Mass transfer of niobium and copper in binary systems obtained by magnetron sputtering

D V Postnikov[1], A I Blesman[1,2], D A Polonyankin[1,2], S L Ibnoyaminova[1] and A A Teplouhov[1]

[1] Physics Department, Omsk State Technical University (OmSTU), 11 Mira Avenue, Omsk, 644050, Russia
[2] Scientific–educational Resource Centre «Nanotechnology», Omsk State Technical University (OmSTU), 11 Mira Avenue, Omsk, 644050, Russia

e–mail: nano@omgtu.ru

Abstract. This paper provides the mutual low–temperature mass transfer in binary systems obtained by magnetron sputtering of niobium onto a heated copper substrate. Based on the kinetic equation of diffusion, the distribution of the niobium through the substrate's depth at temperatures of 100, 200 and 300 °C is calculated. The method of calculating the concentration profiles of niobium, proposed in the manuscript, was verified using experimental data of energy–dispersive analysis.

1. Introduction

Niobium has a high corrosion resistance and performance characteristics under conditions of temperature influences and is widely used in the automotive, chemical and aerospace industries [1]. Application of niobium in bipolar plates manufacture for hydrogen fuel cells is also explained by its high corrosion resistance in sulfuric acid solutions compared to other transition metals, herewith niobium deposition into plates of austenitic AISI 316L steel can be implemented by magnetron sputtering [2].

At present, superconducting niobium thin films are used in a large number of microelectronic devices, such as Josephson junctions, quantum dot, superconducting quantum interference devices (SQUIDs), coplanar waveguide resonators [3, 4], and superconducting qubits [5]. Thin niobium films formed by spraying–deposition methods are used for manufacture of ultra–large integrated circuits, magnetometers, elementary particle detectors [6], high–frequency cryogenic switches [7] and gyroscopes [8]. Due to the high electrical conductivity, niobium is used for manufacture of such elements of micro electromechanical systems (MEMS) as wave filters, nanomechanical oscillators of microwave superconducting resonators [9].

In comparison with other superconductors, niobium has the highest critical temperature (T_C=9.23 K) and lower critical magnetic field (H_{C1}(0)=143.24 kA/m) and can be deposited to substrates of various materials [10]. The magnetron sputtering method is used for thin niobium coatings deposition on the internal cavities (cells) of superconducting radio–frequency resonators (SRF) of elementary particle accelerators.

Magnetron sputtering of niobium on the cavities of oxygen–free copper, which has a high conductivity, provides technological and economic advantages in comparison with the production of

resonators from the bulk niobium [11]. One of the ways to improve the functional characteristics of SRF (including higher magnetic field gradients in comparison with macroscopic superconductors) is to form two–layer structures by magnetron sputtering. Such structures consist of superconducting and insulating layers (for example, Nb/MgO) and provide the best shielding of the internal surfaces of SRF resonators [12]. Sputtering of niobium is applied for covering the cavity's inner walls, made of oxygen–free copper with high conductivity (OFHC copper), to increase the quality factor and reduce the surface resistance of the cavities. The advantages of this approach are the better thermal stability of OFHC copper, its insensitivity to the magnetic field of the earth and the possibility of coating from a material with a high critical temperature (niobium, coating thickness of about 2 μm) [13].

Niobium magnetron sputtering onto a graphite substrate followed by high–temperature annealing of films with a thickness of 8 to 12 μm in the temperature range from 800 to 1800 °C is carried out for niobium carbides' formation (Nb_2C and NbC) and application in aggressive (corrosive, erosive) environments [14]. Heating leads to an increase in the hardness of the niobium coating and its adhesion to graphite, and also to a decrease in the porosity of the coating [15]. Investigation of thermal diffusion transfer in binary systems «niobium–zirconium dioxide stabilized with yttrium oxide (Y_2O_3–ZrO_2)» in the temperature range from 780 to 1000 °C allows the authors [16] to obtain an empirical relationship between the diffusion coefficient of niobium, the energy of its activation, and the pre–exponential factor.

Based on the literature review, it could be concluded that the method of magnetron sputtering is widely applied to the formation of thin niobium coatings of various functional designation. In a number of works, the increase in the physicochemical and mechanical characteristics of niobium films is achieved both during their deposition by heating the substrate and during subsequent annealing. For example, during the condensation of high–energy niobium ions with simultaneous heating of the substrate, a synergistic effect occurs, consisting in the epitaxial growth of niobium films with a low defect concentration [17].

A significant influence on the properties of binary systems is also rendered by the mutual thermal diffusion, which leads to a transition layer formation from the coating's and the substrate's atoms. The theoretical and experimental investigation of the mutual mass transfer of niobium and copper is carried out in the paper when a niobium coating is sputtered to a heated copper substrate.

