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Carbon-limited Dissolution of Oxygen in Niobium

This article deals with results of the invsetigations connected with limitation of oxygen dissolution in niobium by means of creating of the carbide protective coating on the niobium surface or forming of the solid solution of carbon in niobium. It is shown that the carbide coating increases essentially the life time of the niobium parts for vacuum equipment and is consumed as a result of interaction with oxygen. The carbon dissolution in niobium does not hinder redox reaction at the $Nb(C)/Nb_2O_5$ boundary and causes the conductivity increase of the dielectric film Nb_2O_5.

1. Introduction

Niobium is widely used both in industry for making of various vacuum equipment parts, stable at high temperatures and as the base of layer systems $Nb-Nb_2O_5$ used in various electronic solid state devices (JACKSON, CAMPBELL).

It has been shown that impurities in niobium significantly affect the properties of this metal (FROMM, GEBHARDT). The most active interstitial impurity in niobium is oxygen (FROMM). If oxygen concentration is near to the oxygen solubility limit in niobium, the fragile destruction of niobium takes place even at small mechanical loading (FROMM). Since the equipment parts from niobium are used usually at hard conditions (high temperatures $T < 2100$ K, aggressive environment etc.) the problem of stable protective coating formation on the niobium is very actual.

The known protective coatings (SAMSONOV, EPIK) do not provide the necessary degree of niobium protection that was proved by thermodynamical analysis. Alloys of niobium with carbon are very promising for protective coating. In the present study the transformation of the structure and chemical composition of carbide protective coating on the niobium surface in oxygen environment as well as degradation processes in bilayer $Nb-Nb_2O_5$ at high temperatures were investigated.

It was shown (BOIKO et al.) that degradation of the $Nb-Nb_2O_5$ bilayer is caused by redox reaction at the interphase boundary Nb/Nb_2O_5 and is responsible for the inrease of Nb_2O_5 conductivity. Taking into account that carbide coatings are an effective barrier for dissolution of the oxygen in niobium (SAMSONOV, EPIK) we have studied the possibility to suppress the redox reaction at the Nb/Nb_2O_5 boundary also by enrichment of niobium by carbon.

2. Sample preparation and investigation techniques

The niobium foil with thickness $h = 5 \cdot 10^{-4}$ m was electrochemically polished and annealed during $t = 30$ min at the temperature $T = 2300$ K in vacuum $P = 2 \cdot 10^{-4}$ Pa. Main impurities in niobium foil were (in ppm): Ta, <800; Fe, <70; Si, <70; Ti, <80; W, <80; C, <100; O, 300; N, <100; H, <10. The foil surface was coated with graphite layer and annealed at $T = 1770-1820$ K in vacuum $P = 8 \cdot 10^{-4}$ Pa during 60 min. Samples were cut out from foil and exposed in oxygen atmosphere at $P = 2 \cdot 10^{-3}$ Pa and $T = 2100$ K examined with one-hour period of exposure.

The chemical composition of foil was monitored by laser and secondary-ion mass-spectrometry (LMS and SIMS) methods. The laser with a power of 10^{13}–10^{14} Wt/m^2 and duration of shot 10–20 ns was used for LMS. The argon ions with the energy of 3–5 keV were applied for SIMS. The possible error in the chemical analysis was 50 ppm. Besides that, the phase composition of the samples was determined by X-ray analysis with cobalt K$_\alpha$ radiation.

The samples for study of degradation and electrical properties of bilayers Nb–Nb$_2$O$_5$ were prepared in the following way. The foil was doped by carbon with different concentrations by niobium and acetilenum C$_2$H$_2$ interaction at $P = 2 \cdot 10^{-1}$ Pa and $T = 1900$ K. The maximum carbon concentration in surface foil layer was 500 ppm. The Nb$_2$O$_5$ film with $h = 1 \cdot 10^{-7}$ m was grown on the niobium by electrochemical oxidation in 0.01 M aqueous solution of phosphoric acid at room temperature and was a stoichiometric compound. The second electrode was 0.01 M aqueous solution of vinegar acid. The heat treatment for stimulation of redox reaction at the Me/Me$_2$O$_5$ boundary was applied at $T = 525$ K and $P = 2 \cdot 10^{-4}$ Pa during 60 min. The parameter characterizing the extent of degradation was the relative increase of the electrical capacity C of the layer systems Nb(C)–Nb$_2$O$_5$-electrolyte after annealing of the bilayers Nb(C)–Nb$_2$O$_5$ in comparison with unannealed ones. According to (PALATNIK et al.), the increase of the electrical capacity is connected with decrease of the efficient thickness and increase of the dielectrical constant of Nb$_2$O$_5$ as a result of interaction between metal and oxide under annealing that causes a deficiency of oxygen in Nb$_2$O$_5$ film.

3. Results and discussion

The X-ray investigation showed that the bilayer carbide coating on the surface of the metal after high temperature vacuum annealing of niobium coated with graphite layer have been formed. The upper layer with $h = 1.52 \cdot 10^{-5}$ m was NbC phase and lower layer with $h = 1.5 \cdot 10^{-5}$ m was the Nb$_2$C phase. They had solubility ranges according to the equilibrium diagram Nb–C.

