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Development of oxide diffusion-barrier on refractory metals

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A new approach to the development of diffusion-barrier coatings which can effectively reduce the interaction of refractory filaments such as tungsten and tantalum with a nickel-alloy matrix is presented. This consists of reacting the oxide film deliberately grown on these metals with a nickel coating prior to fabricating the composite. The nickel-oxide film reactions proceed under vacuum conditions in the temperature range 650 to 800° C with the formation of intermediate phases which produce sufficiently strong bonds for composite strengthening.

The details of the reaction mechanisms are not known but two types of reaction are identified. Type 1 which is a common reaction to both the Ni/oxide/Ta and the Ni/oxide/W systems constitutes a displacement reaction at the Ni/oxide interface leading to the formation of new phases and type 2 is controlled by the bulk diffusion of nickel through the compact oxide film with the development of a diffusion zone at the oxide/substrate interface. Type 2, which is only observed in the Ni/oxide/W system, is believed to confer remarkable chemical stability at 800° C *in vacuo.*

1. Introduction

Since the refractory metals (Nb, Ta, Mo and W) have excellent high temperature mechanical properties, substantial interest has been shown in their utilization as the high-temperature reinforcement of superalloy matrices [1-5]. In their study of tungsten alloy fibre-reinforced nickel-base alloy composites, Petrasek and Signorelli [6] have demonstrated that the properties of tungsten become attractive despite its high density. However, chemical incompatibility of the fibre and matrix can be a serious problem in metal matrix composite development [6, 7]. While metallurgical reactions between the matrix and the fibre promote bonding for adequate stress transfer, they may also reduce drastically the composite strength by adversely affecting the fibre. In some systems the rate of inter-diffusion and reaction has been reduced through alloying of the matrix or pre-coating the fibre [7-9]. Thus, such aspects as diffusion barriers to reduce the formation of intermetallic compounds are worth investigating.

Oxides are thermodynamically more stable than metals and thus would be less susceptible than metals to interfacial reactions with a metal matrix. An alternate route to forming a barrier layer on the fibre is to purposely grow a thin but adherent oxide film which can be subsequently treated and bonded to the metal matrix. Inter-diffusion and reactions during fabrication of the composite and subsequent use at elevated temperature would be controlled by the rate of formation of intermediate phases (or spinels) at the oxide film-matrix interface and/or the rate of dissolution of the oxide film in the fibre substrate. Reactions between oxide films on zirconium-base alloys and surface-deposited metal layers (e.g. Ni, Cu and Al) have been reported earlier [10] and a recent study [11] has shown that the oxide film can act as an effective diffusion barrier between the zirconium-base substrate and nickel alloy coatings.

It is the purpose of this communication to report the initial results of a continuing study on the feasibility of utilizing the thermally formed oxide film on refractory metals, with particular reference to tungsten and tantalum, as an interfacial diffusion barrier with a nickel matrix. To date our efforts have been directed to the preparation of nickel coatings that firmly adhere to the pre-oxidized metals, the examination of the interfacial reactions that lead to a metallurgical bonding between the nickel layer and the oxide film, and a preliminary assessment of the interfacial strength.

2. Experimental

Commercially pure tungsten and tantalum in the form of sheet stock (0.3 to 3 mm thick) and wire (0.25 mm diameter) were used in this investigation. The samples were prepared by polishing on 600 SiC grit paper followed by an anneal *in vacuo* at 1000 and 750°C for tungsten and tantalum respectively.

2.1. Coating procedure

The annealed tungsten and tantalum samples were oxidized in O_2 at 550 and 650 °C respectively to produce an oxide film 8 to 12 µm thick. The oxide film on tungsten was characterized by an inner protective layer of WO_2 and an outer porous layer of WO_3 while the oxide film on tantalum was identified as Ta_2O_5 with platelets of sub-oxide, TaO_2 adjacent to the oxide film into the substrate.

The Ni-coating was deposited on the pre-oxidized samples in two steps; a thin layer (~ 1 µm thick) was grown by immersing the sample in a Ni-electroless solution which made the surface electrically conductive and then the Ni-layer was built-up to 2 to 8 µm electrolytically.

A metallurgical bond between the Ni-layer and the oxide film was achieved by heat-treating the freshly Ni-coated samples in high vacuum in the temperature range 650 to 800 °C for various periods.

