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DEVELOPMENT OF OXIDATION-RESISTANT COATINGS FOR ZIRCONIUM ALLOYS

by

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ABSTRACT

This research report summarizes the results of a new experimental approach to the preparation of protective coatings for zirconium alloys. It consists in forming a diffusion-barrier type coating at the oxide film/environment interface which is remarkably stable in the temperature range of interest i.e. 5000-6000°C. This is achieved by reacting metal coatings such as nickel, copper, etc. with a pre-formed zirconia film on the alloys.

The report is divided into three parts: firstly, a brief description is presented of the "state of the art" of preparing metallic coatings that adhere strongly to the preoxidized metal; secondly, the interfacial reactions that lead to the chemical bonding of the metallic coatings to the oxide film are characterized; and thirdly the results are given of the oxidation tests that were performed to assess the protective ability of coatings applied on Zircaloy-2 by the various processes employed.


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Développement de revêtements résistant à l'oxydation pour les alliages de zirconium

par

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Résumé

Ce rapport de recherche analyse les résultats d'une nouvelle façon expérimentale d'aborder la préparation de revêtements protecteurs pour les alliages de zirconium. Elle consiste à former un revêtement du type barrière de diffusion à l'interface pellicule d'oxyde/environnement, lequel est remarquablement stable dans l'intervalle des températures présentant un intérêt, c'est-à-dire 500°-600°C. On obtient ce résultat en faisant réagir des revêtements métalliques comme le nickel, le cuivre, etc., avec une pellicule de zircone préformée sur les alliages.

Ce rapport comporte trois parties: premièrement, on donne une brève description de l'état actuel des connaissances dans la préparation des revêtements métalliques qui adhèrent fortement au métal pré-oxydé; deuxièmement, on caractérise les réactions interfaciales qui conduisent à la liaison chimique des revêtements métalliques sur la pellicule d'oxyde; et troisièmement, on donne les résultats d'essais d'oxydation effectués pour évaluer la capacité protectrice des revêtements appliqués sur du zircaloy 2 par les diverses méthodes employées.

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1. INTRODUCTION

1.1 Survey of the Problem

In general two approaches to the protection of any metal from oxidation may be followed: (a) the metal may be alloyed with additions of other metals which induce the oxide film, produced upon exposure, to be protective; or (b) a coating (e.g. diffusion coating, cladding) may be deposited on the metal to provide protection by limiting the access of oxygen to the substrate. Whichever approach is adopted the protection of the metal must be accomplished without altering greatly the desirable mechanical and physical properties (especially high temperature strength and ductility and also, in the case of zirconium, the macroscopic neutron-capture cross section) with which the base metal was originally endowed.

The first approach to protection, that of alloying, has been widely attempted and for high temperature zirconium alloys has, so far, been found wanting. While considerable improvements in oxidation behaviour have been effected by alloying zirconium it would appear that future developments may bring about only marginal improvements. Firstly, because for reasons of neutron economy, only limited amounts of alloying elements having high neutron capture cross sections can be tolerated, and secondly, because even a ten-fold improvement in the oxidation resistance of the presently available zirconium-based alloys would not permit any great degree of confidence in their utilization, without external protection, at temperatures of 500°C-600°C. In brief, at any sufficiently high temperature, where the present generation of high-strength zirconium alloys might remain attractive on the basis of their mechanical properties, no alloys are known with adequate inertness for practical use. The probability of developing such alloys by conventional methods may also be small.

Compared with the extensive research devoted to the elucidation of the mechanism of oxidation of zirconium and its alloys, relatively little effort has been directed towards the development of effective and practical high-temperature oxidation resistant coatings. A fair degree of success in providing adequate oxidation protection of zirconium and zirconium-copper alloys in carbon dioxide up to 650°C was obtained by French researchers with chromium diffusion coatings(4). However no development programme for coatings aimed at the protection of common alloys (e.g. the Zircaloy series) from rapid oxidation in more hostile environments, such as high temperature steam or air, is known.

The overall problem of producing satisfactory protective coatings for zirconium and its alloys may resolve itself into two principal areas. The first has to do primarily with the development of a protective coating composition which will combine with the substrate to form a compatible, useful composite system. The second portion of the problem entails the function of the coating which is to act as a barrier to prevent access
of oxygen to the substrate while itself remaining essentially unchanged throughout the duration of the exposure of the substrate to the aggressive environment.

Compatibility is often a serious problem in protective coating development. Firstly, the coating needs to accommodate itself to conditions of stress imposed by either mechanical or thermal loads and secondly, diffusional stability is an essential requirement, as gross reactions between coating and substrate would inevitably have deleterious effects on substrate mechanical properties. Still further criteria for measuring potential effectiveness of a prospective coating include the development of optimum, economical techniques for its application, which will ensure maximum reliability and preferably the exhibition of some self-healing characteristics in case of accidental damage during the processing and handling of coated parts.

