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Inter-diffusion of carbon into niobium coatings deposited on graphite

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Abstract

The inter-diffusion of carbon (originating from a graphite substrate) into a niobium coating and the fabrication of its carbides by heat treatment in the temperature range of 1073 – 1773 K was studied. The thickness of the Nb_2C and NbC phases formed after heat treatment as well as the inter-diffusion coefficients for the formation of the carbide layers were also studied. It was found that the carbide layer growth displayed parabolic behavior patterns inherent in the growth rate constants (K) of Nb_2C and NbC layers.

By assuming that the inter-diffusion coefficients are independent of concentration, it was possible to determine the inter-diffusion coefficients of carbon D^c into Nb_2C and NbC layers as a function of temperature.

Keywords: Carbon; Carbides; Niobium; Diffusion; Sputtering

1. Introduction

Niobium carbide coatings have great importance in a wide range of applications, in corrosive, erosive and wear environments. In this study we produce niobium carbide coatings on graphite substrates by the deposition of niobium metal followed by heat treatment. The heat treatment forms niobium carbide phases which improve the hardness and reduce the porosity of the coating on graphite [1]. In a previous investigation [1] we showed that the density, morphology, and structure of the niobium layer formed by magnetron radio-frequency (rf) sputtering and of the carbide derived by heat treatment are strongly affected by a negative bias voltage (*Vb*). It was observed that three distinct categories of Nb and NbC layers are formed depending on the negative bias voltage, *Vb*: (a) at $Vb < 50$ V, a singularly nucleated columnar structure of the Nb film is formed, which is transformed into a highly porous NbC coating by heat treatment; (b) at $50\text{ V} < Vb < 80$ V, a singularly nucleated columnar structure composed of a continuously nucleated sub-columnar structure is formed, which is transformed into a dense NbC coating with the highest microhardness, of ~13 GPa; and (c) at $Vb \geq 80$ V, an imperfect structure of the Nb film is formed, which is transformed into a NbC coating with the highest density characterized by brittle fracture and an intermediate range of microhardness.

Several authors [2–6] studied the interaction between Nb and graphite in the temperature range of 1673 – 2573 K, and they determined the carbon inter-diffusion coefficients into Nb_2C and NbC layers, as summarized in Table 1.

Miyake et al. [7] investigated the rate of carbon inter-diffusion and of carbide layer formation, originating from a niobium coating on graphite, and concluded that it is significantly higher than that observed by other authors [2–5] for niobium metal bulk.

Similar results to Miyake et al. [7] were obtained by Isobe et al. [8], who studied carbon diffusivity in molybdenum carbide by measuring the carbide layer growth, in both molybdenum coating on a graphite substrate and in bulk molybdenum that was coupled directly to graphite. They concluded that the inter-diffusion coefficient for coatings is higher and the activation energy is lower than those obtained for the bulk specimen.

The present study was motivated by the lack of detailed information regarding the carbide growth and inter-diffusion coefficients of carbon into niobium coatings at a low temperature regime of 1073 – 1773 K. We therefore investigated the interaction between niobium coatings and graphite substrate by measuring the carbide layers [3,8] and by using Fick's First law to evaluate the average diffusion coefficient.

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Table 1

The growth rate constant and inter-diffusion parameters of carbon into niobium carbide bulk. K_0—growth rate constant, Q_k—activation energy of growth rate, Q_D—activation energy of inter-diffusion, T—temperature

Carbide phase	K_0[m^2/s]	Q_K[kJ/mol]	D_0[m^2/s]	Q_D[kJ/mol]	T [K]	Analysis method	Ref
Nb_2C	$1.57 \pm 0.35 \cdot 10^{-5}$	302.5 ± 25.8	$2.04 \pm 0.57 \cdot 10^{-4}$	295.2 ± 18.2	1673–1973	*	[2]
NbC_{1-X}	$2.65 \pm 0.25 \cdot 10^{-5}$	312.5 ± 11.6	$3.84 \cdot 10^{-9} \exp(23.24x)$	236.4 ± 7.1	1673–1973	*	[2]
Nb_2C	$3 \cdot 10^{-5}$	337.4	–	–	1973–2573	*	3
NbC	$1.76 \cdot 10^{-3}$	402.2	$7.6 \cdot 10^{-4}$	368.9	1973–2573	*	3
Nb_2C	$2.2 \cdot 10^{-6}$	287.7	–	–	1700–2090	–	4
NbC	$4.5 \cdot 10^{-6}$	305.3	–	–	1700–2090	–	4
Nb_2C	$5.9 \pm 0.5 \cdot 10^{-7}$	260.1 ± 14.1	–	–	2173–2573	*	5
NbC	$1.1 \pm 0.1 \cdot 10^{-4}$	344.9 ± 9.1	–	–	2173–2573	*	5
$NbC_{0.75}$	–	–	$8.8 \cdot 10^{-10}$	138.5	1873–2273	**	6
$NbC_{0.98}$	–	–	$1.0 \cdot 10^{-10}$	133.8	1873–2273	**	6

*Layer growth.

