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Report Prepared by
Robert A. Rapp
The Ohio State University Research Foundation
1960 Kenny Road
Columbus, Ohio 43210

under

Subcontract 19X-8B154C

for

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
Managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
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Research sponsored by the U.S. Department of Energy,
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FINAL REPORT
SUBCONTRACT 19X-8B154C

PACK CEMENTATION DIFFUSION COATINGS FOR Fe-BASE AND REFRACTORY ALLOYS

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Project Information: Nov. 1, 87 till Dec. 31, 97; \$923,133.; Dr. R. Judkins

Objective: Develop an improved scientific understanding of the halide-activated pack cementation process which will result in codeposition of several elements into diffusion coatings on steels and refractory alloys. Characterize and test these protective coatings in high temperature and aqueous corrosive environments, present and publish the results, and transfer the technology to industry.

ABSTRACT

With the aid of computer-assisted calculations of the equilibrium vapor pressures in halide-activated cementation packs, processing conditions have been identified and experimentally verified for the codeposition of two or more alloying elements in a diffusion coating on a variety of steels and refractory metal alloys. A new comprehensive theory to treat the multi-component thermodynamic equilibria in the gas phase for several coexisting solid phases was developed and used.

Many different processes to deposit various types of coatings on several types of steels were developed: Cr-Si codeposition for low- or medium-carbon steels, Cr-Al codeposition on low-carbon steels to yield either a Kanthal-type composition (Fe-25Cr-4Al in wt. %) or else a $(Fe,Cr)_3Al$ surface composition. An Fe_3Al substrate was aluminized to achieve an FeAl surface composition, and boron was also added to ductilize the coating. The developmental Cr-lean ORNL alloys with exceptional creep resistance were Cr-Al coated to achieve

excellent oxidation resistance. Alloy wires of Ni-base were aluminized to provide an average composition of Ni_3Al for use as welding rods. Several different refractory metal alloys based on Cr-Cr_2Nb have been silicided, also with germanium additions, to provide excellent oxidation resistance. A couple of developmental Cr-Zr alloys were similarly coated and tested.

The Cr-Si-rich ferrite coatings have proven to be very resistant to high temperature cyclic oxidation and to pitting corrosion in aqueous solutions. This process has been patented, and was licensed for industrial application (e.g. for waterwalls of utility boilers) by Babcock & Wilcox. Mixed pure metal powders in the pack have been used to achieve ferritic Fe-Cr-Al coatings with excellent oxidation resistance. Nearly all of the previously mentioned achievements have been published and presented in professional meetings.

Several other efforts to develop coating processes were not entirely successful. The development of a welding rod for the ORNL Fe_3Al alloy did not yield reproducible coating compositions or growth kinetics. A significant effort to produce Duriron-type (Fe-18Si-5Cr) coatings on steels was not successful, and literature for the intrinsic diffusion coefficients suggests that this task cannot be achieved. Also despite considerable trials, there is little evidence that reactive metal additions of Ce or Y could be introduced reliably into coatings by various codeposition processes.

INTRODUCTION

Carbon steels or low alloy steels have served as the workhorse materials in the construction of utility boilers, heat exchangers and other power generation installations. However, these steels suffer from corrosion attack in the forms of oxidation, sulfidation, and deposition-related corrosion in these applications. In particular, sulfidation, resulting from the presence of sulfur in low grade fuel, shortens the service life of these structures considerably. High alloy steels (e.g., stainless steels and nickel-base alloys) may survive in some of these environments, but not in highly sulfidizing gases. Likewise, the associated cost and susceptibility to stress corrosion cracking (SCC) have made these alloys unlikely choices for the major materials of construction for certain applications.

Appropriate coatings, applied to carbon or low-alloy steels, have long been sought as a means to combat these corrosion problems. The coating techniques of physical vapor deposition, chemical vapor deposition, thermal spray and plasma spray have various advantages and disadvantages. The associated high costs for low-pressure vapor deposition equipment limit its acceptability for large scale application. Evaporation and spraying methods constitute line-of-sight technologies, which make them impractical to protect certain geometries, such as the inside walls of heat exchanger tubing. Also, some spray coatings suffer oxidation, high porosity and poor adhesion to the substrate material, leaving them particularly vulnerable to corrosion attack.