2.2. Examination of samples

The inter-diffusion and reactions at the interfaces (Ni/oxide film/substrate) were studied by optical metallography, X-ray diffraction and scanning-electron-probe micro-analysis techniques. The interfacial strength between the Ni-layer and the oxide film on tungsten was estimated by bonding, with an epoxy adhesive, a diffusion-annealed rectangular coupon in sandwich between two similar brass plates that could be gripped in a suitable testing machine. Measurement of the coupon surface area at the interface and the load to separate the coupon allowed calculation of the breaking stress.

3. Results

3.1. As-prepared samples

Photomicrographs of cross-sections, typical of Ni-coated pre-oxidized samples are shown in Fig. 1. The nickel coating adhered well to the oxide film and where gross porosity existed, as for example at the edges, the pores and cracks filled in with nickel during the electroless deposition as shown in Fig. 2. The remainder of this paper will emphasize Ni-coated samples such as these following diffusion annealing.

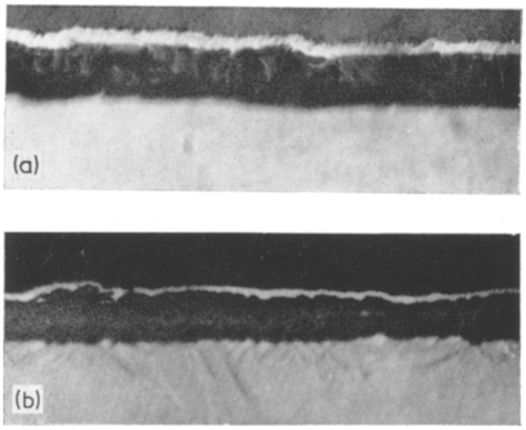

Figure 1 Micrographs of sectioned, as-prepared, samples showing the nickel/oxide/substrate, (a) tungsten (b) tantalum (× 1000).

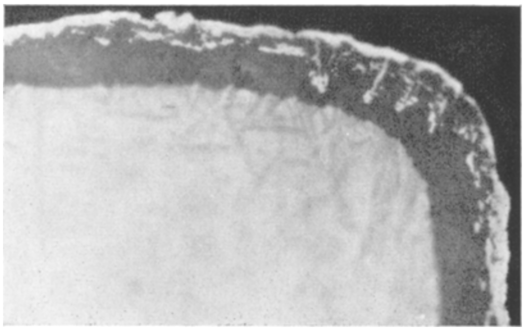

Figure 2 As-prepared tantalum sample showing the penetration of nickel in pores and cracks of porous oxide (× 1000).

3.2. Examination of diffusion-annealed nickel/tungsten oxide/tungsten

Different interfacial morphologies could be achieved with different oxide conditions. Photomicrographs of cross-sections of samples A and B following a heat-treatment at 800°C for 91 h are shown in Fig. 3. Sample A (Fig. 3a) on which a thicker oxide film (12 µm versus 8 µm for sample B) was grown prior to nickel coating revealed a greater degree of Ni/oxide interfacial

