Fundamental aspects of high-temperature corrosion (*)

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Abstract. — Some recent considerations in three widely different aspects of high-temperature corrosion are summarized: 1) reactions at the metal/scale interface in support of scale growth; 2) mass transfer effects in the control of evaporation of volatile reaction products; and 3) the co-deposition of multiple elements for diffusion coatings using halide-activated cementation packs. The climb of misfit edge dislocations from the metal/scale interface can achieve the annihilation of vacancies associated with scales grown by cation diffusion. For scale growth at the metal/scale interface by anion diffusion, the creation of anion vacancies occurs by the climb of misorientation dislocations. For cation-diffusing scales, a blocking of the vacancy annihilation reaction may be achieved by the specific adsorption of reactive elements at the metal/scale interface. The pinning of the interfacial misfit dislocations by segregated reactive elements can explain the changes in growth mechanism, in growth stresses, and in reaction kinetics associated with the reactive element effect for the growth of chromia scales on alloys. Although the vapor pressures of volatile species are readily calculated from available thermodynamic data, the use of these values to predict the kinetics of transport-limited evaporation has not been presented specifically for various substrate geometries and differing flow conditions. The empirical mass transfer relations are evaluated and plotted for the flat plate and tube geometries in the laminar and turbulent flow regimes. A criterion for the stability of a flat interface in selective evaporation from an alloy is still lacking. Despite the inherent difficulty to codeposit two or more elements with greatly differing thermodynamic stabilities for their halide species, cementation coating packs can be designed with selected combinations of powdered masteralloys and halide activator salts whereby elements are codeposited to yield a desirable surface composition. Selected examples for effective aluminizing/chromizing of Ni-base superalloys and for chromizing/siliconizing of steels are presented.

1. Introduction.

A large number of specific topics relevant to high-temperature corrosion will be presented at this Third International Symposium on High-Temperature Corrosion. The topics are too numerous to even list here. The allotted time and space would not permit even a cursory overview of the fundamental aspects for all these topics. Therefore, I have chosen to present some recent considerations on three interesting and important topics. I wish to acknowledge that several colleagues, to be detailed later, have worked with me and contributed importantly for each of these subjects.

(*) Primary lecture.

2. Reactions at the metal/scale interface.

For about seven years, I have worked sporadically with Bernard Pieraggi at ENSCT, Toulouse, on identifying various aspects of the fundamental mechanisms operative during scale growth in the oxidation of metals. This collaboration has been based on identifying logical explanations or novel interpretations for features and characteristics of scale growth which are well known from the experimental literature. Our inquiries began by questioning the detailed mechanism by which vacancies from the scale interact with the metal/scale interface during scale growth by outward diffusion of cations. At this meeting, we will present a paper which offers a novel explanation for the "Reactive Element Effect" in alloy oxidation. I readily admit that the several mechanisms discussed here certainly require some difficult experimental verification, preferably using high resolution TEM in a hot-stage environmental microscope.

The classic question concerning the growth of scales at the scale/gas interface by the outward diffusion of cations over vacancies is "What happens to the vacancies from the scale at the metal/scale interface?" In early studies, Dunnington *et al.* [1] and Tylecote and Mitchell [2], and more recently Francis and Lees [3], suggested that such vacancies were injected into the metal substrate and could diffuse over great distances (at least several mm) before they would be annihilated by an interface or some other vacancy sink. However, dislocation-laden metals cannot support the vacancy supersaturation needed for massive vacancy injection and long-range diffusion. Pieraggi and Rapp [4, 5] have offered an alternative mechanism for vacancy annihilation at the metal/scale interface which is consistent with the arguments of Harris [6, 7].