A variety of pack cementation diffusion coatings have been used in the aerospace, chemical, and utility industries for about 75 years. These coatings can be inexpensively produced, they are strongly adherent to the substrate, and they are rather versatile in terms of enriching an alloying element at the surface. In fact, the long history of these diffusion coatings gives them a psychological handicap, as they may not be considered "high tech" or "trendy", and decades of occasional inadequate or shoddy application by various industrial shops may have created an unfavorable general reputation for the process. Furthermore, in the past, the pack cementation process was only practiced to add a single element to the substrate; this restriction has limited the ability of the coating to protect the workpiece from a variety of corrosion conditions.

Often, the best corrosion protection is provided by an enrichment at the surface of two or more beneficial alloying elements, which can produce a very favorable "synergistic effect" in corrosion protection. Sequential diffusion deposition of two or more elements on carbon steels and low-alloy steels can be done in industry; however, the additional (labor-intensive) furnace runs and the resulting irregular concentration profiles do not make this practice attractive. So to modernize and improve the practice of halide-activated pack cementation coatings, a means was needed to codeposit two or more elements simultaneously in the proper concentrations. However, such a process faces an inherent difficulty analogous to the electroplating of an alloy, where different elements generally exhibit greatly differing standard half-cell reduction potentials. As shown in our research, the analogous difficulty in codepositing elements by pack cementation is the greatly differing standard Gibbs energies of formation of the various volatile halides for the different metallic components of interest.

The principal goal of this DOE-sponsored research was to provide an improved scientific understanding for the halide-activated pack cementation process, which could lead to the controlled coating of various steels with two or more alloying elements in one thermal process step. As detailed in the following, this approach has achieved significant success and has led to the development of a number of different coatings with superior high-temperature and aqueous corrosion resistance in laboratory (with some industrial) testing. The Cr-Si processing technology has been transferred for application by industry, and other processes are also available without patent restrictions.

PROCESSING ACHIEVEMENTS

Research conducted at The Ohio State University (OSU) on this project has focused on producing pack cementation diffusion coatings with the codeposition of multiple alloying elements during a single furnace run. The early stages of this codeposition technology relied on the use of previously manufactured masteralloy powders which are relatively expensive. By the use of a masteralloy in the pack, the thermodynamic activity of the normally favored element could be reduced, such that with the proper choice of halide activator salt(s) and process temperature, codeposition, e.g. of Cr-Si or Cr-Al into steels, became possible.

More recently, this DOE-sponsored project has focused its effort in reducing the material cost, optimizing the diffusion process, understanding further the high temperature gas chemistry, and interacting with industry. For example: 1) The "common component effect" has been elucidated, which provides a basis for an effective choice of the halide activators in the cementation pack. 2) The costly masteralloys used in earlier pack chemistries have been eliminated; instead, inexpensive elemental powders are currently used in the cementation packs. These should also be better suited to rejuvenation in an industrial process. 3) By optimizing the activator(s), the coating time has been shortened to reduce the required energy input for the coating process. The extent of decarburization of the steel has been minimized, and the formation of the undesirable blocking chromium carbide layer on carbon-containing steels has been avoided. 4) Numerous trial runs have been conducted in response to inquiries from industry. 5) Extensive high-temperature and aqueous corrosion tests have been conducted at OSU and in the industrial laboratories of B & W and ABB. 6) The important results have been published in the open literature and presented orally at international conferences. A compendium of reprints of the papers and patents published under this project is attached in an Appendix. In addition, reports were published annually in the Proceedings of the Fossil Energy Materials Conferences conducted by ORNL. In the following, some brief accounts are given for the various project tasks. The reference numbers cited in the text refer to the relevant project publications listed in the Appendix.

Thermodynamic Analyses: The "Common Component Effect"

After the introduction by Mark Harper[8,10,14] of the combined use of a chloride plus a fluoride salt to achieve codeposition of Cr and Si into steels, a more general analysis and understanding of the use of dual activators seemed to be needed. Ning He and Dr. Ge Wang[18] cooperated to run numerous different SOLGASMIX-type computer-assisted calculations of the equilibrium partial pressures for packs containing pure Cr and pure Si powders with various combinations of activators: single salts, fluoride and chloride salts with a common cation, and fluoride and chloride salts with different cations. The conditions (activators) suitable for the codeposition of Cr and Si have been identified in this way, and these predictions have been verified experimentally. The theory about the "common component effect" and its application to the codeposition of Cr-Si was presented as an invited talk at a Materials Chemistry Conference in Vienna, and was published in the journal High Temperature Science.[18]

