Title

INTERACTIONS BETWEEN COATINGS AND SUBSTRATES AT ELEVATED TEMPERATURES

Authors

Whittle, D.P.
Boone, D.H.

Publication Date

1981-08-01

LBL-13350

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

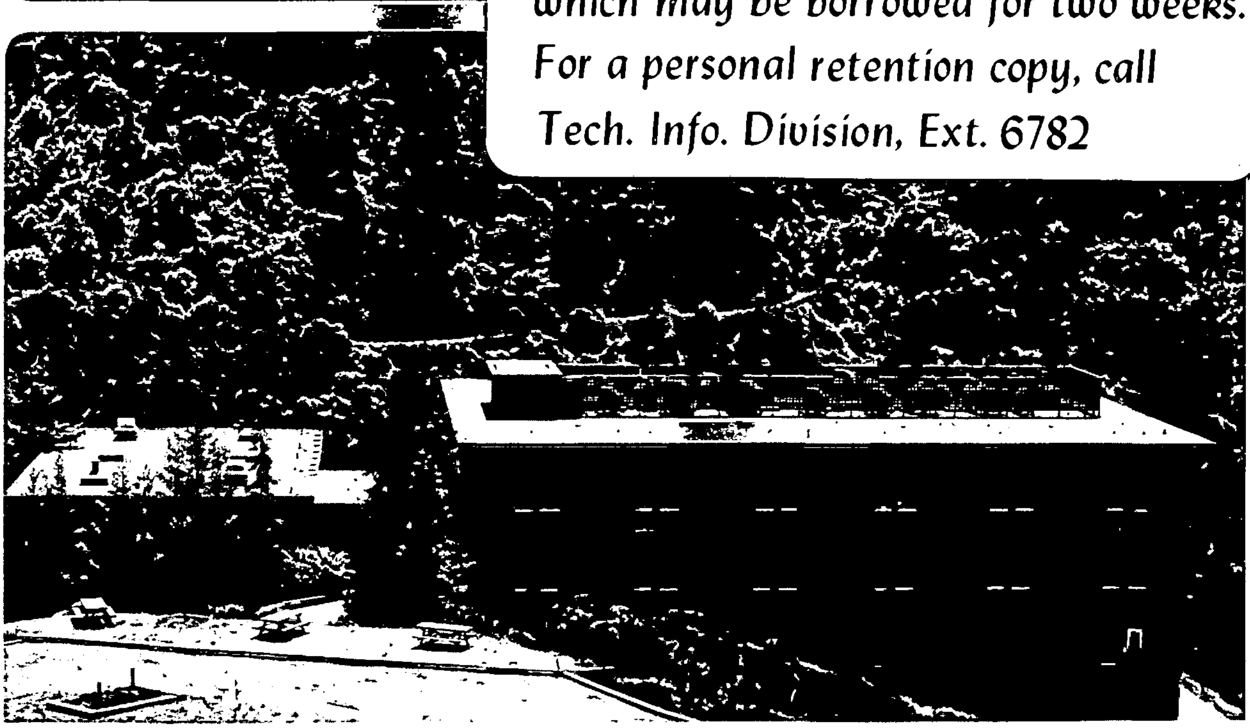
Materials & Molecular Research Division

Presented at the Second Conference on Advanced Materials for Alternative Fuel Capable Heat Engines, Naval Postgraduate School, Monterey, CA, August 24-28, 1981