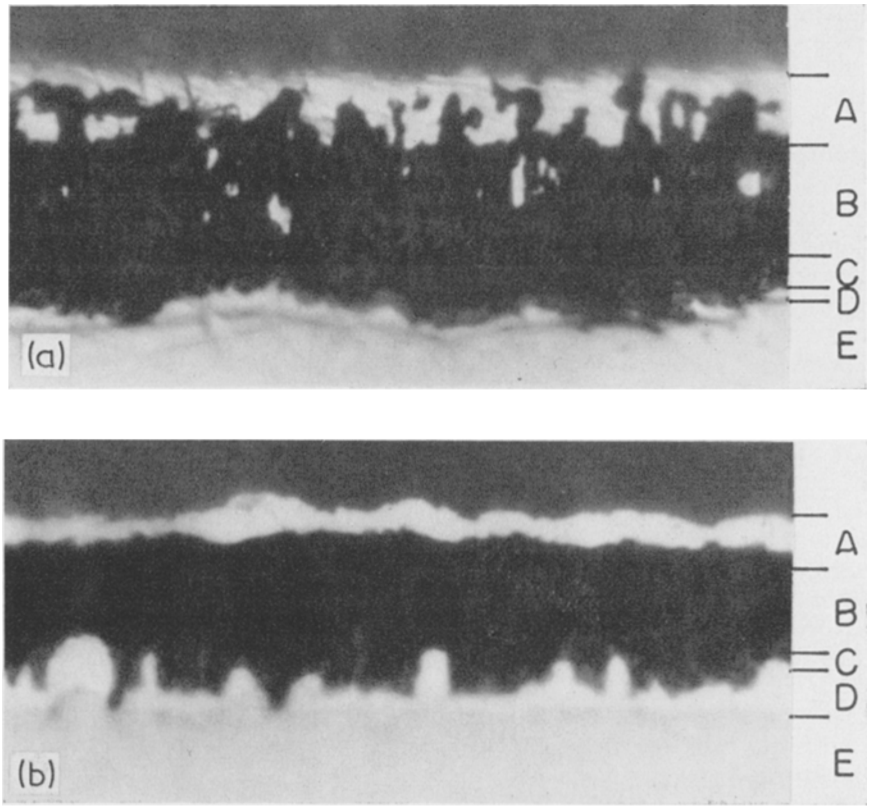

Figure 3 Comparison of cross-sections of nickel-reacted pre-oxidized tungsten samples following diffusion annealing, 800°C *in vacuo*, for 91 h. (a) Sample preoxidized to give an oxide film 12 μm thick. (b) Sample pre-oxidized to give an oxide film 8 μm thick (× 1660).

reaction leading to a continuous but jagged interface. Under polarized illumination, the columnar oxide on both samples appeared red with yellow or white patches randomly dispersed throughout. However, other interfacial features appeared significantly different. At the Ni-oxide interface of sample A a dendritic intermediate phase (greyish-purple) had developed and extended well into the Ni layer whereas in sample B this interface was relatively smooth with some evidence of the intermediate phase as described for sample A. A transition diffusion zone characterized the oxide-substrate interface of both samples but again appeared different in nature when viewed at high power on the optical microscope. In sample A the transition zone consisted of a dark-brown oxide layer 1 to 2 μm thick exhibiting light-yellow spots of sub-oxide and below it a white sub-zone (Ni-rich layer as seen later) extending into the substrate. In sample B the white sub-zone (∼ 3 μm thick) dominated the transition zone (see Fig. 3b) although light-grey platelets of sub-oxide could be noticed at the base of the oxide film.

X-ray diffraction confirmed the presence of the intermediate phases which were detected early in the diffusion annealing period i.e. after 1h at 800°C. Following a 40 h anneal (and up to a total of 100 h so far investigated), no noticeable change could be detected at either of the interfaces using the present analytical techniques. Quantitative analysis of the reaction products is under way to assess systematically the interfacial reactions, however the values of the lattice parameters compiled so far indicate that the new phases, in general, correspond more closely to nickel tungstates ($NiWO_4$) than to nickel-tungsten compounds [12].

Fig. 4 shows a series of micrographs of sample B following a 40 h diffusion annealing, obtained with the scanning electron microscope and the microanalyser. These confirm the extent of a substantial Ni-diffuse layer at the oxide/substrate interface and also show the remarkable

