

The Sulfidation and Oxidation Behavior of Sputter-Deposited Nb-Al-Cr Alloys at High Temperatures

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Sputter-deposited Nb-Al-Cr alloys, 3-5 μm thick, have been prepared on quartz substrates as oxidation- and sulfidation-resistant materials at high temperatures. The oxidation of the alloys in the Ar-O₂ atmosphere of an oxygen partial pressure of 20 kPa follows approximately the parabolic rate law, thus being diffusion controlled. Their oxidation rates are almost the same as or even lower than those of the typical chromia-forming alloys. The multi-layered oxide scales are formed on the ternary alloys. The outermost layer is composed of Cr₂O₃, which is mainly responsible for the high oxidation resistance of these alloys. In contrast to sputter-deposited Cr-Nb binary alloys reported previously, the inner layer is not porous. TEM observation as well as EDX analysis indicates that the innermost layer is a mixture of Al₂O₃ and niobium oxide. The dispersion of Al₂O₃ in niobium oxide may be attributable to the prevention of the formation of the porous oxide layer. The sulfidation rates of the present ternary alloys are higher than those of the sputter-deposited Nb-Al binary alloys, but still several orders of magnitude lower than those of conventional high temperature alloys. Two-layered sulfide scales are formed, consisting of an outer Al₂S₃ layer containing chromium and an inner layer composed of NbS₂ and a small amount of Cr₂S₃. The presence of Cr₂S₃ in the inner protective NbS₂ layer may be attributed to the increase in the sulfidation rates.

Keywords : Nb-Al-Cr alloy, sputter deposition, oxidation, sulfidation

1. Introduction

It is well known that high temperature corrosion of metallic materials in sulfur-containing atmospheres is much severer than in purely oxidizing environments.¹⁾ The rapid or often catastrophic degradation of common metals results from high defect density in sulfides formed, due to large deviations from stoichiometry of sulfides.^{2,3)} Low melting points of common metal sulfides compared with corresponding oxides are also attributed to their rapid degradation in sulfidizing atmospheres. Refractory metals, such as niobium, molybdenum and tantalum, are exceptional and they reveal high resistance to sulfide corrosion; their sulfidation rates are comparable to the oxidation rates of typical chromia-forming alloys.³⁾ Low defect density or low defect mobility of refractory metal sulfides is responsible for their high sulfidation resistance.^{2,4)} Thus, high temperature alloys with refractory metals have received attractive attention as candidate materials resistant in sulfur-containing atmospheres.

The iron-, cobalt- or nickel-base alloys containing up to 30 wt% of refractory metals, however, reveal still relatively high sulfidation rates at high temperatures,⁵⁻¹¹⁾

because protective refractory metal sulfide layers cannot be formed uniformly on the alloy surface. When aluminum is added up to 9 wt% as a third element, the sulfidation rates reduced significantly,¹²⁻¹³⁾ but "pest" phenomenon has been observed for these alloys since these alloys are heterogeneous. Therefore, the common metal alloys containing refractory metals do not possess sufficient sulfidation resistance at high temperatures. Alternative materials are refractory metal alloys or refractory metal intermetallic compounds without common metals. Since refractory metals are not resistant in purely oxidizing environments at high temperatures, alloying with aluminum, chromium or silicon is needed to provide oxidation resistance to refractory metals. Recently, Al-refractory metal and Cr-refractory metal alloys with wide composition ranges have been prepared by sputter deposition.¹⁴⁻¹⁷⁾ It has been reported that the sulfidation rates of refractory metal-Al alloys are further lower than those of the corresponding sulfidation-resistant refractory metals.¹⁴⁻¹⁶⁾ The Cr-refractory metal alloys also have high sulfidation resistance, although their sulfidation rates are almost the same as or slightly higher than those of the corresponding refractory metals.¹⁷⁾ In contrast, the oxi-