INTERACTIONS BETWEEN COATINGS AND SUBSTRATES AT ELEVATED TEMPERATURES

D.P. Whittle and D.H. Boone

August 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

INTERACTIONS BETWEEN COATINGS AND SUBSTRATES AT ELEVATED TEMPERATURES

by

D. P. Whittle
D. H. Boone

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

INTRODUCTION

The durability of directly fired heat engines operated on minimally processed coal-derived liquid fuels is expected to be dependent on the surface stability of combustion zone components. From previous experience with gas turbine engines burning highly refined fuels in both clean environments such as experienced in air-craft propulsion, as well as in marine and industrial environments where a variety of types and levels of contaminants are present, it was found that the use of some type of protective coating is mandatory. As a result, three principal types of protective coatings have developed: diffusion aluminide coatings in the early fifties, overlay-type coatings in the sixties and finally, the recent, ceramic or thermal barrier coatings. At first sight, this order of development also represents what might be anticipated to be an increasing independence of the substrate, and indeed this was one of the driving forces in the evolution of newer coatings. As the superally substrates became stronger and more complex, and in the process less corrosion resistant, their ability to provide beneficial elements and "coatability" to diffusion-type coating systems was drastically reduced. Nevertheless, as discussed in what follows, it is slowly being realized that overlay coatings, particularly metallic overlays and probably also the ceramic thermal barrier-types are far from independent of the substrate, and there is a real need to understand the type and extent of interactions which can occur. In essence, it is now no longer possible to develop superalloy substrate compositions independently of consideration of the need to apply a coating.

This paper then examines the three major types of coatings - diffusion aluminide, overlay and thermal barrier coatings, and in particular concentrates on the effects of substrate elements interferring with or enhancing the corrosion resistance properties of the coating. The effects of coating elements diffusing into the substrate and influencing its mechanical properties are not considered.

DIFFUSION ALUMINIDE COATINGS

Diffusion aluminide coatings are produced principally via a pack cementation process. The extent of substrate interaction depends critically on the process used and two types have been identified (1): 'inward' and 'outward' coatings formed in high and low Al activity packs respectively. The inward, and to a lesser extent the outward, type coating has an external zone which is strongly dependent on the initial substrate. This is a significant feature that can both improve or degrade the oxidation and hot corrosion resistance. For example, the MC-type carbides of the base alloy often extend out to the coating surface providing the origin for defects which can favor the local oxidation of the coating. In addition, loss in nickel from the substrate to the coating can result in σ-phase formation. Improvements in the protectivity of simple aluminides can sometimes be achieved via some form of pretreatment. For example, the adverse effect of titanium from the substrate interferring with protective oxide formation can sometimes be avoided by depositing a 15-30 μm of a nickel-base alloy on the component prior to aluminizing (2).

In a more positive sense, however, addition of elements such as chromium or noble metals like platinum are considered. While the level of chromium enrichment which can be achieved is limited, enrichment of the substrate in chromium followed by a separate or sequential inward aluminizing step can result in enhanced hot corrosion resistance, particularly in the low and intermediate temperature regime. An alternative method of introducing chromium into aluminide-type coatings involves the incorporation of chromium-rich particles from the pack using a low aluminum activity pack, and hence an outward growing aluminide. However, it is difficult to control the inclusion mechanism, since the quantity of chromium-rich particles included depends on the quality of the pack-component contact.

The incorporation of platinum or possibly other noble metals by predepositing 5-10μm of Pt prior to aluminizing, either via a high or low activity process leads to coatings of excellent quality. Lifetime improvements, particularly in the intermediate temperature range, 800-1000°C, can be achieved.

The mechanism by which chromium and platinum improve the protectivity of the simple aluminides is not well understood, but is being related to their effect on the structure and behavior of the initial Al_2O_3 layer which forms on exposure to an oxidizing environment. Using a deep etching technique, which selectively removes the coating, allows direct examination of the underside of the surface oxide at its interface with the coating. Figure 1 shows a typical example of the underside of an Al_2O_3 scale formed in 100 h at 1000°C on a platinum-modified coating on IN 738. Comparison with other systems, and at various stages of exposure indicates that one difference is the much finer Al_2O_3 grain size found on the platinum modified aluminide. Studies are continuing.

Currently, there is also considerable interest in active element additions to aluminide coatings, similar to those in overlay coatings. Again, one route to achieve this, is via additions to the substrate. It has been reported (3) that Hf diffusing from the substrate alloy to the coating was responsible for the improvement in oxidation resistance of Rene 125 over Rene 80. Recent work on aluminized IN 738 containing different levels of Hf indicates that indeed the active element can have an effect on the coating behavior, but that this again depends on the type of aluminide coating (4).

