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Oxygen-Tantalum Interaction in Niobium

This article deals with results of the investigation of oxygen dissolution in niobium foil containing tantalum impurity. Experimental data show spatial separation of oxygen and tantalum in niobium if the oxygen concentration is near to the oxygen solibility limit in niobium at room temperature. Tantalum atoms move to the foil surface, and there is more oxygen in the foil volume than near the foil surface. Enrichment of niobium foil surface by tantalum influences strongly the oxygen diffusion across the foil and foil surface ability to electron injection.

1. Introduction

Niobium-based layer structures are widely used in electronics as parts of various solid state devices (Jackson et al.; Palatnik et al. 1978). It has been verified that the extent of impurities in niobium significantly affects the performance characteristics of such devices (Palatnik et al. 1994; Shamir, Atzmony). The most active interstitial impurity in niobium is oxygen, that has the maximum dissolved energy in comparison with other typical interstitial impurities (nitrogen, hydrogen, carbon) (Fromm). Tantalum is the main substitution impurity in niobium. These metals (Ta and Nb) themselves have much in common in their crystalline structure and chemical and physical properties (Fromm, Gebhardt).

In the present study peculiarities of oxygen dissolution in niobium containing tantalum impurity were investigated.

2. Samples and experimental technique

The object investigated in this paper was niobium foil with a thickness $h = 5 \cdot 10^{-4}$ m. The foil was electrochemically polished and annealed during $t = 30$ min at the temperature $T = 2300$ K in a vacuum $P = 2 * 10^{-4}$ Pa. Concentrations (C) of the main impurities in niobium were: tantalum $C_{Ta} = 500$ ppm, oxygen $C_O = 200$ ppm, other impurities $C \leqq 50$ ppm.

Dissolution of oxygen in the niobium foil was performed due to the sample exposition during various times in the environment of oxygen at $T = 1950$ K and $P = 2 \cdot 10^{-3}$ Pa. Solid state oxygen diffusion from niobium and tantalum powders to the foil was used also. The powders containing $C_O = 1.2 \cdot 10^4$ ppm were sintered with the foil at $T = 1950$ K, $P = 8 \cdot 10^{-4}$ Pa during $t = 30$ min. The experiments on sintering were performed on tantalum foil also as niobium foil.

The chemical composition of foils 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 a period of flash $10 - 20$ ns was used for LMS. The argon ions with the energy of $3 - 5$ keV were used for SIMS. Besides that, the period of the crystal lattice (a) and microhardness (H_V) of foils were determined. The value a was determined by X-ray analysis with cobalt Kα radiation. The value H_V was determined by the Vickers method using a load of 0.1 kg.

For the investigation of the niobium surface property of electron injection the Nb$_2$O$_5$ film with $h = 1 \cdot 10^{-7}$ m was grown by electrochemical oxidation in 0.01 M aqueous solution of phosphoric acid at room temperature. The clipping probe made of the same material as the base metal was used to apply voltage (V) to the Nb$_2$O$_5$ film during electrical measurements. According to Koda et al. the current (I) flowing through Nb$_2$O$_5$ in the layer structure Nb – Nb$_2$O$_5$ – Nb in the field of nonlinear IV characteristic has injection nature.

Fig. 1. Microphotograph of the cross-section of a niobium foil with diamond pyramid indentations

9×10^{-5} m

3. Results and discussion

Figure 1 presents a microphotograph cross-section of a niobium foil with diamond pyramid indentation. Figure 1 shows that the foil has a large crystal grains as the foil thickness. The values a and H_v in the volume of the crystal grains increased regular by increase of C_O in niobium (FROMM, GEBHARDT), changing from $a = 3.300$ Å and $H_v = 7 \cdot 10^7$ kg/m^2 for the initial foil to $a = 3.308$ Å and $H_v = 3 \cdot 10^8$ kg/m^2 for the foil with $C_O = 2.2 \cdot 10^4$ ppm. This last C_O value is near the oxygen solubility limit (C_l) in niobium at $T = 300$ K (TAYLOR, DOYLE).

With further dissolution of the oxygen in niobium the values a and H_v are practically constant in the crystal grains volume. The peak values H_v are observed near the grain boundaries as a result of the supersaturated solid solution Nb(O) decay and precipitation of niobium oxide phases.

Distribution of impurities across the niobium foil is displayed in Figure 2, where one can see that the distribution of the oxygen (curve 1) and tantalum (curve 2) in niobium at low C_O is nearly homogeneous. At $C_O \approx C_l$ the tantalum moves to the foil surface (curve 3) and there is more oxygen in the foil volume than near the foil surface (curve 4).