duction resistance of the Al-refractory metal and Cr-refractory metal alloys is not sufficient, because a continuous alumina or chromia layer is not formed on these alloys. The addition of small amounts of silicon to Al-Nb and Al-Mo alloys improve considerably their oxidation resistance; their oxidation rates are comparable to the typical chromia-forming alloys.¹⁸⁾⁻²⁰⁾ As well as silicon, the addition of chromium is also expected to improve the oxidation resistance of Al-Nb alloys, since it is known that simultaneous additions of aluminum and chromium are more effective in enhancing the oxidation resistance of common metals than the individual addition of these elements.²¹⁾ Thus, in the present study Nb-Al-Cr alloys have been prepared by sputter deposition, and their oxidation and sulfidation behavior has been examined under isothermal conditions.

2. Experimental

Nb-Al-Cr alloy films, 3-5 μm thick, were sputter-deposited on to quartz substrates (10 x 10 x 1 mm) using Vacuum Products SP-2C dc magnetron sputtering facilities. The targets used were a 99.999% pure aluminum disk of 6 mm in thickness and 100 mm in diameter, on the sputter-erosion region of which niobium and chromium discs of 20 mm in diameter were symmetrically placed. The compositions of the alloy films were controlled by changing the number of small disks. During sputter deposition, substrate holders were rotated around central axis of the chamber as well as their own axis to obtain alloy films with uniform composition and thickness. The chemical composition of the alloys was determined by electron probe microanalysis and the structure was identified by X-ray diffraction using Cu $K\alpha$ radiation. All the as-deposited alloy films were amorphous. The compositions of the films prepared are listed in Table 1. In order to secure high resistance both to sulfide and oxide corrosion, all the alloys prepared contain about 40 at% of niobium.

The sulfidation and oxidation experiments were carried out under isothermal-isobaric conditions at temperatures ranging from 1073 to 1273 K in a He-S₂ atmosphere of

a sulfur partial pressure 1×10^3 Pa and in an Ar-O₂ atmosphere of an oxygen partial pressure 2×10^4 Pa, respectively. Change in the weight of the specimens during sulfidation and oxidation was monitored continuously using electronic microbalance. The accuracy of the balance was 10 μg . The details were described in the previous paper.¹⁵⁾

After the sulfidation and oxidation tests, phase identification of the reaction products on the specimens was carried out by $\alpha - 2\theta$ mode X-ray diffraction. The surfaces and fractured cross-sections of the specimens were observed using JEOL JSM-6300F field emission scanning electron microscopy (SEM). The composition of the scales was also analyzed using JEOL JSM-5400 scanning electron microscope equipped with WDS facilities. Further, TEM observation was performed using JEOL JEM-2000FX transmission electron microscope equipped with EDX facilities. Electron transparent sections, about 10-20 nm thick, of the specimens oxidized and sulfidized were prepared by ultramicrotomy.

3. Results and discussion

3.1 Oxidation behavior

Fig. 1 shows the parabolic plot of the oxidation kinetics for sputter-deposited Nb-29Al-29Cr alloy at several temperatures. The oxidation follows apparently the parabolic rate law after an initial slight rapid weight gain. The initial rapid weight gain up to about 0.15-0.2 mg cm^{-2} at all temperatures is caused by absorption of oxygen in the alloy, since the oxide scales with their thickness corresponding to the weight gain do not form during this

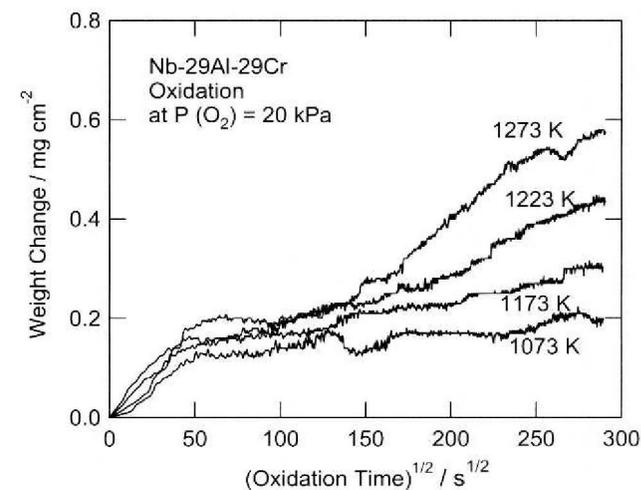


Fig. 1. Parabolic plot of the oxidation kinetics for the sputter-deposited Nb-29Al-29Cr alloy at several temperatures.