Aluminide coating of more advanced alloy substrates, such as directionally solidified and oxide dispersion strengthened alloys produces additional problems. The development of unwanted porosity between coating and substrate is often observed. Recent studies with oxide dispersion strengthened alloys (5) have indicated coating void formation and the resulting spallation occurs primarily in the coating inner zone and is delayed, but not prevented, by a larger more dispersed zone produced by outward type coatings on high aluminum content alloys. In addition, the thickness and structure of aluminide coatings particularly the inner coating zone on ODS alloys was a strong function of substrate alloy composition. Increased aluminum levels and possible refractory strengthening elements appeared to be beneficial. For all the ODS alloys and aluminide coatings studied, the coating systems appeared to have insufficient protectivity to match the available mechanical properties. The lack of stability was manifested by both coating void formation and resulting spallation and aluminum diffusion into the substrate.

OVERLAY COATINGS

Overlay coatings, applied by physical vapor deposition, both electron beam and sputtering, and plasma spraying, allow more flexibility in composition selection. Substrate effects are still observed. However, the amount of published information available is rather limited, since these interaction effects are only just being recognized. In addition, the complexity of the system and various proprietary interests are also involved. Hf from IN 738+Hf was found to improve the hot corrosion resistance of a CoCrAlY type coating (6). The coating process also has an influence, Gupta (7) found that diffusion of Hf from a DS MAR-M200+Hf substrate into an EB PVD coating occurred at a substantial faster rate than into a NiCoCrAlY coating prepared by plasma spraying. Ti has also been found to diffuse rapidly into EB PVD CoCrAlY coatings and accumulate at the interface between the surface Al_2O_3 and the coating.

At this point, it is of interest to briefly examine which elements from the substrate are likely to influence, either in a beneficial or detrimental way, the corrosion resistance of the coating. Some of these are listed in Figure 2. Elements like tungsten, molybdenum and niobium may contribute to acid fluxing in conjunction with sulfate deposits on the surface. Titanium and hafnium may contribute to improved scale adhesion in some instances, but in others may compete with the aluminum in scale formation and reduce the protectivity of the surface oxide. In general, it is not possible to broadly classify a particular element as beneficial or deleterious. It depends on the concentration of the element concerned, and perhaps more critically, on the type of conditions being considered: at high temperature, oxidation is the primary degradation mode, whereas at lower temperatures hot corrosion due to the presence of molten salts is more important with the nature of the deposit also being critically temperature dependent.

Equally, it is important to examine how fast the various elements can diffuse through a typical overlay coating. Figure 3 shows very approximately the time taken for the concentration of an element from the substrate to reach 10% of its value in the substrate at the surface of a 125 μm thick coating. These calculations are based on diffusion coefficients taken from Diffusion Data (8), and consequently, do not take into account the possible variation of diffusion coefficients with composition, or perhaps more importantly with coating structure, as discussed later. It is clear from Figure 3 that at temperatures above 1100°C, virtually any substrate element can penetrate the surface coating in a relatively short period, while below 1000°C, it is perhaps surprising to see any effect of the substrate on the surface properties of the coating.

Studies at the Naval Postgraduate School (6, 9) of the potentially beneficial effects of platinum as an interlayer between the superalloy substrate and the

EB-PVD applied CoCrAlY coating suggest that the essential effect of platinum may be its strong interaction with Ti (forming on Engel-Brewer type phase (10)). In this manner, platinum limits the movement of Ti through the coating to the surface either during the coating process or during subsequent exposures at elevated temperatures. The effect of substrate composition and the presence of a platinum interlayer is shown qualitatively in Figure 4. Since these results are for accelerated (<100 hr) hot corrosion testing at 700°C any effect on the surface oxide protectivity must have been present in the as-coated condition or very shortly thereafter.

Studies of the PVD process has indicated the occurrence of a certain amount of surface mixing during the deposition process. The presence of any bias, so-called ion plating, is known to accelerate this interaction (11).

The as-deposited coating structure consists of an open, columnar oriented grain structure through which substrate elements could rapidly move by surface diffusion (12). Subsequent processing is used to densify this structure, but may be microscopally incomplete; Jacobsen reports the presence of ∿100 Å diameter channels through several type of "fully dense" overlay coatings (13). Increased deposition times, temperatures and the presence of surface ion activity could accelerate this movement. Crane and Boone detected the presence of platinum, ∿2%, on the surface of a 150 μm thick EB-PVD CoCrAlY coating as applied over a 5 μm platinum layer (14). Previously, calculated diffusion rates do not predict this very high rate of substrate interaction.