Codeposition Processes for Steels

A processing scheme involving two halide activator salts was developed to enable codepositing Cr + Si so that an enriched ferrite surface layer could be grown without the formation of a blocking Cr carbide surface layer. In fact, the Cr-Si codeposition into steels was achieved by the use of pure powders of Cr and Si, instead of the earlier Cr-Si masteralloy technology. In short, in a single-pack two-temperature-step process, the ferrite-stabilizing Si must be transported to the surface (via volatile fluorides) at a low temperature, e.g. 830°C. During this step, the carbon in the steel is rejected into the austenite core before the $CrCl_2$ vapors in the pack reach a sufficient vapor pressure to add Cr at a higher temperature, e.g. 1150°C. Once the ferrite case is initiated, the inward rejection of carbon in front of the growing ferrite permits the addition of Cr solute to the ferrite layer without $Cr_{23}C_6$ formation.

US patents 5,364,659, 5,492,727 and 5,589,220 on the general subject of "Codeposition of Chromium- and Silicon-Diffusion Coatings in Fe-Base Alloys Using Pack Cementation" resulted from part of the project work. Babcock & Wilcox cooperated with OSU in submitting these patent applications and has received an exclusive license to practice this technology.

A similar scheme using pure Al and Cr powders with a dual halide activator was later shown to be applicable (and easier) for the codeposition of Cr + Al into steels to generate an $(Fe,Cr)_3Al$ surface composition. A paper describing this research was published in Oxidation of Metals.[21]

In general, codeposition has been successful in depositing Cr-Al, Cr-Si, Cr-Si-V, Cr-Si-Ce coatings on low-carbon steels, Cr-Al on several different austenitic steels, Al and Al-B to transform Fe_3Al to FeAl.[12]

Codeposition Processes for Refractory Alloys

Codeposition of Si and Ge has been achieved for the growth of oxidation-resistant silicide coatings on Cr-Cr_2Nb alloys.[20] Even a relatively small soluble addition of GeO_2 into a protective SiO_2 glass film promotes a large increase in the expansion coefficient and a decrease in the viscosity, factors which greatly improve the cyclic oxidation behavior for such a coating. This study has been published in the journal Materials Science and Engineering.[20]

Aqueous Corrosion Resistance of Cr-Si-RE Coatings on Steels

In the MS thesis by Endang Pangestuti, pack cementation coatings with compositions on the order of 35Cr-4Si (and with or without a small concentration of either cerium or vanadium) were tested by scanning potentiometry in laboratory-simulated seawater. The coatings were deposited onto both 304 and 316 austenitic steels, as well as interstitial-free and low-carbon steels. The pack contained a mixture of elemental Cr and Si powders to produce the Cr-Si, Cr-Si-Ce and Cr-Si-V coatings. The additions of Ce and V to the Cr-Si coatings were found to provide important improvements in the pitting resistance, i.e. extension of the passive plateau to higher oxidizing potentials and reduction of the passive current density.[17] Even for applications in high temperature fossil fuel systems, e.g. coal gasification units, aqueous corrosion resistance is important in resisting attack by hydrolyzed deposits during downtime.

Pack Cementation Coatings to Form Welding Rods for NiAl and FeAl

Because of their inadequate fabricability to support wire drawing, the structural alloys Ni_3Al and Fe_3Al developed principally at ORNL required the creation of welding rods by another means. In fact, these intermetallic phases each also contain a number of other alloying elements to optimize their properties. In this research, an attempt was made to aluminize wires of the Ni-base and Fe-base alloy compositions corresponding to the ORNL-developed Ni_3Al and Fe_3Al materials, except that the compositions of the wires to be coated were low, or devoid, of Al. Then the goal was to deposit coatings sufficiently rich in Al so that the average compositions corresponded to those for the intermetallic phases. For the Ni-base alloy, an external coating of Ni_2Al_3 was grown. For this system, suitable conditions (pack composition, temperature, and times) were found to achieve the goal. As a most favorable aspect for the growth of this coating, the external Ni_2Al_3 layer grew dominantly by the inward diffusion of Al, so that the resulting layer did not entrap pack particles. This research was published in Scripta Met. et Mater.[19]

The analogous problem for coating the Fe-base alloy to create the Fe_3Al average composition was more difficult, as the required Fe_2Al_3 external layer grew by dominant outward diffusion of Fe. In that case, a coating free of pack entrapment can only be grown by an "above pack" arrangement. For the available time and resources, a sufficiently controlled coating process could not be achieved.