Table 1. Composition of the sputter-deposited alloys prepared.

Alloy	Nb (at%)	Al (at%)	Cr (at%)
Nb-42Al-14Cr	44	42	14
Nb-35Al-25Cr	40	35	25
Nb-29Al-29Cr	42	29	29
Nb-19Al-32Cr	49	19	32

oxidation time. The presence of oxygen in the alloy phase after oxidation was also confirmed by EPMA analysis of the cross-section of the specimen. Similar oxidation kinetics has been observed for all the ternary alloys prepared in the present study. It has been reported that the oxidation of sputter-deposited Al-Nb alloys with aluminum contents of 50at% or more reveals the pest phenomenon at 1073 K.¹⁵⁾ In addition, at higher temperatures breakaway oxidation occurs for the binary alloys. The oxidation of the sputter-deposited Nb-Cr alloys does not also follow the parabolic rate law in a temperature range of 1073-1273 K, due to the repeated partial breakdown and restoration of the oxide scales formed during the oxidation process.¹⁷⁾ From the comparison of these results and Fig. 1, it is clear that the simultaneous additions of aluminum and chromium to niobium are more effective in improving the oxidation resistance, compared with the addition of aluminum or chromium individually.

The oxidation kinetics of the Nb-Al-Cr ternary alloys with different compositions at 1173 K is shown in Fig. 2. The alloys containing less than 20 at% aluminum or chromium show initially relatively large weight gain of more than 0.2 mg cm⁻² due to absorption of oxygen in alloy, while the initial weight gain for the other alloys containing more than 25 at% of both aluminum and chromium is small. Thus, the additions of sufficient amounts of both aluminum and chromium are effective in suppressing the absorption of oxygen in alloy. The steady state oxidation rate for the alloy with a low chromium content of 14 at% is slightly higher than those of the other alloys, suggesting the necessity of a certain amount of chromium in the alloy to have high oxidation resistance, although the oxidation resistance of the former alloy is still better than that of the Nb-Al binary alloys. The temperature dependence of the parabolic rate constants in the steady state oxidation of the present ternary alloys is plotted together with that of the conventional high temperature alloys (Fig. 3). It has been found that the Nb-Al-Cr ternary alloys possess the oxidation resistance as high as or even better than the typical chromia-forming alloys.

To understand the significant improvement of the oxidation resistance of niobium by simultaneous additions of aluminum and chromium, the characterization of oxide scales formed on the ternary alloys has been carried out. X-ray diffraction patterns of the specimens oxidized at each temperature reveal the presence of Cr₂O₃, CrNbO₄ and NbO. The former two oxides have been also observed for the Nb-Cr binary alloys, but the latter low valent niobium oxide has not been found in the oxides formed on the binary Al-Nb and Cr-Nb alloys.^{15,17)} The formation

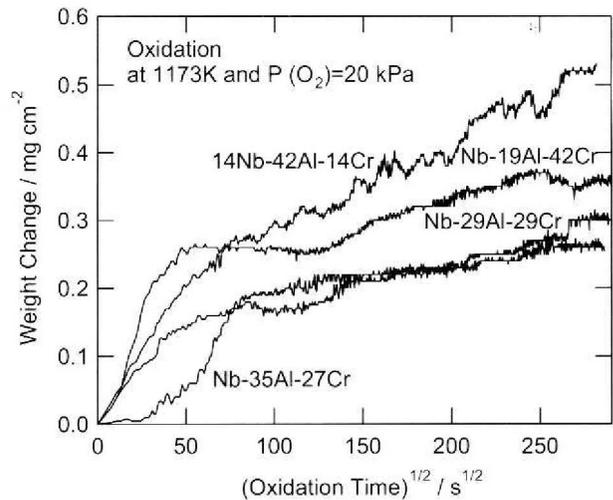


Fig. 2. Parabolic plot of the oxidation kinetics for the sputter-deposited several Nb-Al-Cr alloys at 1173 K.