Spatial separation of the niobium and tantalum in the solid solution Nb(Ta) with unlimited mutual solution of the components (HANSEN, ANDERKO) is caused by minimization of the solution free energy in the availability of the third component oxygen. It is promoted by
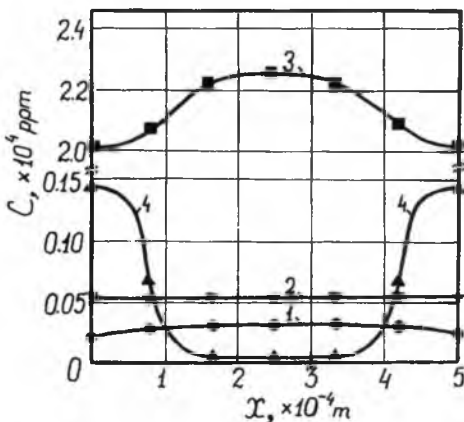

Fig. 2. Distribution of oxygen (1, 3) and tantalum (2, 4) across a niobium foil at low C_O (1, 2) and at $C_O \approx C_l$ (3, 4)
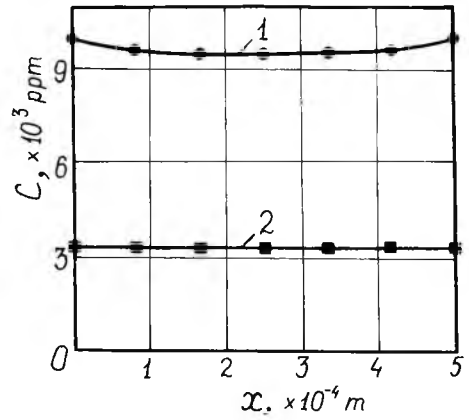
Fig. 3. Distribution of oxygen across foils for oxygen diffusion from tantalum powder to niobium foil (1) and from niobium powder to tantalum foil (2)

the high temperature of the oxygen dissolution and difference of the values C_1 and the free energy (E) of the oxide phases formation for niobium and tantalum (FROMM, GEBHARDT). Particularly, as the value E for Ta_2O_5 is higher than for Nb_2O_5 so it is more energy favourable than that tantalum atoms move to the foil surface, where the probability of oxide phase formation is more probable than in the foil volume.

Figure 2 shows that oxygen diffusion in the nonhomogeneous solid solution Nb(Ta) occurs from the area with lower C_o near the foil surface to the area with higher C_o in the foil volume. That may be caused by increase of the electrochemical potential (φ) of oxygen in Nb(Ta) with increase of the tantalum concentration C_{Ta}. So, the value φ is higher near the foil surface than in the foil volume. Therefore, the oxygen diffusion in nonhomogeneous Nb(Ta) occurs in the direction of the decrease of the value φ.

The limit case of the oxygen diffusion in honhomogeneous Nb(Ta) is the oxygen redistribution between niobium and tantalum. The results of this experiment are presented in Figure 3 where the oxygen concentration in the foil is much higher in the case of oxygen
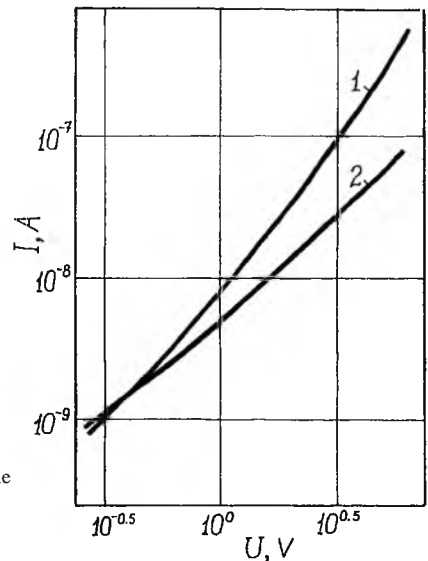

Fig. 4. IV characteristics for the $Nb/Nb_2O_5/Nb$ on the base of the initial (1) and oxygen-saturated (2) niobium foil

diffusion from tantalum powder to niobium foil (curve 1) than in the case of oxygen diffusion from niobium powder to tantalum foil (curve 2).

The oxygen concentration C_o in the niobium and tantalum powders and the diffusion conditions (T, t) were identical in both cases. The oxygen diffusivities in niobium and in tantalum are similar (FROMM, GEBHARDT). That is why the results presented in Figure 3 may be caused by the presence of the energy barrier for the oxygen on the interface between niobium and tantalum. This barrier arises from the higher value φ in tantalum than in niobium. It limits the oxygen diffusion from niobium to tantalum and doesn't limit the oxygen diffusion in the opposite direction.

It is obvious that a similar barrier is formed in the nonhomogeneous solid solution Nb(Ta) between layer with large C_{Ta} adjacent to the foil surface and the foil volume with minimum C_{Ta}. This barrier limits the oxygen diffusion from the volume to the foil surface.

Displacement of tantalum atoms to the surface of the niobium foil saturated by oxygen influences strongly the niobium surface properties, including the ability to electron injection. Figure 4 presents IV characteristics for the structure $Nb - Nb_2O_5 - Nb$ on the base of the initial niobium foil (curve 1) and such one saturated by oxygen (curve 2). The chemical composition of these foils is presented in Figure 2. The Figure 4 shows that the injection current through the Nb_2O_5 film decreases by simultaneous increase of the C_o and C_{Ta} at the foil surface. As the oxygen solubility in niobium leads to decrease of the electronic work function of niobium and hence leads to increase of the electron injection from niobium (ISHCHUK, KANASH), this effect is caused by the enrichment of the niobium surface by tantalum.

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