The Silicide Coating of Steels to form the Fe_3Si (Duriron) Composition

The Fe_3Si composition, especially when alloyed with about 4-6 wt.% Cr, constitutes the metallic composition with the best resistance to inorganic acids such as nitric and sulfuric acids. The corresponding commercial alloy Duriron is brittle and can only be fabricated by casting. Obviously, a Fe_3Si diffusion coating on a steel with more ductility and toughness would find numerous important applications, an opportunity that has been obvious to researchers around the world for at least 50 years. However, for reasons that have not been obvious previously, past research has not been able to grow a dense diffusion coating of Fe_3Si on iron. This search for the "Holy Grail" of coatings became the MS theses for Mingang Zhu and Ted Cruise. Although considerable progress was made, the desired coating process was not achieved. However, the experiments clearly pointed out that significant coating growth occurred by outward Fe diffusion, so that pack pickup was unavoidable unless an "above pack" arrangement was used. According to the limited literature on interdiffusion in the Fe-Si system, the magnitudes for the intrinsic diffusion coefficients for Fe and for Si cross in the range of composition from pure Fe to Fe_3Si. Since in the diffusional growth of Fe_3Si on Fe, vacancies diffuse in the same direction as the component with the lower intrinsic diffusion coefficient, in the Fe-Si system, the vacancies in growing Fe_3Si flow from opposite directions to the Fe-10Si composition, a circumstance which inherently generates voids and a porous coating. The experiments of Ted Cruise could not uncover any halide activator which would avoid the inherent porosity. However, siliciding with some fluoride activators did create a Si surface composition higher than Fe_3Si, a previously unattainable result. At this time, there is considerable doubt that the growth of an Fe_3Si layer on steels can ever be achieved.

CONCLUDING REMARKS

This research demonstrated some considerable improvement in the understanding and development of halide-activated pack cementation diffusion coatings. In addition, it served as a valuable learning and training experience for a number of students and Post-Doctoral researchers. As shown in the Appendix, the important results have been published and presented orally at international meetings. Theoretical and experimental details for the individual topics which are summarized above in this Final Report can be found in more detail in the Abstracts of the project publications listed in the Appendix.

APPENDIX

PROJECT HISTORY

This project was initiated in November 1987, and through December 31 1998, a total of $923,133 has been budgeted for this research. As detailed in the next section, the project has supported the research of 6 MS students , 2 PhD students , and 5 Post-Doc researchers. A list of 21 publications in the open literature follows; many presentations at many conferences were made, but such an accounting list has not been kept. In addition, three US patents have been granted. The participants received a number of Honors and Awards which are also listed.

PRINCIPAL PROJECT PERSONNEL

Principal Investigator:

1. Robert A. Rapp, Distinguished University Professor Emeritus

MS Students:

1. Ed Naylor, Cr-Al coatings for austenitic alloys, engineer for Akzo Chemicals

2. Denis O'Connell, Cr coating mechanism for Fe-Cr ferritic alloys, school teacher

3. Fred Geib, Aluminizing Fe_3Al and Cr-Al coating iron, metallurgist, Timpkin Steel Co.

4. Mingang Zhu, Siliconizing iron, metallurgist, a Cleveland machinery Co.

5. Ted Cruise, Siliconizing-chromizing iron, metallurgist, SeleeCo.

6. Chris McVay, Aluminizing iron and nickel alloys, metallurgist, Allegheny-Ludlum Co.

7. Endang Pangestuti, Aqueous corrosion resistance of Cr-Si coated steels, corrosion engineer for Indonesian Oil Co.

PhD Students:

1. Dr. David Miller, Cr-Al coating of steels, research metallurgist, LTV Steel Co.

2. Dr. Mark Harper, Cr-Si coating of steels, metallurgist, Haynes International.

Post-Doc. Researchers:

1. Dr. Patrick Choquet, Cr-Al coating of steels, research metallurgist, France.

2. Dr. Ge Wang, Cr-Si and Cr-Al coating of steels, senior techn. staff, TRW.

3. Dr. Xiao Ru Wan, Aqueous corrosion resistance of Cr-Si coatings on steels, Assoc. Prof., Beijing Univ. for Aeronautical Eng.

