



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

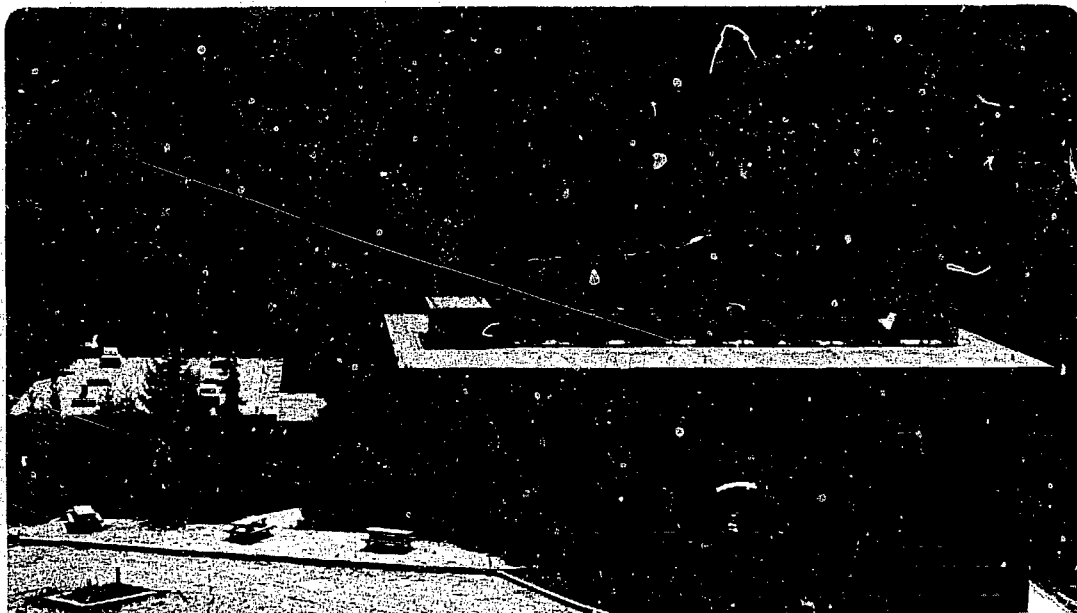
MASTER

Presented at the International Conference on Metallurgical Coatings, San Diego, CA, April 21-25, 1980, and submitted to Thin Solid Films

ADHERENCE OF Al_2O_3 TO CoCrAl COATINGS

D. P. Whittle, D. H. Boone and I. M. Allam

March 1980



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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

D. P. Whittle, D. H. Bocne and I. M. Allam*

Abstract

Adhesion between surface scale and protective coating is an essential requirement of a material possessing good overall oxidation resistance. Poor adhesion can lead to exfoliation of the oxide in response to thermal cycling, or mechanically applied stresses, resulting in enhanced oxidation rates. Marked improvements in scale/substrate adhesion can be obtained via the formation of protrusions of oxide growing into the substrate. These act to key the protective scale to the surface and are more effective when a uniform distribution of small oxide pegs can be achieved. Thus, the structure of the coating, the type of "rare earth addition," and its concentration are all important and this has been examined using EB-PVD CoCrAl coatings containing a variety of elemental additions. These have been subjected to both isothermal and cyclic oxidation in the temperature range 1000-1200°C. The coating/scale interface and the development of pegs growing into the coating has been examined in detail by dissolving away the underlying metal + coating using a Br-methanol

* Present address: SRI International, Menlo Park, California.

⁺To be presented at International Conference on Metallurgical Coatings, San Diego, California, April 1980, and submitted to Thin Solid Films.

solution. The distribution of the pegs provides a good qualitative assessment of the oxide scale adherence. Results have been compared with earlier studies on cast CoCrAl alloys containing various additions.

Introduction

Adhesion between surface scale and substrate is an essential requirement for an alloy or coating possessing good overall oxidation resistance. Poor adhesion can lead to oxide spallation in response to thermal cycling, or mechanically applied stresses, resulting in enhanced oxidation rates. Marked improvements in scale-substrate adhesion, however, can be achieved via a "rare earth effect" whereby addition of a small amount of a rare earth element to heat-resisting alloys or coatings produces significant increases in the resistance to cyclic oxidation. This effect is no longer limited to rare earth elements: additions of other oxygen active elements, or of fine distributions of stable oxides, are equally, if not more efficient.