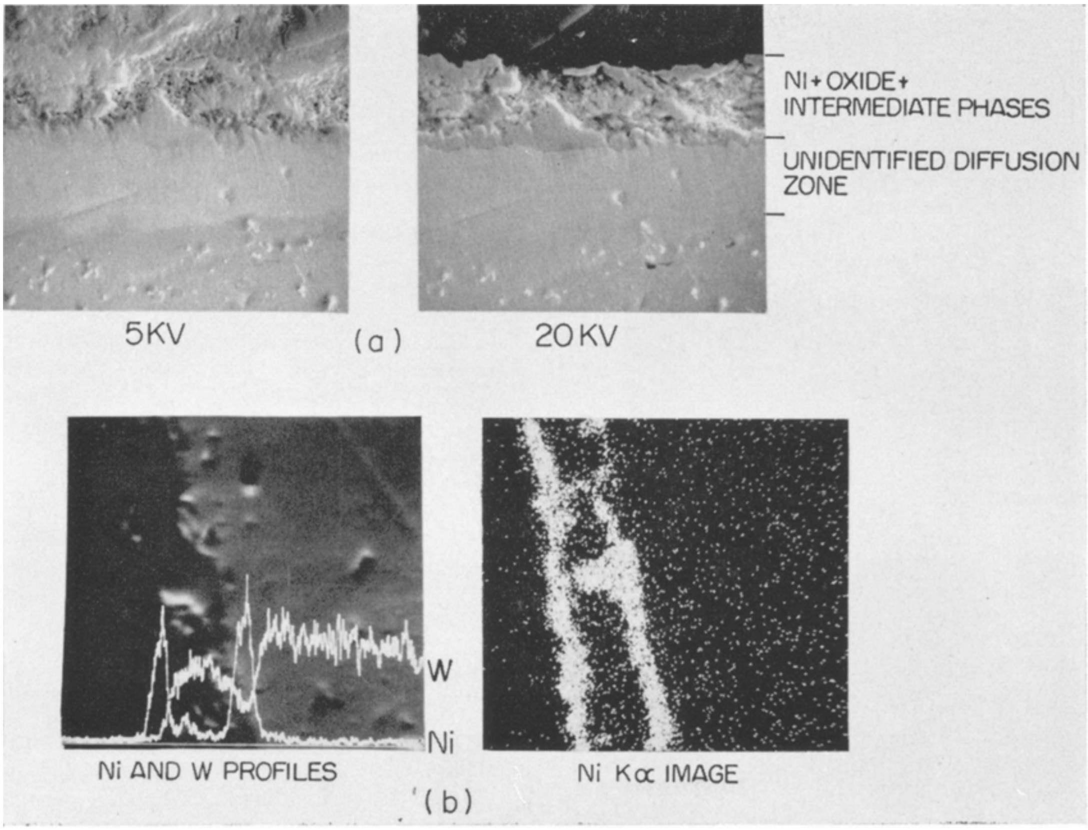

Figure 4 Scanning electron micrograph (a) and electron probe trace (b) showing interfacial continuity in Ni/oxide/W sample reacted at 800° C *in vacuo* for 40 h (approx. × 1500).

structural continuity at both interfaces. Upon increasing the SEM voltage from 2 to 20 kV, a wide contrast band appeared below the Ni-diffuse layer into the metal substrate. As no nickel is detected in this band it is possibly a polishing artifact associated with the depth of penetration of oxygen beyond the oxide/metal interface.

3.3. Interfacial tensile strength of the nickel/tungsten oxide

The coupons (2 × 1.3 × 0.3 cm^3) used in this test had been oxidized to produce an 8 μm thick oxide film, then were Ni-coated ($\sim$ 2 μm thick layer) and diffusion annealed at 800°C for 11 h. The microscopic reactions in these samples resembled closely those of sample B described in Section 3.2. The bond strength was measured in four separate runs and although in all cases between 80 and 90% of the separation was through the epoxy-adhesive the test established that the bond strength between either the Ni/oxide interface or the oxide scale itself was at least 4000 psi (28 MN m^{-2}). Microscopic examination of the separated oxide clearly revealed the sites of the intermediate phases and/or the nickel that connected the Ni-coating to the substrate as suggested by the Ni$K\alpha$ image (Fig. 4b).

3.4. Examination of diffusion-annealed nickel/oxide/tantalum

In contrast to the bulk process Ni/oxide reactions under Section 3.2 above, the interaction of nickel and tantalum oxide was confined to the Ni/oxide interface. Fig. 5 is a typical microscopic reaction and shows an optical micrograph/electron probe trace composite of a Ni-coated sample that had been heated *in vacuo* at 800°C for 8 h. The Ni$K\alpha$ signal in the probe scan shows a concentration plateau corresponding to the broad region of the intermediate phases at the Ni/oxide interface clearly revealed after etching (Fig. 5b). X-ray diffraction confirmed that the reaction products