The potential effect of coating structure is also seen in the studies by Gupta (7). An oxide at the "splat" boundaries of a plasma deposited MCrAlY might serve to accelerate the substrate diffusion of some elements (although the grain boundary path length from the substrate to the surface of a plasma deposited structure is clearly longer and more tortuous than for the perpendicularly aligned PVD boundaries). However, if the diffusing species is more oxygen active than the boundary oxide, interaction can occur, thereby effectively blocking the movement of certain elements such as Hf as proposed by Gupta. The possiblity thus exists for selective transport of substrate elements to the coating-oxide surface. Hf moves much more rapidly in an EB-PVD coating than a plasma sprayed system. However, less potentially beneficial elements than Hf such as Ti may also be found at the surface of a PVD coating. Also, the "beneficial" effect of a platinum interlayer on high Ti content substrates may be deleterious if it blocks the movement of Hf as it would be predicted to do (6). The variables of substrate composition, coating composition and processing, and the use of interlayers appear to be increasing and additional studies and information are required to optimumly use these systems in increasingly severe environments.

Another important effect, that of coating thickness, on the degree and rate of interaction has been recently noted by Morral and Barkalow together with development of a method of normalizing measurements on coatings of varying thicknesses (15). Diffusion distances and the "reservoir" of coating elements are considered in their calculations. Such effects may account for some of the apparent scatter in results observed in some test programs.

Finally, in such discussions as this, it is appropriate to note that in these phenomena where extremely small levels of certain elements can have very large effects on protectivity, it is important to consider some of the inherent limitations of analytical techniques often used in their study. In a multi-phase, columnarly oriented structure with potential channel like diffusion paths, the critical levels of substrate elements such as Ti may be undetected by all but, the most sensitive (timeconsuming and expensive) techniques. For these and other reasons, little hard data are available as yet on the specific elements and their threshold levels for detectible effects on coating protectivity.

CERAMIC THERMAL BARRIER COATINGS

Finally, ceramic coatings are currently being actively considered since these provide both a thermal barrier, allowing hotter gas temperatures, and an apparent inert barrier to isolate the metallic components from the corrosive environment. Potential substrate effects are still evident. Most ceramic coating designs use an intermediate metallic bond coating to improve the adhesion of the ceramic coating. This, of course, is susceptible to all the interactions referred to above. The bond coating is usually pre-oxidized before the ceramic coating is applied but the effects of this, and the influence of the substrate, on the mechanism of adhesion, oxide to oxide are not well understood. In addition, there is also the possibility of destabilization of the ceramic, especially ZrO_2 a prime candidate, by elements diffusing from the substrate and into the ceramic.

CONCLUDING REMARKS

Table 1 summarizes the various observations which have been discussed. From this it is clear that there is a real need for a coordinated study of the interaction between coating and substrate and its subsequent effect on coating behavior is of vital importance. Considerably more understanding and data are required, particularly relating to the effects of low, but significant, concentrations of elements such as titanium, hafnium, platinum, etc., although it is recognized that there are some analytical limitations. The initial oxide, and in particular its interface with the surface coating, appears to be the critical area.

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

REFERENCES

1. G. W. Goward and D. H. Boone, Oxid. of Metals, 3 (1971).
2. R. Pichoir, "High Temperature Alloys for Gas Turbines," App. Sci. Publ. (1979) pg. 191.
3. P. Aldred, paper presented at the National Aerospace Engineering and Manufacturing Meeting, Los Angeles, November 1975.
4. J. R. Exell, M.S. Thesis, Naval Postgraduate School, Monterey, CA. (1981).
5. D. H. Boone, D. A. Crane and D. P. Whittle, Thin Solid Films, to be published.
6. R. N. King, M. S. Thesis, Naval Postgraduate School, Monterey, CA. (1980).
7. D. K. Gupta, Thin Solid Films, 73 (1980) 477.
8. Diffusion Data, Ed. F. H. Wohlbier, Trans. Tech. Publ.
9. D. E. Bush, M.S. Thesis, Naval Postgraduate School, Monterey, CA. (1979).
10. L. Brewer and P. R. Wengert, Met. Trans. 4, 83 (1973).
11. R. D. Bland, G. J. Kominiak and D. G. Mattox, J. Vac. Sci. and Tech. 11, 4 (1974).
12. D. H. Boone, T. E. Strangman and L. W. Wilson, J. Vac. Sci. Tech. 11, (1974) 641.
13. B. E. Jacobson, private communication, 1981.
14. D. A. Crane and D. H. Boone, Lawrence Berkeley Laboratory unpublished work (1981).
15. J. E. Morrel and R. H. Barkalow, submitted for publication, Scripta Met. (1981).