4. Dr. Yrong He, Siliciding of ORNL Cr-Nb Alloy, Post-Doc. NASA-Lewis Lab.

5. Dr. Minhui Zheng, advanced computer studies, Columbus, OH.

PROJECT PUBLICATIONS IN OPEN LITERATURE

1. D. M. Miller, S.C. Kung, S.D. Scarberry and R.A. Rapp, "Simultaneous Chromizing-Aluminizing Coating of Austenitic Stainless Steels", Oxid. Metals, 29, (1988) 239; ibid, Thermochemistry of Alloys NATO-ASI Series, C286, H. Brodowsky and H.J. Schaller, Eds., (1987) pp. 547-558.

Chromium and aluminum were simultaneously codeposited by diffusion into austenitic stainless steel substrates, by a single step pack cementation process, The mechanisms for the formation of diffusion-coated products on 304 and 316 stainless steels and on Incoloy 800 are discussed. The formation of the brittle beta outer layer was minimized by variations in the pack composition and activator. The coated 304 and 316 steels exhibited excellent scaling resistance upon oxidation in air at 1000 C.

2. R. A. Rapp, "Pack Cementation Coating of Steel for High Temperature

Applications", paper 131, Corrosion 88, NACE.

The thermodynamics and the mechanism for the growth of diffusion coatings on steels by the pack cementation method were outlined.

3. V. A. Ravi, P. Choquet, and R.A. Rapp, "Thermodynamics of Simultaneous Chromizing-Aluminizing of Alloys in Halide-Activated Cementation Packs", MRS International Meeting on Advanced Materials, Vol. 4. Tokyo (1989), pp. 483-500.

The equilibrium partial pressures of the gaseous species in halide-activated cementation packs have been determined with a computer program SOLGASMIX. The activities of Al and Cr have been incorporated into the calculations and the results indicate that codeposition of Al and Cr is possible using NaCl, $AlCl_3$, or NH_4Cl as activators and Al-Cr masteralloys with compositions between 90 and 95 w/o Cr. In contrasting the coating of Ni or Fe substrates, the partial pressures of Ni halides are considerably lower than those of the Fe halides, indicating that displacement reactions occur when Fe substrates are coated.

4. V. A. Ravi, P. Choquet and R. A. Rapp, "Chromizing-Aluminizing Coating of Ni- and Fe-Base Alloys by the Pack Cementation Technique", Oxidation of High Temperature Intermetallics, T. Grobstein and J. Doychak, eds., TMS, Warrendale, PA, (1989) pp. 127-145.

Because of large differences in thermodynamic stabilities of the various halides of Al and Cr, the simultaneous deposition of Cr and Al in a halide-activated cementation pack is only possible for very specific, limited combinations of conditions. Computer-assisted computations of the equilibrium vapor pressures for given binary Cr-Al masteralloys and given halide salts identify the necessary pack conditions. Chloride activator salts, not fluorides, are required to chromize/aluminize alloys in a single step. Coatings on pure Ni, Ni-20Cr, and superalloy IN 731 offer microstructures and compositions which promise good mechanical properties and oxidation/corrosion resistance.

5. P.A. Choquet, M.A. Harper, and R.A. Rapp, "Chromizing-Aluminizing and Chromizing-Siliconizing Coating of a Ferritic Steel", Proceedings of the 7th European Conference on Chemical Deposits from a Gas Phase, Perpignan, France, June 1989.

Simultaneous deposition of Cr-Al and Cr-Si as diffusion coatings for a ferritic steel (Fe-12Cr) substrate have been carried out using the pack cementation method. The simultaneous codeposition of Cr with Al is thermodynamically possible for chloride-activated packs when the activity of Al is about three orders of magnitude lower than the Cr activity; for Si-Cr codeposition, the activity of Si must be approximately one order of magnitude lower than that for Cr. The experimental tests of the theory agree reasonably with the predictions, and the resulting coatings promise improvement in resistance to oxidation and corrosion.

6. P.A. Choquet, E.R. Naylor and R.A. Rapp, "Simultaneous Chromizing and Aluminizing of Iron-Base Alloys", Materials Science and Engineering, A121, (1989) pp. 413-418.