1.2 Approach to the Problem

From the preceding survey it is apparent that the common approach followed in developing protective "diffusion-coatings" possesses serious drawbacks in that their processing is likely to affect the substrate mechanical properties and, because of their direct contact with and generally strong affinity for the substrate, they often lack the chemical stability over the times required at the operating temperature. A promising, although not yet completely practicable, scheme for protecting zirconium and its alloys and possibly the refractory metals is based on the reaction of protective coatings with pre-oxidized metals or alloys. This system can provide a "double-indemnity" protection, preventing both gross oxidation (because of the inherent oxidation resistance of metal coating selected) and substrate contamination via the presence of a barrier of oxide at the coating/substrate interface. The principles involved are the following: (a) the ZrO₂ film is metallurgically and thermophysically compatible with the substrate; (b) protective coatings having satisfactory matching properties can be bonded to the ZrO₂ film; (c) the interfacial reactions are minimal at the temperatures of interest as the composite-system involves an intermediate component with low reactivity.

The work described in this report is a summary of the results of several exploratory studies which have been undertaken to assess the potential of this approach to preparing high-temperature oxidation resistant coatings for zirconium and Zircaloy-2. The report is divided into three parts: in Part I, a brief description is presented of the "state of the art" of preparing metallic coatings that will adhere strongly to the preoxidized metal; in Part II, the interfacial reactions that lead to the chemical bonding of the metallic coatings to the oxide film are studied; Part III summarizes the results of the oxidation tests that were performed to assess the protective characteristics of the coatings utilized.
2. METHODS OF COATING PRE-OXIDIZED ZIRCONIUM ALLOYS

2.1 Sample Preparation

Samples of Zircaloy-2 and crystal bar zirconium (batches Bh or Bn, and Be respectively)* measuring 2 cm x 1 cm x 0.3 cm were cut from sheet stock with the long dimension parallel to the rolling direction. All corners and edges were rounded to a radius of about 0.5 cm to minimize edge effects during subsequent treatment of the samples. In addition, a limited number of paddle, spherical and disc shaped samples were utilized to facilitate certain coating procedures.

The surface preparation employed was the standard procedure of abrasion followed by pickling in a nitric/hydrofluoric acid bath. The samples were then weighed on a microbalance, annealed at 750°C for 1 hour in a vacuum of about 2 x 10^{-6} torr and oxidized in the same furnace system at between 550°C-600°C in commercially pure O_2 to produce oxide films of pre-determined thicknesses.

2.2 Coating Procedures

A variety of methods was employed to produce mainly coatings of nickel, aluminum, copper, chromium and nickel-aluminide on the pre-oxidized samples. These fall into three categories:

(i) electroless immersion treatments followed by electroplating,
(ii) physical and chemical vapour deposition,
(iii) plasma-arc spraying.

(a) Electroless Nickel and Copper Plating\[7-9\]

Electroless plating is an autocatalytic, selective reduction of metal ions at the surface of a catalytic substrate immersed in an aqueous solution. Non-catalytic substrates (e.g. oxidized zirconium) need to be activated before film deposition. Amongst the numerous formulations that have been developed for plating non-conductive materials, such as plastics and ceramics, the following solutions and procedures were adapted to plating our samples:

*The materials were supplied by Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada.*
The freshly oxidized samples were immersed for 20-30 sec. in a wetting agent; then successively immersed for 2 min. in a solution of stannous chloride followed by a solution of palladium chloride; the samples were well rinsed in deionized water after each immersion. The composition of the solutions for the activation process is listed in Table I. This treatment activated the zirconium oxide sufficiently for either Ni or Cu deposition to begin; once deposition started in the Electroless solutions, forming a metallic film on the substrate, it continued due to the auto-catalytic nature of the deposit.

Freshly activated substrates were immersed in Electroless nickel or copper solutions at a controlled temperature and pH value, and the time of deposition was used to adjust the film thickness. The compositions of the most successful solutions used are listed in Table II.

Metallic layers up to 1 \( \mu \)m thick adhered well to the oxide film, penetrating deeply into any cracks or large pores in the oxide. Thicker layers tended to crack and flake off due to residual growth stresses. The Electroless coatings proved to be too thin and porous to offer effective protection to the substrate on their own. However, they provided an excellent base upon which thicker and more protective coatings could be built, either electrolytically or by other processes.

(b) Electroless Aluminum Plating

This process is based on the use of a catalyst to decompose solvated aluminum hydride. Aluminum films were produced on pre-oxidized samples by employing three successive steps: 1) catalyst application, 2) aluminum hydride application, 3) decomposition in an oven. All operations had to be performed in a controlled atmosphere enclosure to exclude oxygen and moisture. Reference 10 gives the composition of the solutions that were used.