TABLE I

OBSERVATION SUMMARY

* A strong effect of substrate composition exists on the protectivity of the applied coating.
  - either beneficial or detrimental depending upon specific elements.
* The substrate effect is greatest for diffusion aluminides.
  - depends on type of aluminide and use of addition elements.
* The substrate effect is less for overlay type coating.
  - Cladding Systems
    - depends on thermal diffusion and could be predictable with sufficient data.
    - interdiffusion a significant factor at high temperatures.
  - Thermal Spray Systems
    - grain boundary effects important
      - selective barriers for oxygen active elements.
      - selective paths for other elements?
  - Physical Vapor Deposition Systems
    - aligned boundaries - short circuit diffusion, can be beneficial or detrimental.
    - process sensitive.
* The use of platinum (or possibly ohter) intermediate layers can be beneficial or detrimental.
  - intermediate layer dependence similar to overlay systems.
  - ceramic-oxide bonding possibly dependent on interaction (not well understood).
  - degree of ceramic stability dependent on interaction.

FIGURE CAPTIONS

Figure 1. SEM examination of underside of protective Al_2O_3 oxide grown on platinum modified aluminide coating using LBL deep detching technique. Structural features of oxide-metal interface surface are being compared with oxides grown on other aluminide and overlay coatings to understand differences caused by interaction with substrate elements.

Figure 2. Schematic drawing of coating-substrate interactions and potential elements of interest.

Figure 3. Plot of calculated substrate diffusional interaction time for an element ot appear at the surface of a 125 µm single phase fully dense coating layer, as function of temperature.

Figure 4. Qualitatively comparison of relative 700°C hot corrosion resistance of 125 µm thick EB-PVD applied CoCrAlY coating as affected by substrate composition, and presence of platinum interlayer (6).