Many detailed studies have been carried out and these have been reviewed recently.¹ Although a number of factors may be involved in accounting for the active element effect, such as the disappearance of voids at the substrate/scale interface,^{2,3} an improved chemical bonding between oxide and substrate,⁴ or modification to the growth characteristics and/or the plasticity of the scale,⁵ the most significant appears to be the development of oxide protrusions or pegs at the oxide/substrate interface which anchor the scale to the substrate.^{3,6,8} The greatest beneficial effects are achieved when a fine, uniform distribution of small oxide pegs is formed, since these are more efficient in keying the scale to the substrate. As a consequence of this latter point, the distribution of the active element, or the oxide dispersion in the alloy or coating is the critical factor since this determines the eventual distribution of the oxide pegs. Studies by Gupta⁹

indicate differences between electron beam deposited and plasma sprayed coatings of the same composition may be related to the differences in distribution and form of the yttrium. In cast CoCrAl alloys, Hf was found to be a better addition than Y since the latter tended to segregate to the alloy grain boundaries as an intermetallic.⁸ Furthermore, oxide additions were better still, since the distribution of the oxide particles, which are the sites around which the scale pegs eventually develop, could potentially be more closely controlled. With metallic additions, the active element was converted to an oxide dispersion by internal oxidation during exposure: there is thus, less scope for modifying its distribution.

The prime use of CoCrAl compositions, however, is as protective coatings, when it is clear that the structure of the coating, and in particular the distribution of the active element, will depend on the coating process, and be different than cast alloys. The present work, therefore, examines the behavior of a number of EB-PVD CoCrAl coatings containing various addition elements, and in particular concentrating on the development of oxide pegs at the alloy/scale interface.

Experimental

The coatings were prepared by Airco Temescal under DOE contract No. ET-78-C-03-2156. This latter program was a study¹⁰ of the ability to deposit multi-element coatings with low vapor pressure additions; some samples represent addition levels higher than might be used in actual practice. The coatings were prepared on an IN738 substrate in the form of a 3/4" x 2-1/4" x 1/8" plate. Coating compositions and thicknesses are given in Table I.

Table I. EB-PVD Coating Compositions.

Thickness	Co	Cr	Al	Act. Element
m	wt. %			
120	bal.	28.2	10.7	0
125	bal.	20.1	10.1	4.9 Y
100	bal.	24.0	9.0	1.6 Si
135	bal.	20.8	9.6	3.6 Ti
100	bal.	19.6	8.8	6.6 Zr
120	bal.	23.0	9.0	1.4 Hf

Oxidation samples were cut from the coated plates and had typical dimensions of 3/4" x 3/4" x 1/8"; the cut ends of the samples were uncoated. Oxidation was carried out in air at both 1000°C and 1200°C under isothermal and cyclic conditions (20h cycles). For the most part because of excessive interdiffusion with the substrate, oxidation at 1200°C was too severe and most of the coatings were completely consumed after 200 h exposure. As a consequence, most of the detailed observations reported below and for samples oxidized at 1000°C.

The morphology of the scale/substrate interface was studied by chemically stripping the scale and examining its underside. Scales were stripped by dissolving away the substrate using a 10% bromine in methanol solution. The detached scales were then rinsed in methanol, collected on copper grids and examined in the scanning microscope.

Results

Figure 1 compares the morphological features, as viewed in section, of the Al_2O_3 scales formed after 240 h oxidation at 1000°C on the CoCrAl coatings containing the different additions. The grain structures fall into two broad categories. A columnar-type structure with the grains orientated in the growth direction and single grains penetrating almost completely through the scale section. This is typified in Figure 1a by the oxide formed on the Hf-containing coating; the oxide on the Y-containing coating is very similar.

The second type of oxide has an equiaxed, granular-type of structure, and is shown in Figures 1b and 1c. These are the scales formed on the coating with no addition, and that containing Zr respectively. The scale formed on the Si-containing coating also has the same type of structure. The grain size of the oxide parallel to the growth direction is very similar in both columnar and granular scales.