Although a good deal of effort went into adapting this process to our requirements, the quality of the films (i.e. uniformity, adherence and composition) fell far short of what is claimed in the literature; thus on the basis of our experience with oxidized samples this process is not recommended.

(c) Evaporated Films

Deposits of metallic films (Al, Cu, Cr and Mo) on pre-oxidized samples were achieved in a standard vacuum evaporator at a pressure of \( \approx 10^{-5} \) torr and in an ion-pumped stainless steel vacuum system at pressures better than \( 10^{-7} \) torr. In the former system the metals were vaporized in a heated tungsten boat, whereas in the latter they were evaporated by a 2 kW electron beam gun.
The primary advantages of this process are that multilayer coatings can be prepared and their thicknesses can be reasonably well controlled. The adherence of the films to the substrate, particularly those films prepared in the ultra-high vacuum system, compared well with the Electroless process. The uniformity of the films, however, could be poor unless care was taken to rotate the sample during the evaporation. To minimize this problem, disk-shaped samples, coated on one side only, were used to evaluate the protective ability of these films.

(d) Chemical Vapor Deposition(11,12)

Chemical vapor deposition, as a technique for preparing oxidation resistant coatings, has been investigated in a preliminary fashion. The objective was to compare the quality of chromium deposits on our pre-oxidized samples obtained from the thermal decomposition of chromium carbonyl (e.g. Cr(CO)_6) with those prepared by evaporation or by electro-deposition. The apparatus used for steady-state evaporation and carbonyl decomposition was basically that described in reference 12. One considerable drawback with this process was the embrittlement of the coating by small amounts of co-deposited carbon from a side reaction. While the feasibility of the method has been demonstrated, rather extensive investigation would be required to achieve process optimization and hence useful Cr-coatings.

(e) Electro-Deposition

Since the surface of the substrate must be conductive to permit electro-deposition, this process was always used in conjunction with Electroless plating. Single elements can be deposited on the substrate or several elements can be successively deposited in mechanically bonded layers. Nickel and nickel-chromium coatings 2 to 6 μm thick were formed on our pre-oxidized samples by electro-deposition in two solutions supplied by M & T Products of Canada Ltd.* Detailed information regarding the make-up, operation and control of the nickel and chromium plating solutions were obtained from the M & T technical data sheets P-C-323C and P-CF-520.

These baths were developed by the manufacturers to produce crack-free deposits and thereby to provide excellent corrosion protection to the substrate. However, it was found that both the

Ni and Cr deposits contained or developed pores upon exposure to the high temperature oxidation environment. It should be pointed out that the intrinsic porosity of the coatings has a far less deleterious effect during aqueous corrosion than during high-temperature oxidation. It has been observed that the corrosion of nickel plated metals occurs mainly at points where the external corroden has penetrated the coating rather than at the initially existing pores. As discussed later (Section 4) none of the electro-deposits produced on our samples was pore-free even though the directions for the plating processes were closely adhered to.

(f) Plasma-Sprayed Coatings

For the application of metal or ceramic coatings by the technique of plasma spraying a standard plasma spray gun and associated auxiliary equipment was used. Nickel-aluminide coatings were produced by an exothermic reaction using powders (Metco 404 or Cerac 1431) with a particle size 40-80 μm. Argon or nitrogen were used as the arc stabilizing gas while nitrogen was employed for powder transport. The powder was delivered to the torch via a Sylo fine-powder feeder whose feed screw had an adjustable-speed drive for accurate metering of the fine powder. The powder was introduced into the plasma stream through a port located at a distance of about 5 mm from the nozzle outlet and inclined at an angle of 5° against the direction of travel of the gas stream. The sample was rotated during the spraying operation to ensure an even coating.

The operating conditions of the spray gun (e.g. arc power, arc gas flow rate, torch to sample distance) were optimized empirically to achieve the highest density of deposit, as determined by metallographic techniques. The following settings gave the best results:

- Arc power: 400-450 amps at 40 volts
- Torch-sample distance: 7 to 10 centimeters
- Arc gas flow (Ar): 150 cubic feet per hour
- Powder feed: 13 on the feed control indicator dial.

*The equipment - Thermal Dynamics F40 plasma torch - was loaned by the Chalk River Nuclear Laboratories.*
Efforts to produce useful ceramic coatings (e.g. $\text{Al}_2\text{O}_3$) were discontinued as they generally exhibited unacceptable microscopic porosity.

In summary, of the various methods that were employed to produce metallic coatings on preoxidized samples of zirconium alloys, the Ni-Electroless immersion followed by nickel electropolating apparently offers the greatest potential for development. As discussed in Section 3 of this report, once the nickel layer has been metallurgically reacted with the oxide film any of the conventional application methods can be subsequently used (e.g. hot dipping, pack cementation). The plasma-spraying technique also shows promise for preparing coatings tailored for specific thermal and chemical properties if the microscopic pores in these could be sealed by either an infiltration process or the use of composite powders. In any future studies these aspects should be emphasized.