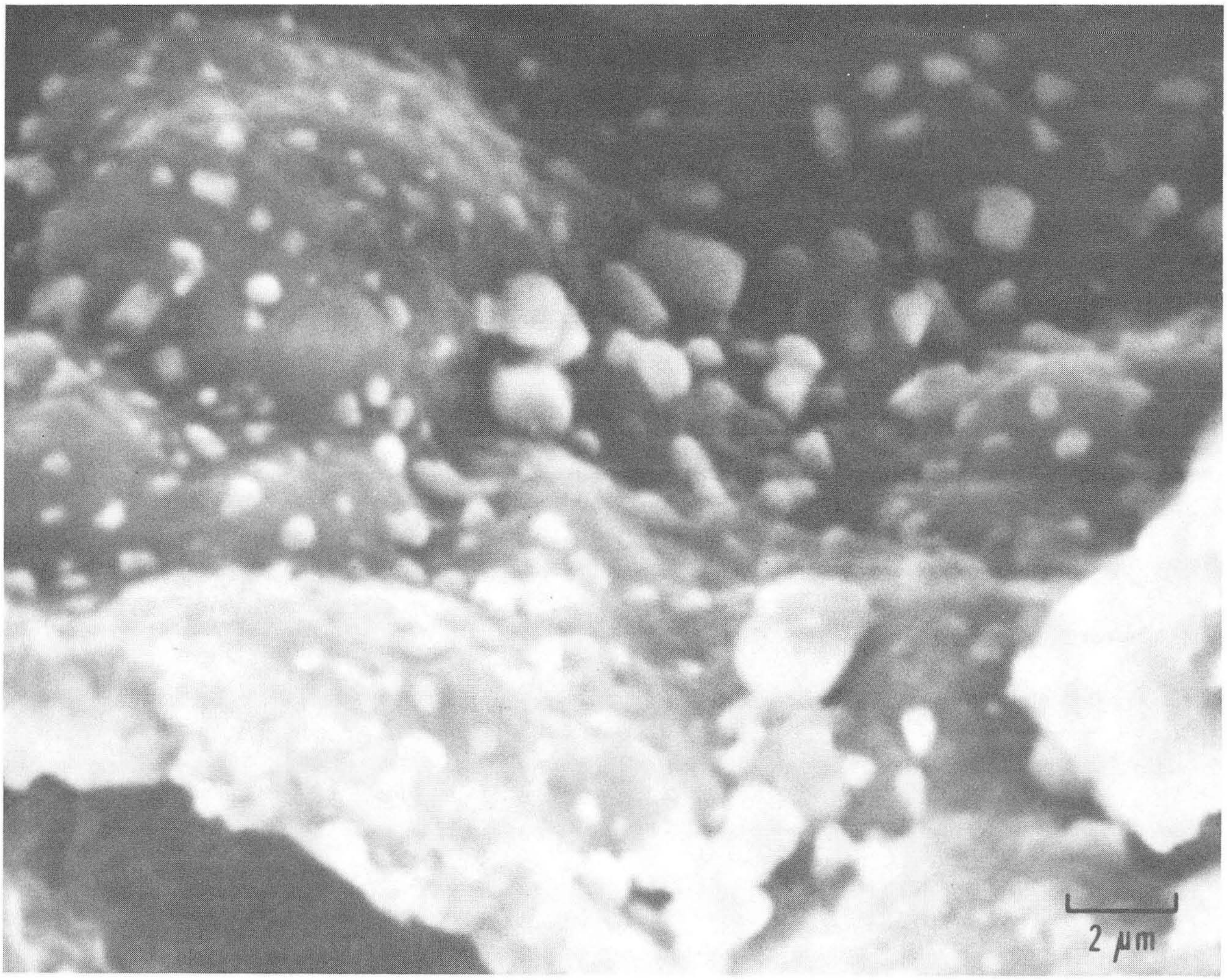
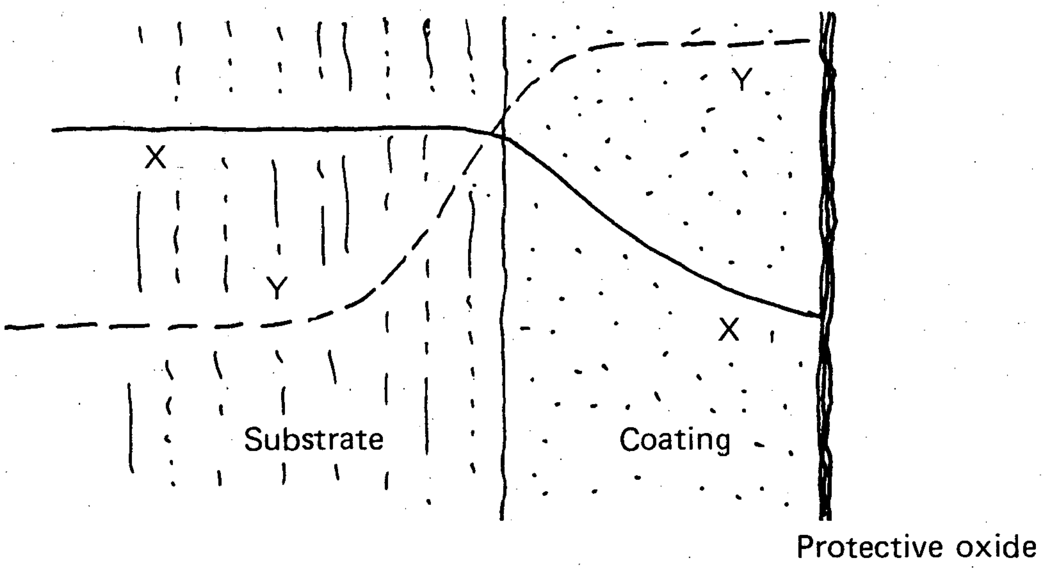


Figure 1.