The Ti-containing coating behaved somewhat differently. In some sections the scale showed a columnar-type of growth, although this was not as pronounced as with the Hf- and Y-containing coatings. In other sections, Figure 1d, the Al_2O_3 scale had a plate-like structure, again orientated in the growth direction.

Figure 2 compares the undersides of the Al_2O_3 scales after the substrate has been dissolved away. Again these fall into a number of categories. With the Hf-containing coating, Figure 2a, the underside of the oxide has an irregular appearance with numerous fingers of oxide penetrating out of the scale into the substrate. These are the oxide pegs referred to earlier. They are more angular in nature than those

observed with cast CoCrAlHf alloys,⁸ and also more abundant. However, this latter factor may well be related to the higher Hf content, 1.5% compared to the 0.3-1.0% in the cast alloys. In spite of this, Hf could not be detected by EDAX analysis of the undersides of the oxide.

Figure 2b shows a second-type of scale underside, typical of the granular Al_2O_3 scales formed on the Si- and Zr-containing coatings. Here the protrusions are less pronounced, and in relation to our earlier work,⁸ this type of morphology would not give as an adherent scale as that shown in Figure 2a. The third type of appearance of the scale underside is shown in Figure 2c and d, for the scales formed in the Ti-containing coating and the addition-free coating respectively. These have a plate-like morphology, and in fact EDAX analysis of the feathery plates indicates significant concentration of Ti. This occurs both for the Ti-containing coating, and more significantly, for the addition-free coating, Figure 2d. Both the Y- and Si-containing coatings also show significant Ti concentrations, and oxide platelet formation at the scale/coating interface. The Ti has presumably diffused out through the coating from the IN 738 substrate. Again these poorly distributed pegs and platelets are unlikely to produce the maximum scale/substrate adherence.

Typical sections through the coatings after the 240 h exposure at 1000°C are shown in Figure 3. The Hf-, Ti-, Si- (shown) and addition-free coatings all show an even band near to the surface of the coating which is depleted in the β -CoAl phase. The Zr- and Y-containing coatings, the latter is shown in Figure 3b, show a much more irregular loss of

the β -phase from the coating. However, these features do not appear to be related to the type of Al_2O_3 scale produced.

Discussion

A number of significant features have arisen from this investigation so far. Firstly, the undersides of the Al_2O_3 scales formed on CoCrAl-type coatings show similar morphologies, in terms of oxide peg development, as these on equivalent cast alloys studied earlier,⁸ except that the differences between the various addition elements are less pronounced. Earlier⁸ it was suggested that during oxidation the active element was converted into an internal oxide and that the Al_2O_3 grew inwards by oxygen diffusion along the incoherent interface between matrix and internal oxide encapsulating these particles. The peg distribution so developed was thus very dependent on the distribution of the active element in the substrate, and on comparing Y and Hf in cast alloys there was substantial differences. Y tended to segregate to alloy grain boundaries, whereas the more soluble Hf was more uniformly distributed. As a consequence, scale adhesion on the Hf-containing cast CoCrAl alloy, with its more uniform peg distribution, was much better. Segregation of this type is less pronounced with PVD coatings.

A second important feature is related to the apparent segregation of Ti to the scale/coating interface, and particularly to its ability to diffuse from the substrate through the coating. Ti is not an active element in Al_2O_3 -forming alloys, in the sense that its oxide is less stable than Al_2O_3 : the oxides of Si and Zr are also less stable than Al_2O_3 . Nevertheless, Ti does appear to be oxidized forming platelets,

although whether this was beneficial to the scale adherence has not been established.

The predominance of columnar-type of scale growth on the Hf and Y-containing coatings, as opposed to the more granular structure may also be important. Similar differences were observed⁸ earlier between Hf and Y containing and addition-free cast CoCrAl-alloys. The absence of columnar grains in the addition free coating, and those containing Si and Zr, which are not active elements, implies that there is continued nucleation of Al_2O_3 at the coating/scale interface, and thereby less propensity for oxide peg development. As such, adhesion of the scale would not be particularly enhanced, and maybe this can be related to there being no internal oxidation of the addition element. Interestingly the columnar-type scales also appear to grow more slowly than the granular-type oxides, at least if the appearance of Ti at the scale/coating interface is related to the consumption rate of the coating.