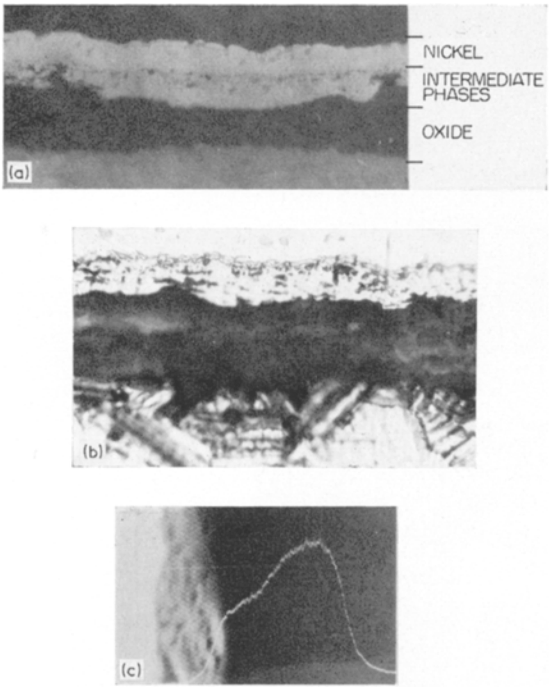

Figure 5 Diffusion annealed Ni/oxide/Ta sample, 800° C *in vacuo*, after 8 h. Optical micrographs (a) and (b) before and after etching respectively showing the gross reaction at the Ni-oxide interface (× 830). (c) Electron probe trace of Ni across the sample showing the broadness of the reaction zone at the Ni-oxide interface (approx. × 750).

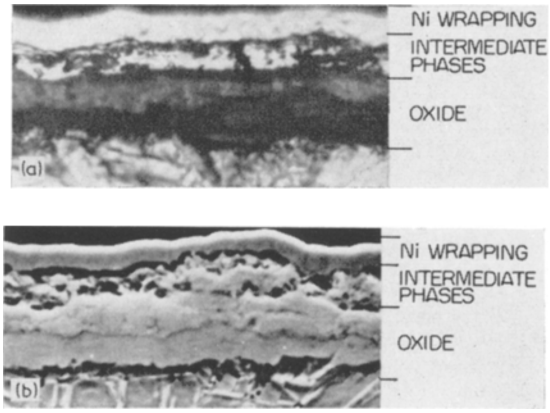

Figure 6 Optical (a) and scanning electron micrograph (b) of a reacted Ni/oxide/Ta sample emphasizing the substantial reaction at the Ni-oxide interface (× 830).

at the Ni/oxide interface were mostly the intermetallic Ni-Ta compounds that were obtained with a Ni/Ta diffusion couple with perhaps also a number of lines corresponding more closely to the composition $NiTa_2O_6$.

Fig. 6 shows the optical (a) and scanning electron (b) micrographs of a sample that had been coated with a thin Ni-layer (~ 2 μm) and reacted *in vacuo* at 750°C for 2.5 h. The thin nickel layer was intentionally applied in this case to allow the nickel to be completely consumed as a result of the reaction with the oxide film during a normal vacuum anneal. The reacted sample was subsequently Ni-plated again, before sectioning and polishing, to prevent mechanical surface damage and then etched to reveal the intermediate phase. Although porosity does appear to have developed in the reaction zone, the structural continuity is remarkable. The laminar appearance of the oxide film probably results from the stoichiometric variation across it. Certainly the dark oxide layers observed under semi-polarized illumination at both interfaces is indicative of hypostoichiometric Ta_2O_5 oxide [13].

4. Discussion

4.1. Reactions

There seems little doubt that the bonding of nickel to the oxide film of both tungsten and tantalum involved diffusion controlled chemical reactions. However, from the observations presented here, two types of reaction appear basically responsible for the formation of strong bonds. Type 1 reaction, common to both systems is a displacement reaction between the nickel coating and the oxide film leading to the formation of new phases at the Ni/oxide film interface and type 2, peculiar to tungsten, is controlled by the bulk diffusion of nickel through the compact tungsten-oxide film leading to the formation of a diffusion zone at the oxide/substrate interface.

Based on published thermodynamic data, the observed reactions at the Ni/oxide interface are energetically unfavourable in the temperature range investigated. Thus the reduction of the oxide film by the Ni-coating may not proceed unless an intermediate chemical step most likely associated with the non-stoichiometric behaviour of the oxide film is implicated. Present evidence from vacuum anneals conducted at 800°C for periods up to 100 h indicates that while type 1 reaction is time dependent and macroscopic in character producing an interface of compositional variations, type 2 reaction, though time-dependent initially, attains a steadystate equilibrium through the formation of a diffusion zone at the oxide-substrate interface. An analysis of the mechanism and kinetics of the two types of reactions is deferred to a succeeding paper.