Figure 1 shows a schematic illustration of a metal/scale interface assumed to obey a "parallel" epitaxial relationship, i.e. the atomic lattice for the metal is extended in space to constitute the cation lattice of the oxide. Although it is commonly observed in metal oxidation, the

Fig. 1. — Schematic illustration of metal/scale interface with parallel epitaxial orientation showing interfacial misfit and misorientation dislocations [4].

assumption of this specific epitaxial relation only serves to facilitate the visualization of the interfacial structure. Because of the large mismatch in the lattice parameters for the metal and the oxide lattices, the "equilibrium" interface would support a 2-D grid of misfit interfa-

cial dislocations which correspond to extra half-planes (edge dislocations) in the metal. For example, for a $\{100\}$ planar interface in the Ni/NiO system, the "dead" interface would have 2 misfit dislocations for every 13 planes in the $\langle 110 \rangle$ direction for Ni.

Figure 1 also shows schematically the existence of interfacial misorientation dislocations whose Burgers vectors are normal to the interface plane. Figure 2a presents a schematic

Fig. 2. — Schematic illustration of interfacial misorientation dislocations: a) atomic planes at interface; b) equivalence to atomic steps on ledges; and c) introduction by intersection of screw dislocation from the metal.

drawing of the metal and oxide lattice planes at an interface with a minor angular tilt away from the ideal epitaxial interface; the metal planes terminating in the interface correspond to the misorientation dislocations of figure 1. As shown in figure 2b, the misorientation dislocation in the interface may also be considered as a monatomic step (or ledge), in this case introduced by edge dislocations emanating from some glide plane in the metal. Unlike the intrinsic misfit dislocations, the misorientation dislocations must be replenished by dislocations supplied from some source inside the metal. As shown in figure 2c, a screw dislocation from the metal intersects the interface to create not only the steps (ledges) and interfacial tilt, but also to extend itself into the scale. This screw dislocation in the scale can also provide the ledges needed for lattice extension at the scale/gas interface. In both figures 2b and 2c, kinks are shown in the interfacial ledges. Virtually every metal/oxide interface, regardless of the relative lattice orientations, should possess huge densities of misorientation and misfit dislocations. These interfacial dislocations have important, but differing, functions in supporting scale growth on metals.

2.1 VACANCY ANNIHILATION. — For the growth of scales via cation/vacancy diffusion, Vermilyea [8] proposed that vacancies are annihilated at kink sites in ledges at the metal/scale interface. However, if that mechanism would occur, then anion diffusion in the oxide would be required to fill the space resulting from recession/reaction of the interfacial ledge, corresponding to inward oxide growth. Therefore, although an excess of interfacial ledges may be present, they should not participate in vacancy annihilation for cation-diffusing scales.

As shown schematically in figures 3a-d, Pieraggi and Rapp [4] proposed that vacancies are annihilated at the metal/scale interface by the climb of some fraction of the interfacial misfit edge dislocations into the metal, and the rearrangement (increase in spacing) of the remaining misfit dislocations in the interface. This mechanism introduces elastic tensile stresses into the metal and compression into the oxide at the interface, consistent with experimental observations. The generation of excessive growth stresses in this way would activate the glide of dislocations in the oxide. After the climb of some edge dislocations into the metal, corresponding to the annihilation of numerous vacancies, the dislocation may dissociate and glide/return to the interface where an association reaction can reform the misfit dislocation. Thus, this edge dislocation climb/glide sequence can annihilate vacancies at the interface while maintaining intimate epitaxial contact at the metal/scale interface. Obviously, this same model applies for the creation of interstitial cations when these defects are dominant in the oxide. The model does not correspond to that of Vermilyea [8] whereby vacancy annihilation at interfacial ledges was not expected to create growth stresses. Likewise, the model contradicts the vacancy injection mechanism mentioned earlier [1-3].