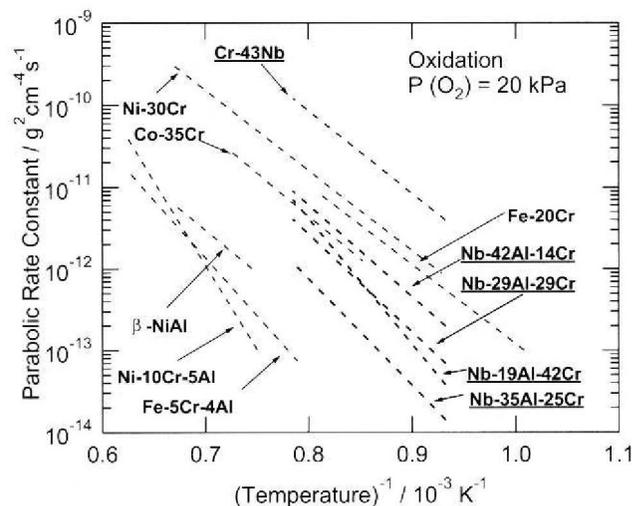


Fig. 3. Temperature dependence of parabolic rate constants for oxidation of the sputter-deposited several Nb-Al-Cr alloys and Cr-43Nb alloy¹⁷⁾ as well as typical alumina- and chromia-forming alloys.

of NbO, which is not stable in the atmospheres of high oxygen partial pressures, suggests the presence of outer protective oxide layer that reduces effectively the oxygen partial pressure in the inner part of the oxide scales. A typical example of the X-ray diffraction patterns obtained using different incident angles of X-ray beam is shown in Fig. 4. The intensity of diffraction lines for Cr₂O₃ is relatively high at the lower incident angle ($\alpha = 2^\circ$), compared with that at the higher incident angle ($\alpha = 10^\circ$), indicating the presence of Cr₂O₃ in the outermost layer

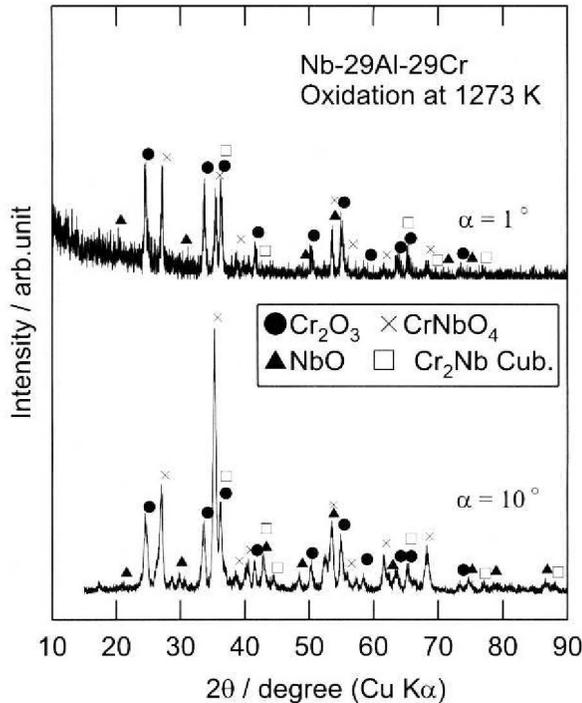


Fig. 4. Glancing-angle X-ray diffraction patterns of the sputter-deposited Nb-29Al-29Cr alloy oxidized at 1273 K for 24 h.

of the oxide scale. Since the diffraction lines for NbO are not clearly visible at the lower incident angle, the NbO should be formed in the inner part of the scale. Similar X-ray diffraction patterns were obtained at all temperatures examined, although the diffraction intensities for oxides relative to those for underlying Cr_2Nb decreased with a decrease in the oxidation temperature. No diffractions lines corresponding to oxide phases containing aluminum were detected from all the specimens oxidized, despite of the highest activity for oxidation among the alloy constituting elements. The absence of the diffraction lines suggests that aluminum may be present mainly as poorly crystalline phases.