Further work is being directed at a closer correlation between the morphology of the Al_2O_3 scale and both the structure and composition of the coating, and the properties of the scale in terms of its overall growth rate and adhesion to the substrate. In this latter respect, a more quantitative assessment of adhesion is required and hopefully this will be provided by low angle erosion studies of the oxide scales. In addition, samples with lower addition element concentrations will be examined and attempts to optimize addition-type and concentration will be carried out.

Acknowledgment

This work has been supported by the Division of Materials Science, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-ENG-48. The coated samples were prepared under DOE Contract No. ET-78-C-03-2156.

References

1. D. P. Whittle and J. Stringer, Phil. Trans., Roy. Soc., London (1979) 309.
2. J. Stringer, Oxid. Metals 5 (1972) 59.
3. J. K. Tien and F. S. Pettit, Met. Trans. 3 (1972) 1587.
4. J. E. McDonald and J. G. Eberhart, TMS-AIME 233 (1965) 512.
5. F. A. Golightly, F. H. Stott and G. C. Wood, Oxid. Metals 10 (1976) 163; J. Electrochem. Soc. 126 (1979) 1035.
6. C. S. Wukusick and J. F. Collins, Mater. Res. Stand. 4 (1964) 637.
7. E. Felten, J. Electrochem. Soc. 108 (1961) 490.
8. I. M. Allam, D. P. Whittle and J. Stringer, Oxid. Met. 12 (1978) 35; 13 (1979) 381.
9. D. Gupta, Thin Solid Films, 63 (1979) 542.
10. D. H. Boone, S. Shen and R. McKoon, Thin Solid Films 63 (1979) 299.

Figure Captions

- Figure 1. SEM sections of the oxides stripped from (a) CoCrAlHf, (b) CoCrAlSi, (c) CoCrAl and (d) CoCrAlTi after oxidation for 240 hr in air at 1000°C. (micron mark = 10 μ m)
- Figure 2. Undersides of the oxides formed as in Figure 1. (a) CoCrAlHf, (b) CoCrAlSi, (c) CoCrAlTi and (d) CoCrAl (micron mark = 10 μ m)
- Figure 3. Cross-sections of the coatings (a) CoCrAlSi and (b) CoCrAlY after oxidation for 240 h at 1000°C. (micron mark = 10 μ m)