2.2 ANION DIFFUSING SCALES. — When the dominant ionic defect in the scale is the anion vacancy (or interstitial), then new scale is grown at the metal/scale interface, upon the release of anion vacancies (or arrival of interstitial anions), as sketched in figure 4. The monatomic interfacial ledges with kinks are synonymous with interfacial misorientation dislocations with jogs, and anion vacancy creation or interstitial incorporation into new oxide lattice corresponds to the climb of these dislocations, or recession/reaction of the ledges, in the interface. In this case, we agree with Vermilyea [8] with regard to the mechanism for scale growth at the metal/scale interface. He inferred that little growth stress is introduced by this mechanism for extensive flat surfaces, because the large volume increase corresponding to the Pilling-Bedworth ratio is simply displaced toward the free external surface. However, for coupons with finite sizes containing edges and corners, voluminous growth of a brittle scale at the metal/scale interface certainly creates cracks and pores which permit the local ingress of

Fig. 3. — Climb of misfit interfacial dislocations to annihilate vacancies and glide return to the interface: a) misfit dislocations at equilibrium spacing; b) upon oxidation, climb of some fraction of misfit dislocations into metal and dissociation and glide/return of dislocations to interface; c) dislocation glide in the oxide; d) two-dimensional view of metal/scale interface during scaling [4].

Fig. 4. — Growth of anion-diffusing scales at metal/scale interface.

gaseous oxidant. Likewise, such metals also usually exhibit a high solubility for atoms of the oxidant. Oxidant dissolution into the metal probably also involves kinks in interfacial ledges by some yet unexplained mechanism.

2.3 GENERALIZATIONS. — The literature provides certain indisputable facts about the characteristics of scale growth at the scale/gas interface (cation diffusion) contrasted to growth at the metal/scale interface (anion diffusion). For cation-diffusing scales, relatively large columnar grains with some growth texture, are grown at the scale/gas interface by the translation of surface ledges dominantly associated with screw dislocations in the scale [9]. At the metal/scale interface, local vacancy annihilation leads to an enrichment in more noble solutes, the adsorption of various oxidized and noble segregants, and in the accumulation (as markers) of oxidized and noble third phases, even superficial dirt initially present at the external surface. Further, as the scale thickens, the vacancy annihilation mechanism can break down if the climbing misfit dislocations get tangled beneath the metal/scale interface, so that interfacial voids are formed. All of these disturbances to the inherently strong epitaxial metal/scale bond lead to the generalization that excellent adherence for such scales cannot be expected.

On the other hand, for scale grown at the metal/scale interface for anion-diffusing compounds, the recession/reaction of interfacial ledges would transfer certain interfacial solutes and particles (as markers) into the oxide. Thus, for this clean interface, the strong epitaxial metal/scale bond should be maintained for anion diffusing scales. In a study of the sulfidation of molybdenum, scale formation at the metal/scale interface resulted in a textured scale forming from a textured Mo substrate [10]. The prism face of the hexagonal MoS_2 unit cell matches very well the $\{110\}$ plane of Mo to provide an ideal epitaxial fit. However, this epitaxy is satisfied for two alternative, but incompatible, orientations of the sulfide lattice. In this case, scale growth at the metal/scale interface consists of repeated nucleation of sulfide grains which cannot intergrow, so that further nucleation is required. For these reasons, anion-diffusing scales are generally fine-grained and very tightly adherent, at least locally near the metal/scale interface. These generalizations are useful in attempting to interpret the reactive element effect (REE) in scale growth on chromia-forming alloys.

2.4 REACTIVE ELEMENT EFFECT. — As outlined in greater detail by Pieraggi at this Symposium, a segregation of large, highly charged reactive element cations to the metal/oxide in-

Fig. 5. — Segregation of large, highly charged reactive element cations to pin misfit dislocations in metal/scale interface.