The fractured cross-sections of the Nb-29Al-29Cr alloy specimens oxidized at three different temperatures are shown in Fig. 5. Apparently two-layered scale, about 3 μm thick, forms at 1273 K. WDX analysis of the oxide scale indicated that the outer layer was composed mainly of Cr_2O_3 , and the inner layer was built up of niobium-rich oxides containing aluminum and chromium. Both layers are non-porous and apparently protective, although cracks are running along the interfaces between alloy and the inner layer as well as between the inner layer and outer layer. Since a porous inner layer forms on the Nb-Cr binary alloys,¹⁸⁾ the formation of non-porous inner layer

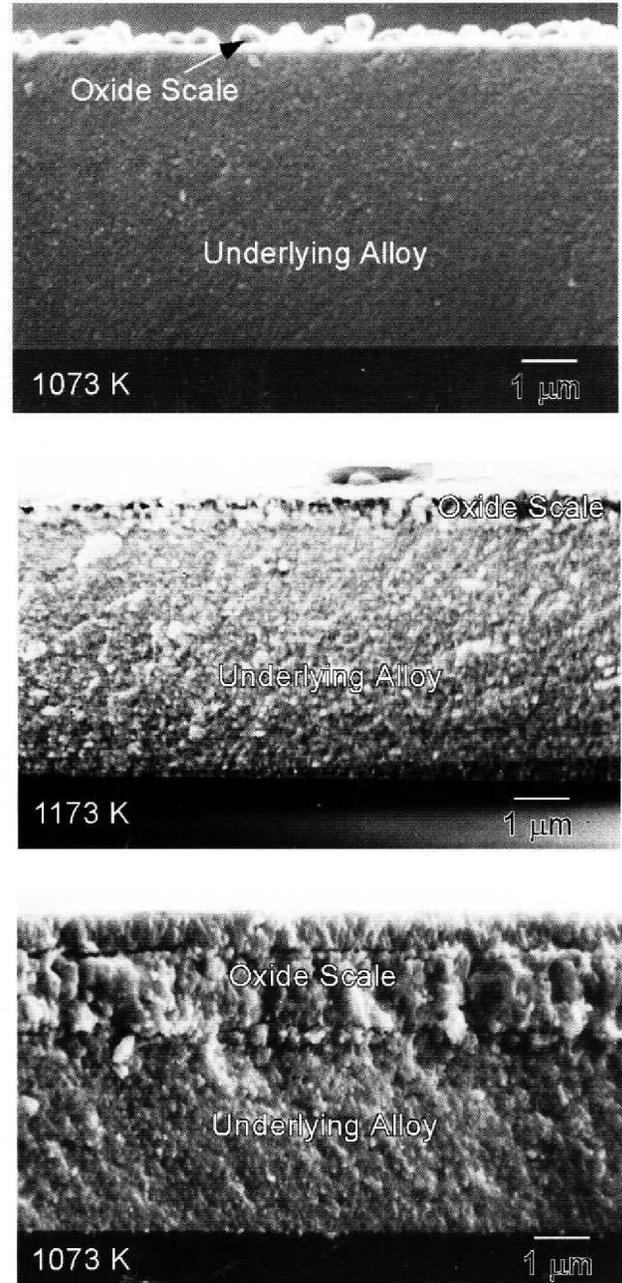


Fig. 5. Scanning electron micrographs of fractured cross-sections for the sputter-deposited Nb-29Al-29Cr alloy specimens oxidized at 1073, 1173 and 1273 K.

should be one of the reasons for the better oxidation resistance of the present ternary alloys. At lower temperatures rather thin oxide scales, less than 1 μm thick, form on the Nb-29Al-29Cr alloy as seen in Fig. 5. The formation of discontinuous cubic block-like oxides is found at 1073 K. At 1173 K, a continuous oxide layer forms, but the layer appears to contain micro-voids, which may be related