4.2. Bond strength

If the complex oxide film interposed between the fibre and the matrix can provide greater chemical stability to the composite system it must not adversely affect the load transfer between composite components. In fact the bond strength (4000 psi minimum) estimated between nickel and pre-oxidized tungsten was found satisfactory for composite strengthening in an exploratory experiment. To check the validity of this strength value, a composite consisting of forty-eight tungsten wires (25 mm long × 0.3 mm diameter) compacted in nickel powder was prepared and fractured in tension. The tungsten wires (pre-oxidized and reacted with nickel as described in Section 3.2) were placed in commercially pure nickel powder (− 325 mesh) twelve in a layer in four alternate layers; these accounted for only about 0.5% of the total volume fraction. The composite was hot pressed at 600°C in an inert atmosphere for 2 h under an applied pressure of 8000 psi then consolidated by heating *in vacuo* at 800°C for 12 h.

Because of the relatively high porosity of the powder compact, the value of the fracture strength of the specimen has little practical significance, but the important result in this experiment is that most of the wires broke, showing that the stress transfer was adequate. Fig. 7 shows micrographs of the surface of the fractured specimen and an enlarged view of a broken wire.

Another important consideration in the development of fibre-reinforced materials is the mechanical compatibility of the composite components or thermal expansion effects. The average thermal coefficients of expansion (in. in.$^{-1}$°C^{-1} × 10^{-6}) for the proposed nickel-tungsten system at 700°C are respectively 15.5 (Ni), 17-18 along *a*- and *c*-axes and −1.3 in the *b*-axis (WO$_3$) and 5.2 (W). Thus on cooling from the consolidation temperature, no serious stresses are expected to develop at the Ni/oxide interface although residual tensile stresses will be induced in the tungsten wires.

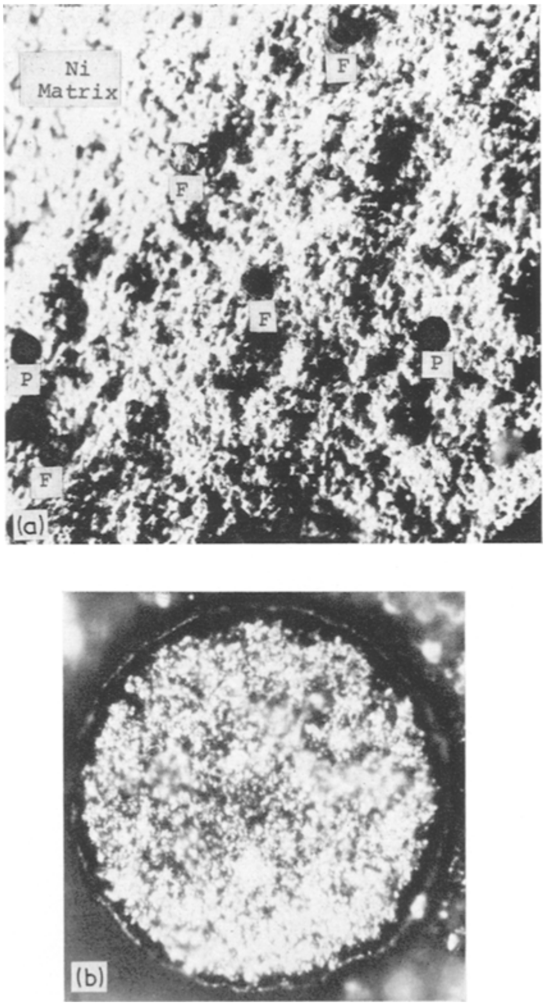

Figure 7 Optical micrographs of tensile fracture face showing (a) fractured (F) and pulled-out (P) tungsten wire (× 26), (b) enlargement of a fractured wire (× 280).

5. Conclusions

1. Nickel has been successfully deposited on and reacted with pre-oxidized tungsten and tantalum coupons and wires. The nickel-oxide film reactions are metallurgical in nature and lead to the formation of sufficiently strong bonds for composite strengthening.

2. Although the details of the reaction mechanisms may be extremely complex, it would appear that two types of reaction are involved. Type 1 constitutes a displacement reaction at the Ni/oxide film interface leading to the formation of new phases and type 2 is the bulk diffusion of Ni through the oxide film with the development of a diffusion zone at the oxide/substrate interface. The Ni/oxide/Ta interaction

is characterized by type 1 while the Ni-oxide/W interaction involved both types.

3. The chemical stability of the reacted Ni/oxide/W *in vacuo* at 800°C is remarkable and it has been attributed mainly to type 2 reaction.

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