interface can explain the four important effects associated with the growth of chromia scales on alloys: 1) reduced rate of parabolic scale growth; 2) improved scale adherence for a very fine-grained scale; 3) lower chromium concentration required to form chromia; and 4) a change in fundamental mechanism resulting in scale growth at the metal/scale interface. This segregation of only a fraction of a monolayer of the reactive element cations (Ce, Y, La cations, etc.) to the misfit dislocations in the metal/scale interface is shown schematically in figure 5. These large cations in the chromia at the interface would stretch the corundum lattice and introduce tensile stress into the metal, as does the climb of the misfit dislocations from the metal/interface in interstitial cation formation. Therefore, the segregated reactive element cations serve to oppose (pin) the climb of the misfit dislocations and thereby poison the interfacial reaction. In the absence of interstitial cation formation, only anion diffusion can occur, with a resultant scale growth at the metal/scale interface. As just discussed, such a scale is inherently fine-grained and tightly adherent. The much slower anion diffusion results in a greatly reduced parabolic growth rate, which in turn, permits a lower Cr concentration to ensure chromia growth [11]. Certainly, this model requires further scrutiny to interpret the various observations from a hundred or more experimental studies, as reviewed recently by Moon [12] and Stringer [13]. An indisputable test of this model for poisoning the interfacial vacancy annihilation reaction would be the demonstration of a drastic reduction in the parabolic rate constant, and scale formation at the metal/scale interface, for the oxidation of a fast oxidizing pure metal such as Cu, Fe, Co or Ni. Of course, to achieve an equivalent difference in sizes between the segregated reactive cation and the metallic lattice, a different choice of reactive elements should be made. Such experiments are currently in progress.

3. Mass-transport-limited evaporation kinetics.

For a number of high-temperature environments, the formation of a highly volatile reaction product competes with scale formation, especially in the reactions of metals and alloys with halogens, e.g. Cl_2 or HCl , in flowing gas streams. The detailed behavior of such reactions has been treated and reviewed in the literature [14-20], so that the essential points for the interpretation of experiments are known. Every young student in a materials curriculum learns to calculate the equilibrium vapor pressures for given volatile species over given condensed phases in given gaseous environments. Yet the important engineering question is the following: "From a knowledge of the local equilibrium vapor pressure, how does one predict the steady-state evaporation behavior for a given set of flow parameters in a given system geometry?" My colleague Ge Wang has been considering this problem.

As one learns from the Wagner [21] analysis for the active/passive oxidation of silicon, for a kinetics problem, the local (interfacial) activity for the oxidant may differ drastically from that in the bulk gas phase. In a gas phase containing a high concentration of an unreactive (inert) component, large gradients in the partial pressures for species can be maintained for a negligible gradient in total pressure. Thus, the stability of any condensed phase, and the vapor pressures for the stable phase(s) at the surface, must be decided from a kinetics condition which usually states that the rate of arrival of oxidant through an effective stagnant boundary layer is equal to the rate of loss of some volatile product. This condition for rate control by counterdiffusion in the gas phase is solved by the existence of some specific local (interfacial) value for the oxidant activity, which might differ greatly [21], or negligibly [22], from that for the bulk gas stream.

3.1 GENERALIZATIONS. — Such analyses lead to certain predictable expectations for the reaction of a pure metal (such as Fe, Ni, or Co) in a halogen/inert gas mixture, as illustrated in figure 6. At relatively low temperatures where the vapor pressure of the volatile halide

is low, a stable condensed scale may form and evaporate slowly at a rate dependent upon the flow rate, but independent of the oxidant activity, of the bulk gas phase. At a very high temperature where the vapor pressure of the metal halide is high, evaporation may consume the reactant upon arrival, so that the local interfacial oxidant activity and the ensuing reaction kinetics should depend upon both the flow rate and oxidant activity of the bulk gas phase. For either extreme, empirical expressions for mass transport through an effective stagnant boundary layer are used to predict/interpret the kinetics.

Fig. 6. — Generalized behavior expected for reaction of pure metal M in H_2/HCl gas to form product MCl_2 with high vapor pressure.