2. Mass transfer model in a binary system

To calculate the niobium distribution through the depth of the «niobium–copper» binary system during the substrate heating, it was used the kinetic equation of diffusion:

$$\frac{\partial c_B}{\partial t} = -\frac{\partial}{\partial x}\tilde{D}\left[1+\left(\frac{P}{E}\right)^2\right]\frac{\partial c_B}{\partial x}+\frac{\partial}{\partial x}\frac{c_A c_B}{kT^2}\left(E_B D_B - E_A D_A\right)\left[2+\left(\frac{P}{E}\right)^2\right]\frac{\partial T}{\partial x} \qquad (1)$$

here c_A, c_B – are the atoms' concentration of A and B type, E_A, E_B – activation energy of atoms' diffusion of A and B type, $D_A = D_{OA}e^{-\frac{E_A}{kT}}$, $D_B = D_{OB}e^{-\frac{E_B}{kT}}$ – the diffusion coefficients of A and B atoms' type, $\tilde{D} = D_B c_A + D_A c_B$ – is the mutual diffusion coefficient, P – distribution of internal stresses, T – is the temperature in absolute scale, k – Boltzmann's constant.

The first summand in equation (1) reflects the mutual diffusion in the binary system by the concentration mechanism; the second summand corresponds to the thermal diffusion under the influence of the temperature gradient. In addition, this model takes into account internal stresses in the crystal lattice, caused by an external impact or an uneven temperature distribution. The diffusion coefficients (D_0) and activation energy (E_a) of niobium and copper used for calculations are presented in table 1 [18].

In accordance with the proposed model [19], the atoms' flow of the coating into the inner layers of the substrate occurs both by the concentration mechanism and by the thermal diffusion mechanism.

Table 1. Diffusion coefficients and activation energy.

| Element	D_0 (m^2·c^{-1})	E_a (kJ/mol)
Nb	$0.376 \cdot 10^{-2}$	381.2
Cu	$1.5 \cdot 10^{-2}$	77.7

3. Experimental results

A niobium coating with a controlled thickness of 2 μm [20] was obtained by the magnetron sputtering method in the ADVAVAC VSM–200 installation at a copper substrate temperature of 200 °C. Analytical part of the study was carried out via scanning electron microscopy by using Jeol JCM–5700 equipped with an X–ray energy dispersive spectrometer JED–2300.

Figure 1 shows the experimental and calculated niobium concentration profiles (through the depth) depending on the heating temperature. Figure 2 shows a micrograph of the cross–section of «niobium–copper» system with the points in which the energy–dispersive spectroscopy (EDS) analysis was performed. To the left of LG10000 point (figure 2), a compound is seen, into which the binary Nb–Cu system was mounted.
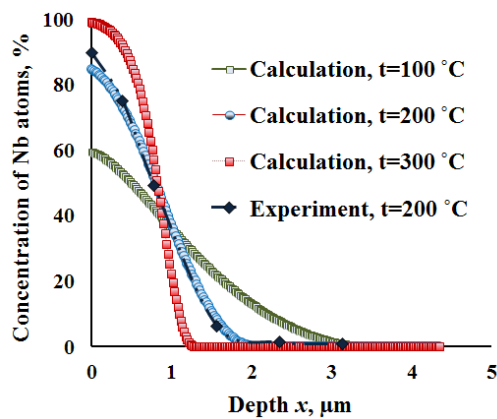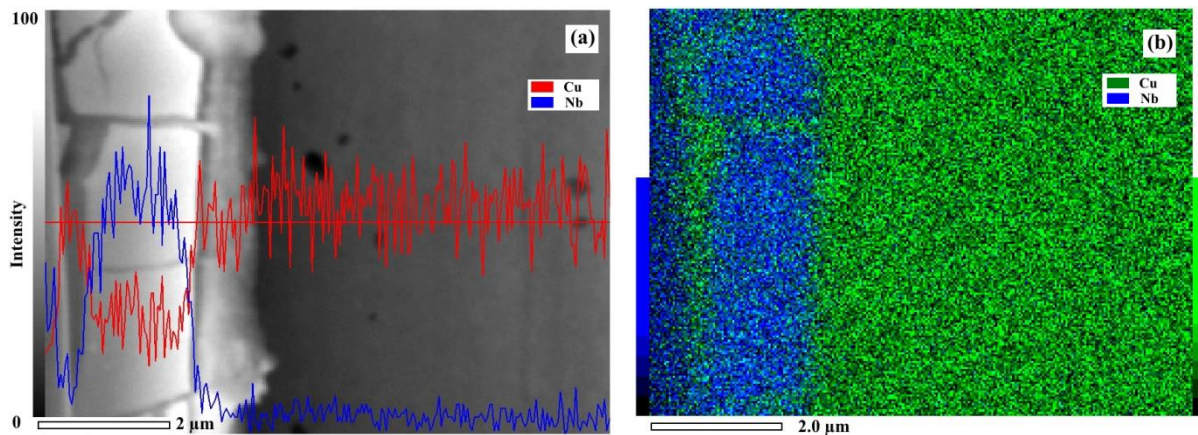