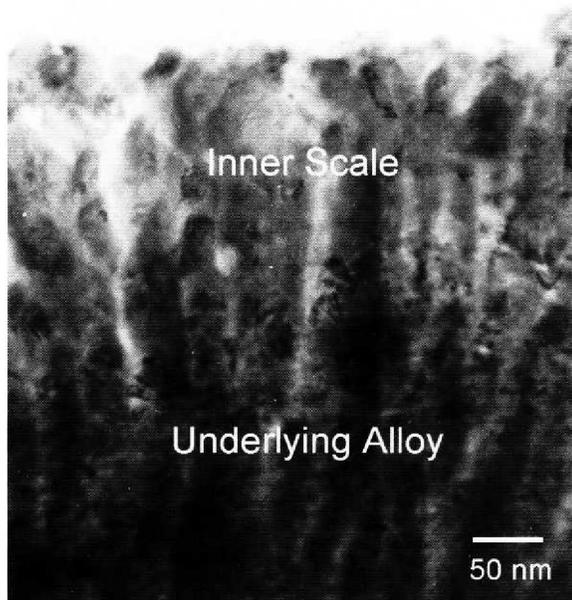


Fig. 6. Transmission electron micrograph of an ultramicrotomed section for the sputter-deposited Nb-29Al-29Cr alloy oxidized at 1173 K for 24 h.

to the formation of cracks in the scale formed at 1273 K.

The oxide scale formed at 1173 K was also observed by transmission electron microscopy. Electron transparent cross-sections were prepared using an ultramicrotomy technique. However, the oxide scale of full thickness was not observed successfully, due to spalling of the outer part of the scale, which was associated with the presence of voids. Fig. 6 depicts a transmission electron micrograph of the inner part of the scale, about 150 nm thick, formed on the Nb-29Al-29Cr alloy at 1173 K. The inner layer consists of grains of 20-30 nm sizes. EDX analysis of several regions of the oxide layer and the underlying alloy layer was also performed using an electron beam of about 20 nm in diameter. As shown in Fig. 7, the inner oxide layer is almost free of chromium, being composed of aluminum and niobium cations. The intensity ratio of aluminum and niobium is strongly dependent on the analytical points, as clearly seen in Fig. 7: at some points almost no aluminum is detected and at some points almost no niobium is detected. Such difference of the composition was not related to the direction of the depth of the oxide layer. Therefore, the inner layer consists of a mixture of Al_2O_3 and NbO. The absence of chromium in this layer suggests that Cr_2O_3 and CrNbO_4 , observed in X-ray diffraction patterns, are formed above this innermost layer, owing to the outward diffusion of chromium during the

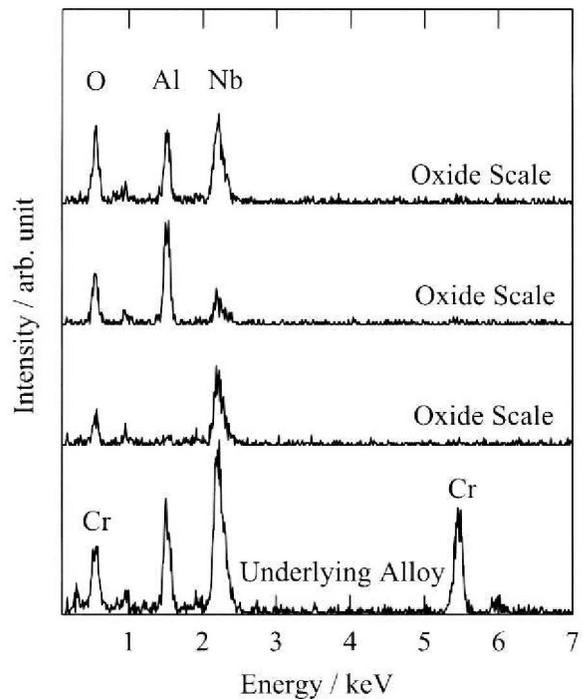


Fig. 7. EDX spectra obtained from the several points in the oxide layer as well as in the underlying alloy of Fig. 6.