**Radio-tracer of powder metallurgy samples.

Kidson [9] showed that using diffusion coefficients and Ficks First law to investigate poly-phase diffusion in binary systems leads to defining the sub-layers as a function of time and temperature.

Therefore, using Fick's law we investigate here the kinetic growth of niobium carbides as a result of the interaction between the Nb coating and the graphite substrate in a temperature range of 1073 to 1773 K. The metallographic cross-sections enable us to distinguish between sub-layers. These are used to evaluate the growth rate of the carbide layers and the mean values of diffusion coefficients of carbon into the niobium carbides formed by heat treatment.

2. Experimental details

2.1. Layer deposition and heat treatment

The niobium layers, typically 8–12 μm thick, are deposited in a custom-designed radio-frequency (rf) magnetron system. The graphite substrates ($10 * 40 * 1.5$ mm^3) are polished with a 600 mesh SiC paper, then ultrasonically degreased, cleaned and mounted on a substrate holder. The sputter Nb target (80 mm in diameter and 6 mm thick, 99.9%) is mounted on an rf magnetron source at a distance of 5 cm from the substrate holder. The base pressure is below 7×10^{-4} Pa and the sputtering process is performed in argon (99.999%) at a constant pressure of 0.7 Pa and an rf input power of 400 W. The substrate holder subjected to $Vb = -80$ V with reference to ground. The maximum substrate temperature resulting from the deposition process is about 473 K. After deposition, the Nb layers are annealed in a vacuum of 7×10^{-4} Pa and in the temperature range of 1073–1773 K for 12 – 480 min. The heating rate is 300°/min and the cooling rate is 200°/min.

2.2. Layer characterization

Phase analysis is carried out using an X-ray diffractometer (XRD) with Cu-Kα radiation ($\lambda = 0.154$ nm) and a graphite monochromator. Scanning electron microscopy (SEM) micrographs of the cross-sections is taken after fracturing the sample by bending tests. Metallographic sections are prepared by standard polishing of the samples at several stages of 600, 1000 and 2400 mesh followed by polishing with a synthetic cloth and 1 μm diamond paste. The metallographic samples are etched in diluted solutions containing nitric acid and hydrofluoric acid. The thicknesses of the NbC and Nb_2C layers, obtained after heat treatment of the niobium coating, are measured by SEM. Measurement of the thicknesses of the sub-layers is enabled by defining the location of interfaces after the chemical etching. These measurements are also verified by depth profile analyses using Wavelength Dispersive Spectroscopy (WDS), and micro-probe analyzer, with energy of 5 keV.

3. Results and discussion

3.1. Growth rate of Nb-C layers

XRD peak patterns of ~10 μm thick were examined after annealing for 3 h at various temperatures (Fig. 1a), and of ~4 μm after annealing for 45 min (Fig. 1b). The depth sensing capacity of the XRD method is about 4–5 μm. Therefore, it is seen that for the thicker films treated at low $T = 1173$ K no carbide phases are detected, while at $T = 1373$ K a Nb_2C phase is detected, but only after treatment at $T = 1773$ K does the treated Nb layer transform to a single NbC phase (Fig. 1a). It is probable that Nb_2C and NbC phases are formed at the interface between the coating and the graphite at 1173 and at 1373 K, respectively. However, these phases cannot be detected in thick films, ≥ 5 μm, due to the depth sensing of the XRD method. Only where the layer is ~4 μm thick, is XRD capable of detecting the whole layer composition revealing the three phases, Nb, Nb_2C and NbC (Fig. 1b). The analyses indicate that only for layers with a thickness lower than the depth sensing capacity of the XRD method is it possible to characterize the entire layer depth and to distinguish between the various phases, whereas for layers =5 μm it is not. Moreover, the thin layer ≤ 5 μm displays (111), (002) and (101) phase orientations of NbC, Nb_2C and Nb, respectively (Fig. 1b). The orientation of the Nb_2C phase changes from (002) to (100) for thicker layers (~10 μm), which is possibly affected by the growth of NbC phase. The XRD analyses suggest that annealed samples with niobium layers of 8–10 μm