3. METAL-COATING/OXIDE FILM INTERACTION

The compatibility of the metal coating with the preoxidized sample includes the chemical interactions at both interfaces i.e. coating/oxide film/substrate and any mechanical effects such as thermal expansion mismatch between the layers of the composite. When considering the chemical stability of selected metal/zirconia systems, one normally relies on the thermodynamics as a starting point from which to predict any possible reactions. Metals which could reduce zirconia at elevated temperatures would have free energy changes ($\Delta F$) for reaction that are negative or close to zero. The nickel/zirconia system, for example has at 800°C, a high positive value for $\Delta F$, indicating considerable thermal stability since the reaction

$$2\text{Ni} + \text{ZrO}_2 \rightleftharpoons 2\text{NiO} + \text{Zr}$$

lies strongly to the left.

As Moore has shown (13), the formation of NiAl$_2$O$_4$ at the interface of the Al$_2$O$_3$/Ni system demonstrates one of the limitations of this approach. Similarly the reaction of titanium and Al$_2$O$_3$ shown as

$$3\text{Ti} + \text{Al}_2\text{O}_3 \rightleftharpoons 3\text{TiO} + 2\text{Al}$$

would not account for the formation of Ti$_3$Al which has been identified as a major reaction product(14). Other types of ceramic-metal reactions that lead to the formation of very strong bonds(15,16) have also been reported. On the basis of these unfamiliar solid-phase reactions, the results of the interaction between the zirconia film of the preoxidized samples and the metal coatings which are presented in this section should not, therefore, be completely unexpected.
3.1 Experimental Procedure

With the exception of the Al-coated samples which were tested for their oxidation resistance immediately after coating, the freshly coated samples were heat-treated in a vacuum of about $10^{-6}$ torr at 800°C for periods of 0.5 to 20 hr. depending on the thickness of the zirconia film grown on the sample prior to coating. The heat-treatment was programmed by means of a slowly rotating cam linked to the control set point of a Barber-C"r manifold temperature controller. The normal operating cycle consisted of a 5.0 hr. heating period followed by 0.5 hr. soaking at 800°C then about a 6 hr. cooling period to room temperature.

Metallography, X-ray diffraction and to a lesser extent scanning electron microscopy and electron microprobe analysis were the techniques used to follow the interfacial reactions resulting from the diffusion anneals.

3.2 Observations

In the first phase of this study a qualitative assessment of the nature of the chemical reaction between nickel coatings and preoxidized samples of zirconium and Zircaloy-2 was made from metallographic observations.

3.2.1 Interfacial Reactions

Micrographs of cross sections of a zirconium sample following various stages of annealing are shown in Figure 1. The oxide film thickness on this sample was an average of 9 μm prior to nickel coating. Following the first annealing cycle little interfacial change could be detected with the optical microscope; however subsequent anneals up to 5 cycles promoted gross reactions between the nickel layer and the zirconium oxide film. With advancing annealing time disintegration of the zirconia into lamellar oxide and a nickel compound appeared to take place. Simultaneously a diffusion zone, which was well resolved by etching in the standard pickling solution, developed at the oxide/substrate interface.

In contrast to the microscopic features described above, the interfacial reaction between the nickel layer and the oxide films (in the thickness range 3-9 μm) on Zircaloy-2 was confined to the Ni/zirconia film interface as shown in Figure 2. The growth rate of the product of the reaction is indicated in Figure 3 which shows a series of micrographs of cross sections of a sample (pre-oxidized to give an average 4 μm thick oxide film and then nickel coated) taken after 1, 2 and 6 annealing cycles. Although the oxide film thickness has decreased appreciably (due to reactions at both interfaces) little thinning has occurred between the second and the sixth annealing cycles. The hard diffusion zone observed at the oxide/substrate interface in the case of zirconium was not so prominent
with Zircaloy-2.

The rate at which the reaction products developed also appeared to depend strongly on the state of the oxide film, i.e. the degree of substoichiometry. For example, a thin oxide film (~3 μm) in the pre-transition state reacted strongly with the nickel coating during 1 annealing cycle, whereas several cycles were required to initiate a reaction between the nickel coating and a thick post-transition oxide film (20-25 μm). Therefore, a pre-oxidized sample which showed a variation in the oxide film thickness similarly exhibited a variation in the development of the Ni/zirconia reaction product. Micrographs in Figure 4 illustrate this phenomenon by showing two areas on the same sample which revealed different reaction features after 6 annealing cycles. Initially the oxide film thickness varied between 18 and 25 μm and was porous. It appears that the Ni/zirconia reaction has started in the thinner areas of the oxide film (Figure 4a); whereas, in the area where the oxide was thicker (e.g. corner of the sample) and cracked, the reaction began internally (Figure 4b) due to the fact that nickel infiltrated the oxide film during the Ni-Electroless immersion part of the preparation of the nickel coating.