3.2 ALLOY REACTIONS. — For the reactions of alloys comprised of components with greatly differing reactivity and vapor pressures in mixed halogen/inert gases, an interesting behavior is observed. Kim and Pickering [19] and Singheiser *et al.* [20] reacted Co-Pt and Co-Pd alloys, respectively, in H_2/HCl gas mixtures, such that the noble metal was unattacked while the very volatile $CoCl_2$ evaporated. Similar to the selective dissolution of the more reactive component from an alloy in aqueous corrosion (e.g. dezincification of brass), the exclusive loss of $CoCl_2$

vapor from a Pd-rich Pd-Co solid solution alloy generates a zone of fine porosity at the alloy surface. In this case, the HCl oxidant and the CoCl_2 product species must counterdiffuse across both the stagnant boundary layer and the porous metal zone, as shown schematically in figure 7a. However, for many experimental and industrial conditions, the thickness of the effective stagnant boundary layer is much greater than that for the porous metal zone. Therefore, the kinetics of evaporation for a 0.9Co-0.1Pt alloy were almost identical to those for pure Co [19], despite the existence of a porous metal zone.

Fig. 7. — Generalized behavior expected for reaction of NM alloy to form volatile MCl_2 Product: a) in H_2/HCl gas; and b) in $\text{H}_2/\text{HCl}/\text{H}_2\text{O}$ gas.

As treated by Singheiser *et al.* [20], as the noble metal content of a Pt-Co alloy is increased, gaseous diffusion in the porous zone, and ultimately solid-state diffusion contributes to the rate control. However, the reaction of an alloy with 0.3Co-0.7Pd still produces a porous zone at the metal surface. An interesting unsolved problem is to predict theoretically, or to demonstrate experimentally, that some critical alloy composition exists at which a flat external interface becomes stable. Such a theory must consider a number of relevant physical properties and experimental parameters.

When an alloy suffering volatilization is further subjected to a second gaseous oxidant, e.g. H_2O or CH_x , then the mechanism shown schematically in figure 7b could apply. In this case,

the second oxidant might stabilize a solid product (with low vapor pressure), e.g. an oxide or carbide. The evaporation reaction could be restricted to an internal loop, whereby the halogen is recycled to carry the volatile component to the surface where the thermodynamically more stable solid product would be formed. The depth of internal attack could be localized (e.g. at grain boundaries) and serious, although the alloy could even gain weight.

The empirical relationships to describe fluid flow over surfaces of various geometries are readily available, but cannot be elaborated here. For industrial practice, as well as laboratory simulation, both laminar and turbulent flow for both flat plates and cylindrical tubes is important. Without providing the complex mathematical relations for the fluid flow, figures 8 and 9 show some calculated depths of selective attack for a binary alloy with given (indicated) halide vapor pressures for one component in H_2/HCl gas streams with the indicated total pressures. Figure 8 describes the evaporation attack of the ID of a cylindrical pipe [23, 24] with laminar and turbulent flow ($v_c = 14$ m/s). Gaseous diffusion through a porous surface layer hardly contributes to rate control, which switches to solid-state diffusion control only after very extended reaction times.

Fig. 8. — Calculated depth of internal attack for a tube of 4.3 cm ID for NM alloy of $X_M = 0.43$ with vapor pressure of 10^{-5} atm.

If one defines an “evaporation ratio” as the ratio of the actual (calculated) evaporation rate to the Hertz-Langmuir gross (equilibrium) flux, then this ratio (α) has the following values for the plot of figure 8: 2×10^{-6} , 2×10^{-4} , and 10^{-2} for 0.01, 1, and 100 m/s flow rates. Figure 9 presents the depth of attack by selective evaporation for a flat plate alloy for both laminar and turbulent flow [25] ($v_c = 40$ m/s). Values of the “evaporation ratio” for figure 9 are: 3×10^{-6} , 3×10^{-5} , and 3×10^{-4} for 0.01, 1, and 100 m/s flow rates. The evaporation ratio is a useful concept since it evaluates rate control by gas phase transport, independent of the magnitude of the vapor pressure. The obvious conclusion from these considerations is that transport-limited evaporation kinetics can be calculated from available expressions when the vapor pressure is known, but the resulting rates of evaporation are very much smaller than those corresponding to the Hertz-Langmuir rates.

