The niobium alloy has the highest heat resistance when covered with single component vacuum-diffused silicon plating layers (see Table 1). The deterioration in protective properties of a silicon plated layer is not due to low oxidation resistance but to its disintegration under the high tensile stresses (Fig. 3). Silicon-plated layer disintegration is even observed when the specimens are slowly cooled from the saturation temperature (see Fig. 1b).

To obtain a protective layer with the lowest residual stresses, a previously chrome-plated niobium layer was covered with silicon (Fig. 1d). The protective surface layer consisted of two zones. The upper (microhardness 1100 kg/mm²) layer was shown by x-rays to consist of chromium- and titanium-rich NbSi₂. The lower zone (microhardness up to 1000 kg/mm²) consists of titanium-, chromium-, and molybdenum-rich Nb₂Si₅. Residual tensile stresses are 30% less than in a silicon layer on niobium (Fig. 3). Such a layer was found to protect the alloy for 100 h at 1200°C (see Table), the protective properties not deteriorating even above the chromium islands.

The study of the heat resistance properties of VN-2 covered with titanium-chromium-silicon layers showed σ_{100} to be no lower than 17 kg/mm² at 1000°C. From the mechanical property investigations on niobium alloys covered with three component titanium-chromium-silicon layers, it was found that the tensile strength and elastic limits were slightly lowered. The hardness parameters of the original alloy were $\sigma_b = 70-80$ kg/mm² and $\sigma_s = 53-55$ kg/mm² respectively. This lowering is due to the fact that the diffused layer is less plastic than the base material, and the composite hardness decreases as a whole.

LITERATURE CITED

1. Refractory Metallic Materials for Cosmic Engineering, Izd. Mir (1966).
2. Refractory Materials in Mechanical Engineering Handbook [in Russian], Izd. Mashinostroenie (1967).
3. E. L. Gerasova, A. N. Sokolov, A. S. Stroeve, et al., Thermal Stability and Thermally Stable Coverings [in Russian], Izd. Nauka, Leningrad (1969).
4. G. V. Zemskov, R. L. Kogan, and V. M. Luk'yanov, Thermal Stability and Thermally Stable Coverings [in Russian], Izd. Nauka, Leningrad (1969).
5. M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York (1958).
6. V. I. Svechnikov, Yu. A. Kocherzhinskii, et al., Study of Heat-Resisting Alloys, 8, Izd. Akad. Nauk, SSR, Moscow (1960).
7. E. P. Ponomarenko, Yu. K. Belov, and L. M. Petrovskaya, Protective Coverings on Metals, No. 3, Izd. Naukova Dumka (1970).