After annealing of niobium with carbide coating in oxygen atmosphere at $T = 2100$ K and $P = 2 \cdot 10^{-3}$ Pa during $t = 30$ min the phase Nb$_2$C with $h = 3.65 \cdot 10^{-6}$ m was found only. By increase of annealing time the thickness of the Nb$_2$C layer was decreasing. In the case of annealing of niobium with carbide coating at $T = 2100$ K and $P = 8 \cdot 10^{-4}$ Pa in passive atmosphere changes of phase composition and thickness of coating were not observed.

Accordig to the data of X-ray investigations, the annealing of niobium with bilayer coating NbC/Nb$_2$C in oxygen atmosphere during 7 hours leads to total disappearance of carbide layers. At the same time the formation of the oxide phase in niobium which embrittles metal was not observed.

The distributions of oxygen (curve 1, 2) and carbon (curve 3) across the niobium foil after annealing during 7 hours in the case of absence (curve 1) and presence (curve 2, 3) of protective coating are displayed in Figure 1. It shows that protective coating on the niobium surface essentially decreases the absorption of oxygen by metal. Homogeneous carbide coating was destroyed due to its interaction with oxygen. The carbon interacted with oxygen with formation of the volatile oxides CO and CO$_2$ as well as dissolved in the niobium foil volume. Mass spectrometry measured carbon concentration on the foil surface was higher that its solubility limit in niobium at the room temperature (FROMM, GEBHARDT) that was possibly caused by small inclusions of residual carbide phase undetectable for X-ray diffraction method.

The tests demonstrated that the life time of niobium foil with carbide coating at high temperatures in aggressive environments was two or three times longer in comparison with an uncoated one.
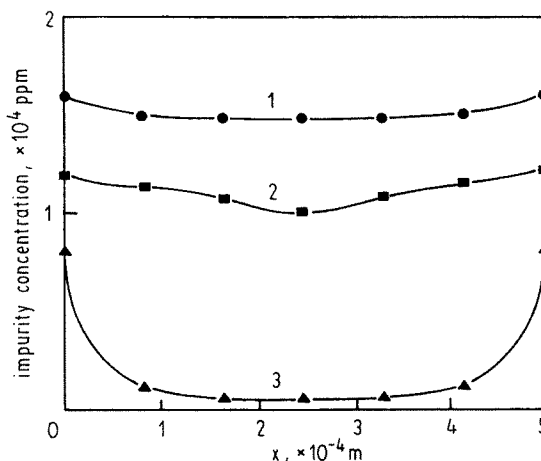
Fig. 1. Distributions of oxygen (1, 2) and carbon (3) across the niobium foil without protective coating (1) and with one (1, 3) after annealing during 7 hours

The dependences of the relative capacity $(C-Co)/Co$ and current I at the constant voltage $U = 10$ V upon the carbon concentration in niobium for systems $Nb(C)-Nb_2O_5$-electrolyte are presented in Figure 2. One can see that the value $(C-Co)/Co$ practically did not change in the whole investigation range of carbon concentrations after one-hour annealing of the bilayers $Nb(C)-Nb_2O_5$. At the same time the electrical current across the system $Nb(C)-Nb_2O_5$-electrolyte at the positive polarization of the base metal is increased with the growth of carbon concentration in niobium. Obviously, it was connected with the formation of the "weak places" in the Nb_2O_5 film by oxidation of metal containing the carbide phase inclusions (VERMILYEA) in the layer adjacent to the niobium surface. These non-oxidation inclusions had formed in the niobium doping by carbon from the gase phase. In such places the thickness of oxide was lower and electrical conductivity was maximum. Because of low carbon solubility in niobium at room temperature such inclusions appear when the carbon concentration is near $1 \cdot 10^3 - 1.5 \cdot 10^3$ ppm (FROMM, GEBHARDT).

The results of this work demonstrated that the formation of the consumable protective coating in the form of niobium carbides allow to suppress temporarily the interac-
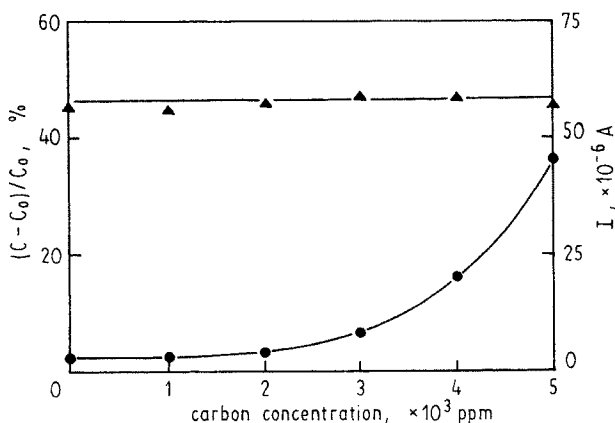

Fig. 2. Dependence of $(C-Co)/Co$ (1) and I at the $U = 10$ V (2) upon the carbon concentration in niobium for the systems $Nb-Nb_2O_5$-electrolyte

tion between niobium and oxygen and hence to increase essentially the life time of the equipment parts made of niobium. The carbon dissolution in niobium does not hinder redox reaction at the $Nb(C)/Nb_2O_5$ interphase boundary and causes the conductivity inrease of the dielectric film Nb_2O_5 because of formation of carbide phases inclusions on the niobium surface.

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