3.2.2 Effect of ZrO₂ Stoichiometry

To establish whether the reaction between nickel and zirconia at 800°C was truly associated with the deviation from stoichiometry of the oxide film, or was purely a natural solid-state reaction such as has been reported for other systems (e.g. BeO/Ni/BeO, Al₂O₃/Ni/Al₂O₃, etc.)

at elevated temperature (above 1000°C), a Ni/ZrO₂/Ni couple was prepared in the following way. A pre-oxidized Zircaloy-2 sample (oxide thickness about 9 μm) was Ni-coated and reacted 2 hours at 800°C in vacuo. The sectioned and metallographically prepared sample revealed a thin reaction band at the Ni-zirconium oxide interface. The oxide film on one side of the sample was stripped by polishing away the metal substrate first mechanically and then chemically in a dilute pickling solution. The bare-side of the oxide film was nickel coated in the usual way thus producing a Ni/ZrO₂/Ni couple, in which one of the interfaces (that of the original oxide surface) had already acquired a thin reaction zone as a result of the first anneal. The couple was then heated in vacuo at 800°C for 16 hr., i.e. an annealing period that would normally produce gross interfacial reactions.

Figure 5 shows an oblique view of the metallographically prepared couple with the optical microscope and the scanning electron
microscope. At the original Ni/zirconia interface (smooth) a thin reaction zone can be seen (Figure 5a) which appears to be unchanged by the subsequent long anneal; at the other Ni/zirconia interface (wavy) no obvious reaction product can be seen. The SEM picture (Figure 5b) confirmed these observations. Thus, one may infer from these results that the degree of chemical activity of the ZrO$_2$ film is reduced considerably by separation from its metal substrate; thus the reactivity must be a consequence of its non-stoichiometric nature when heated in vacuo in contact with the metal.

### 3.3 Identification of the Reaction Products

At the present time an incomplete picture of the reaction products of nickel (or other metallic coatings) with zirconia films still prevails. In conjunction with the metallographic observations under Section 3.2, surface X-ray diffraction analysis of the samples with metallic coatings was generally carried out, and in a few instances electron probe traces were run across the interfaces. The results of these analyses provided sufficient information to identify (at least qualitatively) the main compound formed, gave some indication on its distribution across the interfaces but gave very little information about the kinetics.

#### 3.3.1 X-Ray Diffraction Analyses

The main reaction product in all of the reacted metal coated preoxidized samples consisted of an intermetallic MZr$_x$ (M being the coating element). Intermediate phases of less importance (quantitatively) were observed but have not been identified unambiguously. Very complex diffraction patterns evolved with prolonged heat treatment in vacuo of copper coated samples and with nickel coated samples heat-treated in oxygen partial pressures of $\sim 10^{-3}$ torr. Quantitative microprobe analyses of the intermediate phases forming under various conditions at the Ni/ZrO$_2$ film/substrate interfaces are currently under investigation and the results will be reported in a later paper.

In addition to phase identification, the X-ray analyses were extremely valuable in determining the time of initiation of the reaction between the coating and the ZrO$_2$ film, as well as the extent of development of the intermediate phases during annealing. Figure 6 gives plots of the relative X-ray intensity for the intermetallic Ni-Zr, and Ni as a function of annealing time for three Zircaloy-2 samples preoxidized to give oxide films, 3, 7 and 25 μm thick and identically nickel coated. The effect of the state of the oxide film upon the beginning of the reaction is again clearly demonstrated, Figure 6a. It is also worth pointing out that the migration of nickel (as revealed by the decrease in intensity in Figure 6b) into the thickest oxide is significant even though the reaction products
were not detected until late in the annealing period. This may be explained by the fact that the Ni-zirconia reaction has taken place internally in layers of oxide which have attained some critical value of substoichiometry but are too deep in the oxide film for the X-rays to penetrate to them.

3.3.2 Penetration of the Nickel-Coating into the Oxide Film

It was described earlier (see Section 3.3.1) that nickel coated samples of zirconium and Zircaloy-2 presented, following similar annealing periods, quite different morphological arrangements of the Ni/ZrO\(_2\) film reaction products. While the chemical reaction appeared to be confined to the Ni/zirconia interface in the case of Zircaloy-2, the oxide on zirconium was breaking up with the apparent penetration of nickel into the oxide.