Fig. 9. — Calculated depth of internal attack for a plate of 6.2 m length for NM alloy of $X_M = 0.43$ with vapor pressure of $1.3 \times 10^{-4} \text{ atm}$.

4. Codeposition of diffusion coatings by pack cementation.

Methods for physical vapor deposition (evaporation, sputtering, plasma spray, etc.) of surface coatings generally require large, expensive vacuum chambers and manipulation equipment. Although these PVD processes find application in the thin-film electronics applications, they are not ideally suited for the production of relatively inexpensive, thick diffusion coatings intended to minimize oxidation, hot corrosion, and erosion in high-temperature oxidizing environments. In contrast, the halide-activated pack cementation process is a proven method for enriching single elements (Al, Cr, or Si) into a diffusion coating on various alloys. The conversion of the composition and perhaps the structure for such thick, adherent coatings results in useful coatings for parts of many shapes and sizes for applications in a great variety of systems.

The pack cementation diffusion coating is formed by heating the parts to be coated in a closed (vented) refractory retort, which also contains a powder mixture of the element to be deposited, a dominant amount of an inert filler, and a small amount of a halide salt (fluoride, chloride, bromide). At the processing temperature, the coating element forms volatile halides with sufficient vapor pressure, and solid-state diffusion is sufficiently rapid, that the surface is changed to the desired composition and structure to a desired depth. However, because the thermodynamic stabilities of the various volatile halides for Al, Cr, and Si differ greatly, usually the halide vapor pressures for one element dominate, so that only one element is generally deposited.

However, the oxidation attack of alloys at high temperatures is usually minimized by a combination of two elements. For example, the Kanthal alloy (Fe-base, 20Cr, 4.5wt%Al) exhibits excellent scaling resistance in air at high temperatures. Likewise, high temperature austenitic Fe-Ni-base alloys are protected best, especially in oxidizing-carburizing environments, by compositions containing about 25Cr and 3wt%Si. According to the Wagner model [26], upon initial exposure to an oxidizing environment, such alloys form a protective chromia film, which prevents the rapid oxidation of the Fe or Ni substrate, and thereby avoids the internal oxidation of the smaller Al or Si contents. However, alumina and silica are thermodynamically more stable than chromia, so upon further exposure, these slower growing scales are established at steady state. This synergistic action of two elements (Cr-Al or Cr-Si)

illustrates the need to codeposit two elements in desired concentrations *via* a diffusion coating process. In coating Ni-base superalloys to grow an NiAl layer, the codeposition of some Cr with Al provides improved resistance to hot corrosion attack by thin fused salt films.

My students Robert Bianco and Mark Harper and I have recently reviewed [27] a series of pack cementation studies for the codeposition of various pairs of elements into numerous substrates. Codeposition of two elements in the desired ratio is achieved by using a proper masteralloy, with a proper salt, and a proper filler in the cementation pack. As an approximate condition for codeposition, the net rates of arrival of the metal halide volatiles for the two elements must be in the correct ratio, although their inherent thermodynamic stabilities may differ greatly. The competitive tendencies for various metals to form volatile fluorides and chlorides from different salts have been calculated [28]. To adjust the activities, and thereby the halide vapor pressures, for the desired elements, Neiri and Vandenbulke [29] suggested the use of binary masteralloys such that the component activities can be varied by several orders of magnitude.

A computer-assisted analysis of the complex vapor phase equilibria can be made to select combinations of activator salt, masteralloy, and filler which show promise to achieve the desired surface compositions. With these calculations as a guide, codeposition of Cr+Al, Cr+Si, and Si+Ge (for $\text{Mo}(\text{Si}, \text{Ge})_2$ growth [30]) has been accomplished.