oxide growth. The previous diffraction patterns with different incident angle of X-ray beam reveal that Cr_2O_3 is a main constituent of the outermost layer of the scale. Below the Cr_2O_3 layer, CrNbO_4 is probably present together with poorly crystalline Al_2O_3 . The innermost layer of the scale is composed of NbO and Al_2O_3 as observed in the transmission electron micrograph. The dispersion of Al_2O_3 in the CrNbO_4 - and NbO-containing inner layer is probably attributed to suppression of porous film formation, which occurs on the Cr-Nb binary alloys,¹⁷⁾ and hence the high oxidation resistance is obtained by sustaining protective and continuous outer Cr_2O_3 layer.

3.2 Sulfidation behavior

It has been reported that Al-Nb alloys containing 50 at% or more niobium have higher resistance to sulfide corrosion than niobium.¹⁵⁾ In contrast, the sulfidation rates of the Cr-Nb alloys are higher than those of niobium and increase with an increase in chromium content.¹⁷⁾ Thus, the influence of aluminum and chromium additions on the sulfidation behavior of the niobium alloys is different, although their roles are not yet well understood. When both aluminum and chromium are added simultaneously to niobium in the present study, the sulfidation rates increase, as shown in Fig. 8. Obviously, the sulfidation rates of the Nb-29Al-29Cr ternary alloy are higher than

those of Nb-50Al alloy at both 1073 and 1173 K, indicating that the addition of chromium to niobium increases

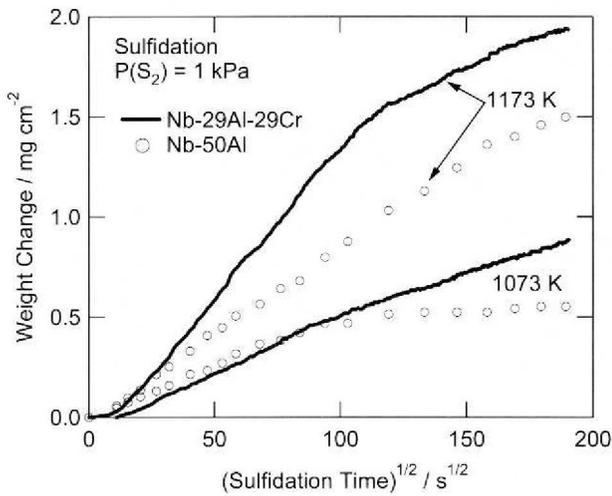


Fig. 8. Parabolic plots of the sulfidation kinetics for sputter-deposited Nb-29Al-29Cr alloy as well as for Nb-50Al alloy¹⁵⁾ at 1073 and 1173 K.

the sulfidation rates even under the presence of aluminum.

X-ray diffraction patterns of the ternary alloys after sulfidation reveal the diffraction lines corresponding to Al_2S_3 and NbS_2 . No diffraction lines corresponding to the chromium-containing sulfides were detected. SEM observations revealed that the sulfide scales formed on the present Nb-Al-Cr ternary alloys consisted of two layers, similarly to the Al-Nb binary alloys.¹⁵⁾ Fig. 9 shows transmission electron micrograph of an ultramicrotomed section of the sulfide scale formed on the Nb-29Al-29Cr alloy at 1173 K. The micrograph reveals only the scale due to detachment of the underlying alloy layer during sectioning by ultramicrotomy. Despite the fact that the scale is highly damaged during sectioning, the sulfide scale consists clearly of two layers. The inner layer has a columnar structure, which is typical of refractory metal disulfides with a layer crystal structure. From EDX spectra shown in Fig. 9, the outer layer consists of aluminum, chromium and sulfur. Since no diffraction lines for Cr_2S_3 were observed from the XRD patterns, chromium should be dissolved in the Al_2S_3 phase. The inner layer contains