Nickel profiles were examined across the interfaces of the reacted samples using the electron microprobe analyser. It was operated with an accelerating voltage of 25 kV and a specimen current of \(\sim 0.1\) A. The beam resolution was \(\sim 0.8\) \(\mu\)m and the rate of transverse was 12 \(\mu\)m min\(^{-1}\). The results shown in Figure 7 indicate that the nickel coating on the zirconium sample (optical micrographs shown in Figure 1e) penetrated through the oxide resulting in a high nickel concentration at the oxide/substrate interface. The nickel penetration into the oxide film on Zircaloy-2 appeared to be relatively shallow (Figure 7b), exception for porous oxide films in which the intermediate phases were also detected in isolated pockets within the oxide. However, in none of the Zircaloy-2 samples examined so far have we detected nickel, above the concentration level normally found in this alloy, at the oxide/substrate interface.

3.3.3 Chemical Stability of the Ni/ZrO\(_2\) Film in Vacuo

It is now apparent that the formation of a diffusion zone at the coating-oxide interface can be initiated rapidly by heating in vacuo at 800°C. One of the objectives of this study was to assess the chemical stability of the Ni/ZrO\(_2\)/substrate complex at a temperature of practical interest, e.g., 600°C.

A Zircaloy-2 sample preoxidized to give, on average, a 8 \(\mu\)m thick oxide film and nickel coated, was first diffusion annealed for 1 hr. at 800°C then held at 600°C in vacuo for 250 hrs. During this time the sample was cooled down at regular intervals to assess the progress of the reactions at both interfaces. Neither surface X-ray analyses nor metallography showed any evidence for changes in either the amount of the intermediate phases or in the oxide film thickness. Based on values of the oxygen diffusion coefficient in zirconium\(^{17,18}\) and the time the sample was held in vacuo at the two temperatures one would have expected complete dissolution of the oxide film following the two annealing periods. Figure 8 shows an electron probe trace/
optical micrograph composite of the sectioned sample after 42 hr. and 250 hr. at 600°C. It can be seen that during this interval no significant changes occurred either metallographically or for diffusion of nickel into the oxide.

3.4 Summary

There seems to be little doubt that the bonding of metal coatings to the oxide films on zirconium and Zircaloy-2 is a bulk process involving diffusion controlled chemical reactions. The reaction products and the processes underlying their formation appear to be basically the same for both types of samples although the morphological arrangement of the intermediate phases differs.

Evidence was obtained that the chemical reactions are promoted by an increasing degree of sub-stoichiometry in the zirconia film. Since on thermodynamic grounds the chemical interaction between the metal coatings and the zirconia film could not be predicted, our knowledge about the non-stoichiometric behaviour in zirconia must be broadened if a basis for understanding the details of the possibly extremely complex reactions is to be found.

The chemical stability of a reacted Ni/ZrO₂/Zircaloy-2 composite at 600°C in vacuo appears excellent by comparison with uncoated preoxidized Zircaloy-2. Although no explanation of this is offered at the present time, the phenomenon may be associated with the strong interaction between Ni atoms and O atoms in the interstitial sublattice at the inner interface. The build-up of a nickel layer at this interface in reacted Ni/ZrO₂/Zirconium composites suggests that this could be a plausible explanation.

4. OXIDATION RESISTANCE OF COATED ZIRCALOY-2

In the light of the results presented in Section 3 it would appear that some of the major requirements in the development of effective high temperature coatings for Zircaloy-2 have been achieved to a reasonable degree; i.e., both the adherence of the metal coatings to the oxidized substrate, and the chemical stability of the system were found to be acceptable. It must be emphasized however that unless the protective coating built onto the preoxidized substrate is impermeable to oxygen or other corrosive media, the system may have little practical value. The intermetallic (or intermediate) phases which develop at the coating/zirconia film interface at reasonably high temperature and in extremely high vacuo (e.g. the O₂ partial pressure at the coating/oxide film is probably equal to the equilibrium partial pressure over ZrO₂ at the inner interface) may chemically be reactive in the presence of oxygen. In evaluating the true effectiveness of a coating, therefore, penetration
or breakdown of the coating rather than weight gain were often found to represent more realistic indicators.

4.1 Experimental Procedure

Zircaloy-2 samples preoxidized to give oxide films 2 to 25 μm thick were coated with either single element (e.g., Ni, Al coatings) or multi-layered coatings (e.g., Ni-Cr, Cu-Al and nickel aluminide) using one or a combination of the application techniques described in Section 2. With the exception of the aluminum coating, the coated samples were given a diffusion anneal prior to the oxidation test. Oxidation was carried out in commercially pure tank oxygen at pressure of about 100 torr in the temperature range 500°-600°C.

A disconcerting feature of the oxidized, coated samples was the formation of surface pustules at weak spots in the coatings. These caused enhanced oxide growth beneath the coating and consequently invalidated much of the weight-gain data. The protective ability offered by the coatings was therefore assessed by either weight gain (whenever appropriate) and microscopic examination at various stages of oxidation or by X-ray diffraction analysis of the coated samples (disc-shaped) oxidized in situ on the diffractometer in a hot stage X-ray chamber(19). Continuous analyses could then be made of the interfacial reactions and the oxide growth rate beneath the coating, by following the increase in peak intensities of the (202) and the (104) lines of monoclinic zirconia as a function of the oxidation time.