Fig. 10. — Microstructure of coating and concentration profiles for 0.5Cr-0.5Mo steel using 90Cr-10Si masteralloy and 97NaF-3NaCl activator diffused at 1050 °C for 16 hours (silica filler) [27].

Figure 10 presents a microstructure and the concentration profiles for a chromize/ aluminize coating of a 0.5Cr-0.5Mo steel. For this particular coating, a 90Cr-10Si(wt%) masteralloy which has a Si activity of only 1.3×10^{-4} was used in combination with a silica filler and a mixed activator of 97NaF-3NaCl (mol.%). Thermodynamic calculations showed that the NaF greatly favors SiF_x volatiles, while NaCl favors CrCl_2 vapors. In fact, the SiO_2 filler was not inert, but reacted with the vapor to form a sodium silicate, which increased the activities of the halogens. The flaw-free microstructure and rather ideal surface composition (32Cr-2.8Si) results in an extremely low cyclic oxidation rate in air at 700 °C, as shown in figure 11 for a slightly different steel. Such very slow oxidation kinetics ($< 0.2 \text{ mg/cm}^2$ after 4.5 months) can only be explained in terms of a steady-state silica film, even for this very low temperature. Silicon has also been introduced into several austenitic alloys intended for service at much higher temperatures, and very improved oxidation behavior was noted [27].

Fig. 11.

Fig. 12.

Fig. 11. — Cyclic oxidation kinetics in air of coated steel with surface composition of 34Cr-3Si. each datum point indicates the weight-gain measured after cooling from 700 °C to room temperature [27].
 Fig. 12. — cross-section of René 80 alloy coated at 1150 °C for 24 h. In a pack with 90Cr-10Al masteralloy and 2% ZrO₂ activated by NH₄Cl [27].

Fig. 13. — Cyclic oxidation kinetics in air at 1100 °C for René 80 alloy coated using the indicated activators [27].

Figures 12 and 13 provide a second example of an “engineered” cementation pack coating, here for chromizing/aluminizing a Ni-base superalloy, with the further addition of a small reactive element content. The intention was to grow an adherent NiAl coating with sufficient chromium content to resist hot corrosion attack. Further, two different means were used to introduce into the coating a small content of a reactive element (Y or Zr) during the same isothermal coating treatment: either YCl₃ or ZrCl₄ salts were used as the activators, or else the oxides Y₂O₃ or ZrO₂ were added to the filler in combination with quite unstable chloride

activators.

Table I lists some surface compositions for such coatings, which were processed without physical contact with the pack. Compared to the usual aluminide coating, these compositions contain about 6-8%Cr and a small content of reactive element. These coatings have proven to be superior to a simple aluminide coating in laboratory hot corrosion tests [27]. Furthermore, as shown by the cyclic oxidation kinetics plot of figure 13, at least some of the coatings into which reactive elements were introduced exhibited outstanding performance. This research is continuing.

Table I. — EPMA surface analysis of René 80 substrates coated for 24 hours at 1150 °C.

Activator	Masteralloy	Avg. Bulk Surface Composition (at.%)				
		Ni	Al	Cr	Zr	Y
NH ₄ Cl, ZrO ₂	92.5Cr-7.5Al	47.6	36.2	7.6	0.18	—
ZrCl ₄ , 4wt.%	92.5Cr-7.5Al	49.9	33.4	8.1	0.22	—
NH ₄ Cl, Y ₂ O ₃ 0.02		92.5Cr-	7.5Al	47.9	38.9	6.4-
YCl ₃ , Y ₂ O ₃ 0.01		92.5Cr-	7.5Al	50.2	36.7	6.3-
YCl ₃ , CrCl ₂	92.5Cr-7.5Al	47.7	37.2	7.6	—	0.02
YCl ₃ , CrCl ₂	92.5Cr-7.5Al	50.9	34.8	7.5	—	0.00
ZrCl ₄ , 4wt.%	90Fe-10Al	44.5	40.9	1.9	0.12	—

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