Figure 1. Niobium concentration profiles (through the depth) depending on the heating temperature.
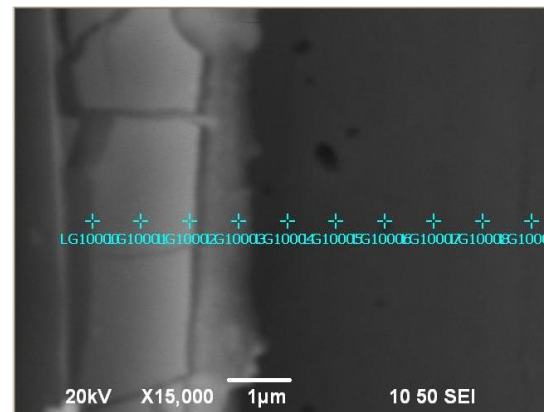
Figure 2. A micrograph of the cross–section of Nb–Cu system with the EDS points.

As can be seen from figure 1, niobium concentration profile obtained by the experimental method coincides with the calculated data within the margin of error.

Figure 3. EDS analysis «along the line» (**a**) and Nb–Cu distribution map (**b**).

The thickness of the transition diffusion layer is determined, which is of the order of 1 μm (figure 3(a)). Based on the analysis of the Nb–Cu distribution map (figure 3(b)), it can be concluded that the diffusion of copper (the element of substrate) into the coating occurs predominantly by the grain boundary mechanism.

4. Conclusions

The kinetic equation of diffusion makes it possible to obtain concentration profiles of niobium through the depth of the copper substrate, which allows to estimate the thickness of the transition layer and to carry out mass transfer simulation without experimental studies.

Niobium concentration profile obtained by the experimental method coincides with the calculated data within the margin of error. In the course of the work it was established that the diffusion of copper (the element of the substrate) into the niobium coating in the temperature range from 100 to 300 °C mainly occurs by the grain boundary mechanism. The flux of niobium ions incident on the substrate with the energy significantly higher than the energy of the lattice thermal vibrations leads to an increase in the mass transfer intensity in the binary system.

References

[1]   Liu E B, Cui X F, Jin G, Li Q F and Shao T M 2012 *Key Eng. Mater.* **525–6** 9–12
[2]   Kim J–H, Jung D–W, Kim S, Hong S, You Y and Kim D 2012 *Vacuum* **12** 1789–94
[3]   Bothner D, Clauss C, Koroknay E, Kemmler M, Gaber T, Jetter M, Scheffler M, Michler P, Dressel M, Koelle D and Kleiner R 2012 *Supercond. Sci. Technol.* **6** 065020
[4]   Broussard P R 2017 *J. Low Temp. Phys.* **1–2** 108–19
[5]   Bruno A, Mengucci P, Mercaldo L V and Lisitskiy M P 2013 *Supercond. Sci. Technol.* **3** 035004
[6]   Esposito A, Nakagawa H, Akoh H and Takada S 1999 *J. Vac. Sci. Technol., A* **6** 3525–28
[7]   De Freitas T C, Gonzalez J L, Nascimento V P and Passamani E C 2016 *Thin Solid Films* **611** 33–8
[8]   Kolosov V N and Shevyrev A A 2014 *Phys. Met. Metallogr+* **8** 786–92
[9]   Kim Y W, Lee S–G and Choi J–H 2011 *Physica C* **21–22** 1193–5
[10] Beebe M R, Valente–Feliciano A–M, Beringer D B, Creeden J A, Madaras S E, Li Z, Yang K, Phillips L, Reece C E and Lukaszew R A 2017 *IEEE T. Appl. Supercon.* **4** 1–4
[11] Cattarin S, Musiani M, Palmieri V and Tonini D 2006 *Electrochim. Acta* **8–9** 1745–51
[12] Beringer D B, Roach W M, Clavero C, Reece C E and Lukaszew R A 2013 *J. Appl. Phys.* **22** 223502
[13] Bemporad E, Carassiti F, Sebastiani M, Lanza G, Palmieri V and Padamsee H 2008 *Supercond. Sci. Technol.* **12** 125026
[14] Barzilai S, Raveh A and Frage N 2005 *Vacuum* **3–4** 171–7
[15] Barzilai S, Frage N and Raveh A 2006 *Surf. Coat. Technol.* **14–15** 4646–53
[16] Kuri G, Gupta M, Schelldorfer R and Gavillet D 2006 *Appl. Surf. Sci.* **3** 1071–80
[17] Krishnan M, Valderrama E, James C, Zhao X, Spradlin J, Feliciano A–M V, Phillips L, Reece C E, Seo K and Sung Z H 2012 *Phys. Rev. ST Accel. Beams* **3** 032001
[18] Heumann T 2007 *Diffusion in Solids* (Berlin–Heidelberg: Springer–Verlag)
[19] Postnikov D V, Blesman A I, Logachev I A, Logacheva A I, Tkachenko E A and Polonyankin D A 2016 *Proc. Eng.* **152** 576–81
[20] Polonyankin D A, Blesman A I, Postnikov D V, Logacheva A I, Logachev I A, Teplouhov A A and Fedorov A A 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **168** 012069