4.2 Results

Typical oxidation results with samples that were coated by the various processes described in Section 2 are given in Table III. In most cases the oxidation test was terminated because of either the detection of a sudden, rapid increase in weight gain of the sample or the appearance of surface pustules.

The nickel coatings (e.g., A.5) offered fairly good protection to the samples, which exhibited accelerated weight gains only at the end of the oxidation period, due to the nearly complete conversion of the nickel coating into nickel oxide as shown in Figure 9. The thickness of the ZrO₂ layer varied between 3 and 5 μm which should be compared with an estimated oxide film thickness of around 40 μm on uncoated Zircaloy-2 oxidized under similar conditions(20). The Ni-Cr coating (e.g., A.6) provided some protection but appeared to be more susceptible to breakdown than the simple Ni coating. Figure 10 shows two photomicrographs of the sectioned sample illustrating (respectively) sound and failed areas of the coating. The thickness of the ZrO₂ layer on this sample varied from a few to many microns. The oxidation of a further Ni-Cr coated specimen was followed on the diffractometer (Figure 11).
The oxidation resistance of the aluminum coated samples (with the exception of the plasma-sprayed samples) was determined "in situ" on the diffractometer by following the development of the (204) and (102) diffraction intensities of the monoclinic ZrO$_2$ layer underneath the coating. The linear absorption of CuK$_{\alpha}$ in zirconia however limits this type of analysis to oxide layers of less than about 10 $\mu$m thick (not including the coating). The effectiveness of the aluminum coating was considered to be inferior to the others; the end of the useful life of this coating coincided with the nucleation of an AlZr intermetallics at the Al/ZrO$_2$ interface. This occurred, in contrast to other coatings, at the temperature of oxidation (e.g. 550°C). The sample (B.5) oxidized to give a thick oxide film prior to coating with aluminum showed much better oxidation resistance. Although this sample showed no sign of coating degradation after 270 hr. exposure to O$_2$ at 550°C, the intermetallics nevertheless gradually developed around 200 hrs.

As suggested by the oxidation results in Table III and the graphs in Figure 12, the Al, Al-Al$_2$O$_3$ and Al-Ni plasma-sprayed coatings provided only marginal protection to the substrate. Attempts to use undercoats (e.g., C.5) and sealers (e.g., C.1) to prevent oxygen from penetrating through the microscopic pores of the plasma-sprayed coatings produced only marginal improvements.

4.3 Summary

Disregarding, at this stage of development, the coating defects that were detrimental to the long-term oxidation resistance of the coated samples, the short-term oxidation behaviour of these composites showed a marked improvement over uncoated Zircaloy-2 oxidized under similar conditions.

The aluminum coating appeared to be the least effective in the protection of oxidized substrates as an AlZr intermetallics formed at the temperature of oxidation and caused the coating to degrade rapidly. This is in contrast to the nickel coated samples which were chemically stable at the temperature of oxidation as long as there was no oxygen ingress through the coating.

Long-term improvements can reasonably be anticipated on the premise that further development of the coating processes will provide us with coatings which are flawless and thermally matched to the substrate.

5. ACKNOWLEDGEMENTS

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REFERENCES


11. L.W. Owen, Electroplating and Metal Finishing, 17 (1964) 296.


TABLE I

Composition of Solutions used for Activation of Preoxidized Samples

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Constituents</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-Flow 200 (wetting agent)</td>
<td></td>
<td>0.5 cc/l</td>
</tr>
<tr>
<td>Sn Cl₂ (sensitizer Soln.)</td>
<td>Sn Cl₂</td>
<td>0.1 g/l</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>0.1 cc/l</td>
</tr>
<tr>
<td>Rinse in deionized H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd Cl₂ (Activator Soln.)</td>
<td>PdCl₂</td>
<td>0.1 g/l</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>0.1 cc/l</td>
</tr>
<tr>
<td>Rinse in deionized H₂O</td>
<td></td>
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</tbody>
</table>