XBB 810-7708



Typical X elements

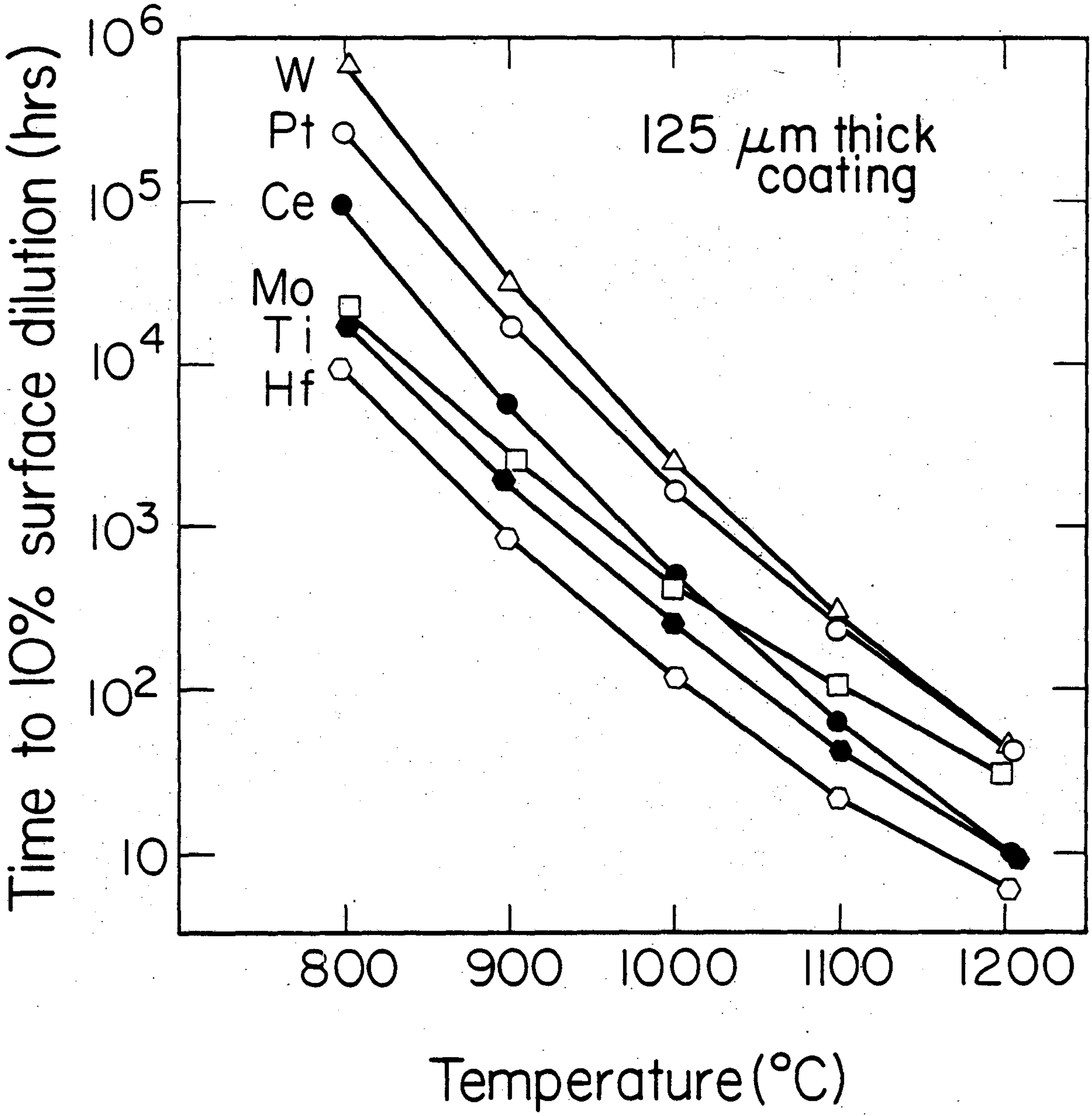
W
Mo } May contribute to
Nb acid fluxing
Ta ?
Ti } Active elements may
Hf contribute to scale adhesion
or compete with Al_2O_3 formation
Pt ?