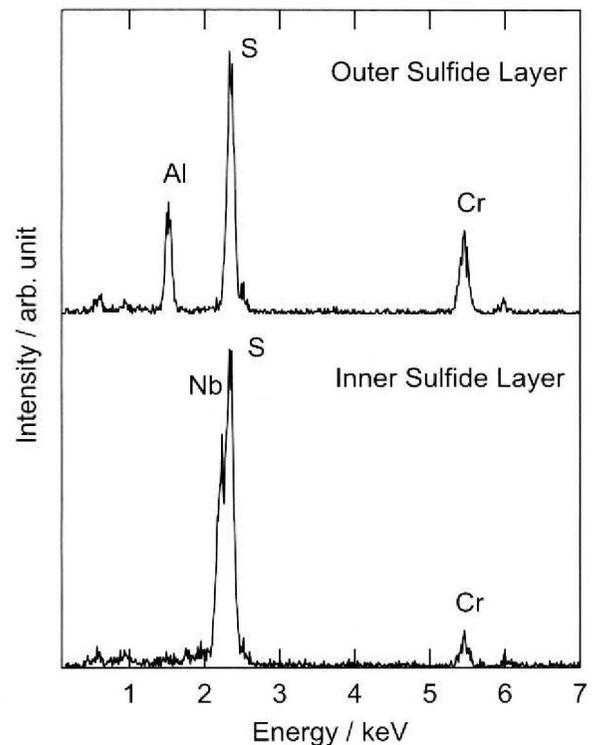


Fig. 9. Transmission electron micrograph and EDX spectra of an ultramicrotomed section for the sputter-deposited Nb-29Al-29Cr alloy sulfidized at 1193 K.

both niobium and chromium, but aluminum is detected in the EDX spectrum obtained from the inner layer of the sulfide scale. From the relatively low intensity of the chromium peak, the inner layer is composed mainly of NbS₂. The selected area electron diffraction pattern of the inner layer revealed the presence of the Cr₂S₃ phase, indicating that the inner layer is a mixture of NbS₂ and Cr₂S₃ with the latter being the minor component. The increase in the sulfidation rates of niobium and Nb-Al alloys by the addition of chromium is, therefore, related to the presence of Cr₂S₃ in the protective inner layer; the heterogeneity of the inner layer reduces the protectiveness of the NbS₂ layer, resulting in the increase in diffusional transport of matter in the inner layer.

4. Conclusions

Ternary Nb-Al-Cr alloy films, about 3-5 μm thick, have been sputter-deposited on quartz substrates, and their oxidation and sulfidation behavior has been examined in an oxidizing atmosphere of p(O₂) = 20 kPa and in a sulfidizing atmosphere of p(S₂) = 1 kPa, respectively, at temperatures ranging from 1073-1273 K. The oxidation resistance of the ternary alloys is as high as or even higher than that of typical chromia-forming alloys, although the ternary alloys reveal initially absorption of oxygen in alloy film. Thus, the simultaneous additions of aluminum and chromium are very effective in enhancing the oxidation resistance of niobium. The oxide scales consist of Cr₂O₃, CrNbO₄, NbO and poorly crystalline Al₂O₃. The outermost layer is Cr₂O₃, being mainly responsible for the high oxidation resistance of the alloys. Unlike on CrNb alloys, the inner layer on the ternary alloys is not porous. The presence of Al₂O₃, together with CrNbO₄ and NbO, in the inner layers should avoid the formation of the inner porous layer.

In contrast, the ternary alloys reveal higher sulfidation rates than niobium and Nb-Al alloys at high temperatures, although their sulfidation rates are still several orders of magnitude lower than those of conventional high temperature alloys. The sulfide scales consists of two layers, comprising an outer (Al, Cr)₂S₃ layer and an inner layer of a mixture of NbS₂ and Cr₂S₃. The heterogeneity of the

inner protective layer possibly results in the increase in the sulfidation rates of the ternary alloys.

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