TABLE II

Electroless Ni and Cu Solutions

<table>
<thead>
<tr>
<th>Nickel Bath</th>
<th>Copper Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactic acid: 90.08 cc/l of H₂O</td>
<td>Copper sulphate (anhydrous): 3.60 g/l</td>
</tr>
<tr>
<td>Stannic chloride: 35.06 g/l</td>
<td>Sodium hydroxide: 3.75 g/l</td>
</tr>
<tr>
<td>Nickel sulphate: 26.29 g/l</td>
<td>Sodium potassium tartrate: 25 g/l</td>
</tr>
<tr>
<td></td>
<td>(Tetrahydrate)</td>
</tr>
<tr>
<td>Sodium hypophosphite: 63.59 g/l</td>
<td>Formaldehyde (35-40%): 10 cc/l</td>
</tr>
<tr>
<td>Solution Temp., °C: 85 ± 2°C</td>
<td>Solution temp. °C: 70-75°C</td>
</tr>
<tr>
<td>pH (adjusted with NaOH) = 5.5</td>
<td>pH (adjusted with H₂SO₄) 7.0</td>
</tr>
<tr>
<td>Test No.</td>
<td>ZrO$_2$ Film (Pre-Oxidation) Thickness (μm)</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>A.5</td>
<td>~4.5</td>
</tr>
<tr>
<td>A.6</td>
<td>4</td>
</tr>
<tr>
<td>A.10</td>
<td>2</td>
</tr>
<tr>
<td>A.11</td>
<td>2</td>
</tr>
<tr>
<td>B.2</td>
<td>7</td>
</tr>
<tr>
<td>B.4</td>
<td>2</td>
</tr>
<tr>
<td>B.5</td>
<td>25</td>
</tr>
<tr>
<td>C.1</td>
<td>3</td>
</tr>
<tr>
<td>C.2</td>
<td>3</td>
</tr>
<tr>
<td>C.5</td>
<td>5</td>
</tr>
</tbody>
</table>

*(E) Electroless; (ED) electrodeposition; (M) vacuum deposition; (P) plasma spraying
AFTER TWO ANNEALING CYCLES

AFTER FOUR ANNEALING CYCLES

AFTER FIVE ANNEALING CYCLES

A - Ni coating  B - zirconia layer  C - diffusion zone  D - substrate

FIGURE 1 Cross-sectional appearance of nickel coated zirconium with increasing annealing time at 800°C. (a) and (b) 1 hr.; (c) and (d) 2 hr.; (e) and (f) 2.5 hr.
FIGURE 2  Cross-sectional appearance of nickel coated Zircaloy-2 after 6 annealing cycles (3 hr.) at 800°C. Note that the reaction Ni/ZrO₂ appear confined to the coating/oxide film interface.

A - nickel coating; B - reacted layer; C - zirconia layer; D - substrate
FIGURE 3 Nickel coated Zircaloy-2 sample showing the progress of the reaction at the Ni/ZrO\textsubscript{2} interface after various annealing periods at 800°C (a) 0.5 hr; (b) 1 hr; (c) 3 hr.
FIGURE 4  Two areas of the same sample after 3 hr. annealing at 800°C, showing the beginning of the Ni/ZrO₂ reaction at the interface (a) and within the oxide (b) due to the penetration of the Ni-Electroless coating. The original oxide film (18-25 μm thick) was porous.
FIGURE 5 Optical micrograph (a) and SEM (b) of an Ni/ZrO$_2$/Ni couple. Heated in vacuo at 800°C for 16 hr. The thin reaction zone observed at the outer Ni/ZrO$_2$ interface had formed prior to stripping the ZrO$_2$ film from its substrate.
FIGURE 6  Variation of the reaction product (NiZr) and Ni diffraction lines with annealing time at 800°C. The effect of oxide film thickness on the start of the reaction is indicative of the state of the oxide.
FIGURE 7  Penetration of nickel into the oxide film on (a) zirconium and (b) Zircaloy-2. Top left - Electron image of sample as in Figure 1(e) x 3000. Top right - optical micrograph of Zircaloy-2 sample after 4 hr. vacuum anneal at 800°C x 1000. Bottom photos; Left - nickel profile across the interfaces Ni/ZrO$_2$/Zr x 3000. Right - Electron image and superimposed nickel profile across the interfaces Ni/ZrO$_2$/Zircaloy-2 x 3000.
FIGURE 8  Coated Zircaloy-2 sample vacuum annealed at 800°C for 1 hr. then heated at 600°C in vacuo for 250 hr. Observations after (a) 42 hr. (b) 250 hr. revealed chemical stability of the Ni/ZrO₂/substrate at 600°C.
FIGURE 9  Cross section of nickel coated Zircaloy-2 sample (A.5) after oxidation at 600°C for 72 hr. NOTE the nickel coating was partly converted into its oxide.

FIGURE 10  Cross section of (duplex) Ni-Cr coated Zircaloy- sample (A.6) after oxidation at 575°C for 150 hr. (a) good area of the sample showing sound and protective coating; (b) breakthrough in the coating that led to rapid growth of the ZrO$_2$ layer.
FIGURE 11 X-ray analysis of Zircaloy-2 samples oxidized "in situ" on the diffractometer. (a) Oxidation of uncoated sample at 500°C (b) Oxidation of Ni-Cr coated sample at 580°C. The variation of the (10$\bar{4}$) and (20$\bar{2}$) line intensities of monoclinic ZrO$_2$ as a function of oxidation time is used in estimating the extent of oxide film thickening.
Comparison of oxidation kinetics of aluminum coated and uncoated Zircaloy-2 samples at 500°C.