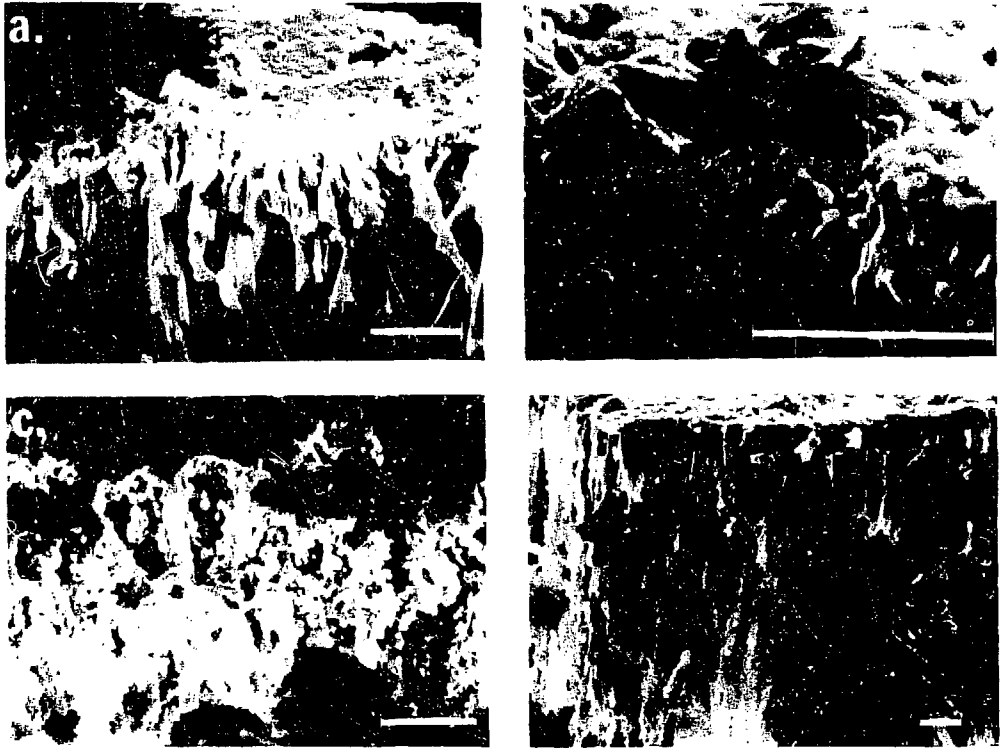


Fig. 1

XBB803-3491

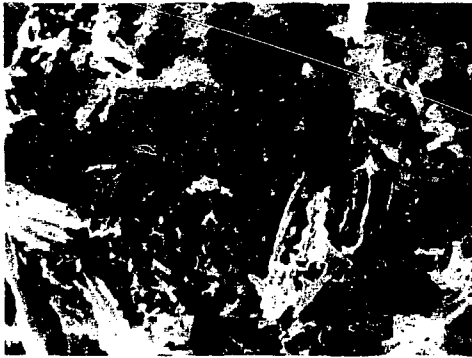
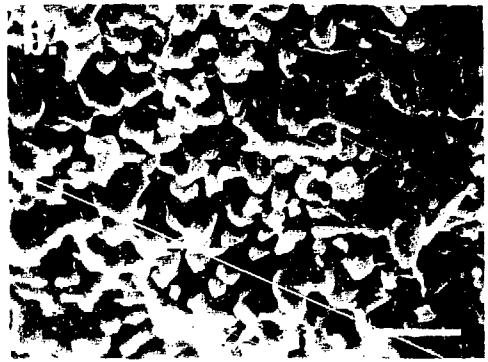
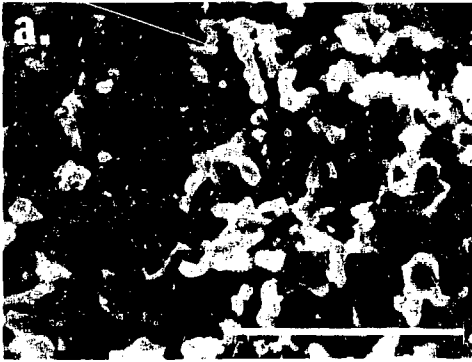


Fig. 2

XBB803-3492

```

      jpart=j-1)*nev
      i=jpart+1
      j=i+part+1
      phold=ccplx(0.,0.)
      do 150 k=1,nev
        kpart=(k-1)*nev
        ik=kpart+1
        jk=kpart+j
        phold=phold*cc((ik)*phase(k,jac(j,k)
150      continue
        pl(j)=phold
        p(j)=phold
250      continue
300      continue
      return
      end

c
c  function argue follows.
c
      function argue(ev,t)
c
c  reduces a large trigonometric argument (the product
c  of ev and t) to a small one
c
      twopi=6.283185308
      w=ev/twopi
      tw=w
      rw=w-tw
      it=1
      rt=t-rt
      a1=tw*rt
      i1=1
      r1=a1-1
      a2=rt*rw
      i2=a2
      r2=a2-1
      argue=(r1+r2+rw*rt)*twopi
      return
      end

c
c  subroutine afind follows.
c
      subroutine afind(mats,schar)
c
c  routine to project the singlet character out of
c  those states originating in the singlet manifold.
c
      common/blk4/nblk1(32),nev1(6),nblk1(6),inev1(6),loc1(32)
      common/blk5/nblk2(32),nev2(6),nblk2(6),inev2(6),loc2(32)
      common/blk6/p1,p2
      common/blk8/nangs,nblk1,nblk2
      dimension mats(4,256)
      complex pl(256),p2(256),scoat
      schar=0.
      do 400 i=1,nangs
        i1=mats(i,1)
        i2=mats(i,2)
        i3=mats(i,3)
        i4=mats(i,4)
        i1=nblk1(i1)

```