Typical Y elements

Al
Cr
Y
Pt

XBL 818-11444

Figure 2.



XBL 818-1191

Figure 3.

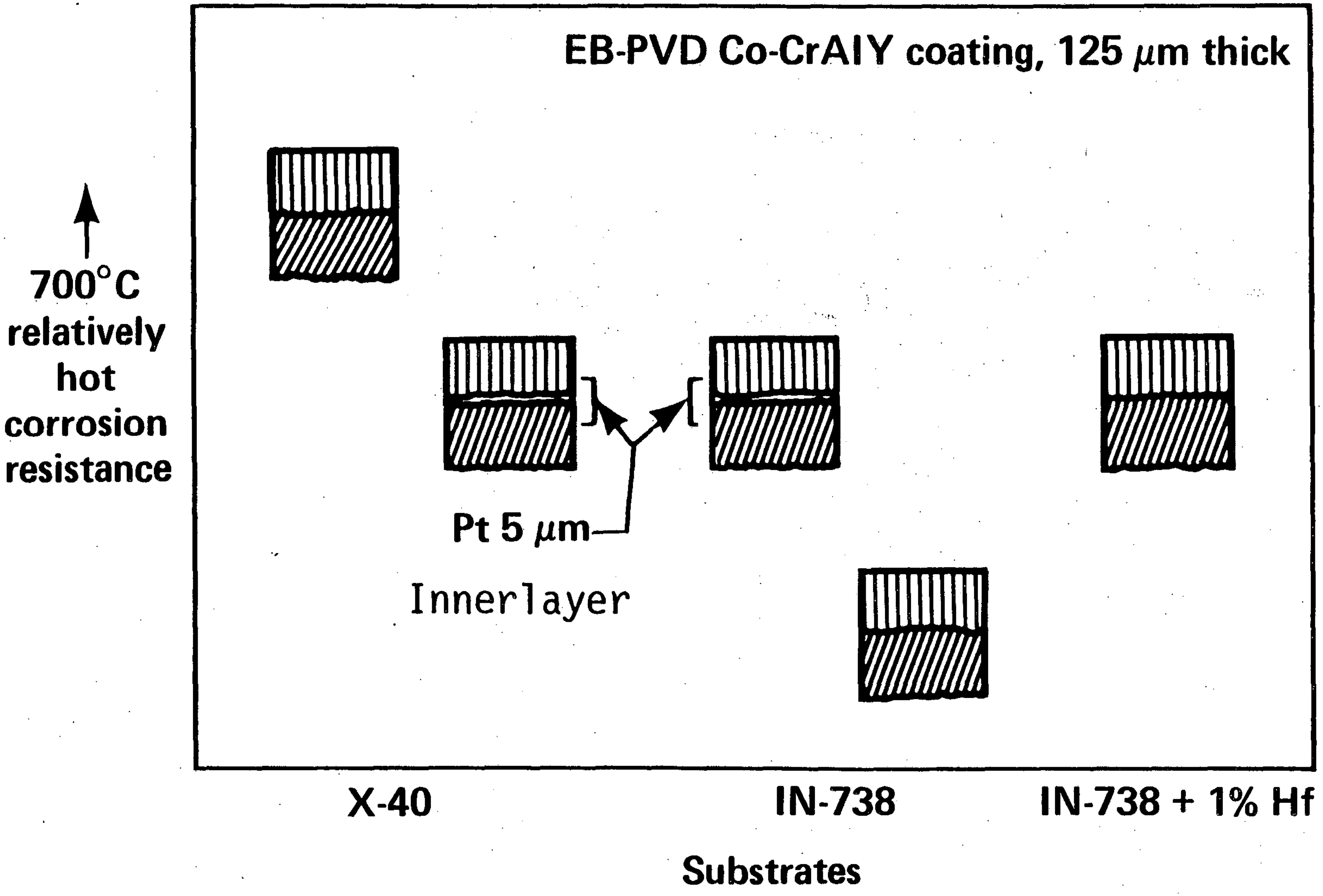


Figure 4.

XBL 818-11351

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720