Simultaneous deposition of Cr and Al into Fe-base alloys has been achieved by a pack cementation process. Specific conditions were identified which incorporate a small concentration of Ti into the Cr-Al coating on a ferritic steel (Fe-15Cr) substrate. Pack compositions and processing conditions were demonstrated which avoid both the formation of an external carbide layer on a 2.25-1Mo-0.15C steel, and the formation of a brittle external NiAl layer on austenitic stainless steels.

7. R.A. Rapp, "Pack Cementation Coatings of Steels for Fossil Fuel Environments", Corrosion 1989, NACE, paper #532.

Computer-assisted SOLGASMIX calculations serve to identify the proper pairs of Cr-Al binary masteralloy composition and halide activator salt to balance the arrival fluxes of Cr- and Al-halide species to the substrate surface so that specific surface compositions can be achieved. Such calculated predictions were tested experimentally for different types of alloys: Fe-2.25Cr-1Mo, Fe-12Cr, 304 SS, and Incoloy 800.

8. M.A. Harper and R. A. Rapp, "Codeposition of Chromium and Silicon in Diffusion Coatings for Iron-Base Alloys Using Pack Cementation" Fourth International Conference on Surface Modification Technologies, Paris, 1990.

The codeposition of Cr and Si into low-alloy steels has been achieved using the pack cementation process. Surface compositions of the coatings are 20-40 wt% Cr and 2-4 wt% Si. Cyclic oxidation tests of coated coupons show a dramatic decrease in the oxidation kinetics of the substrate material.

9. M.A. Harper and R. A. Rapp, "Chromized-Siliconized Diffusion Coatings for Iron-Base Alloys by Pack Cementation", Paper #66, Corrosion 91, NACE 1991; ibid Materials Performance, Sept. (1991) pp. 41-44.

The codeposition of Cr and Si into a 2.25Cr-1.0Mo-0.15C steel, Alloy 800, and 304 stainless steel has been achieved using the pack cementation process. The ferritic coating produced on the Cr-Mo steel was approximately 225 microns (9mils) thick, whereas the inward diffusion of Cr and Si produced a two-phase structure of ferrite plus austenite for the 304 stainless steel. Cyclic oxidation testing in air for the coated Cr-Mo steel and 304 stainless substrates showed a dramatic decrease in the oxidation kinetics compared to the uncoated alloys.

10. M.A.Harper and R. A. Rapp, "Chromized-Siliconized Pack Cementation Diffusion Coatings for Heat-Resistant Alloys", in Heat-Resistant Materials, K. Natesan and D.J. Tilack, Eds., ASM Internat., (1991), pp. 379-386.

Chromium and silicon were codeposited into various alloys by the pack cementation process. The ferritic coating on a 2.25Cr-1.0Mo steel had a surface composition of Fe-38wt%Cr-3Si. This diffusion coating was produced using a 90Cr-10Si masteralloy and a "double activator" consisting of a molten salt solution of 95 mol%NaF-5%NaCl. For 304 stainless steel, the inward diffusion of Cr and Si produced a two-phase structure of ferrite and austenite at the surface. For austenitic Alloy 800, about 3wt%Si was added to the surface without effecting a phase change. Cyclic oxidation in air for these coated alloys showed a dramatic decrease in oxidation kinetics compared to the uncoated alloys.

11. R. Bianco, M.A. Harper, and R.A. Rapp, "Codeposition of Elements in Diffusion Coatings by the Halide-Activated Pack Cementation Method", Journal of Metals, Nov. (1991), pp. 68-73.

The codeposition of two or more elements in a halide-activated cementation pack is inherently difficult because of large difference in the thermodynamic stabilities for their volatile halides. However, computer-assisted analyses of the pack equilibria have identified suitable combinations of masteralloys and activator salts. The codeposition of Cr plus Al, or Cr plus Si, by pack cementation has yielded diffusion coatings with excellent resistance to high-temperature oxidation and corrosion for a wide range of alloy substrates.

12. F.D. Geib and R.A. Rapp, "Diffusion Coatings for Iron Aluminide Fe_3Al by Halide-Activated Pack Cementation", Processing and Manufacturing of Advanced Materials for High Temperature Applications, V.A. Ravi and T.S. Srivatsan, Eds., TMS Warrendale, PA, (1992) pp. 347-360.

The intermetallic compound Fe_3Al has excellent high-temperature corrosion resistance and is being developed for 600-700°C service in low-P_{O2} sulfidation environments. The sulfidation resistance of Fe_3Al-5Cr-0.5Nb is poor because the formation of Fe-, Cr-, and Al-sulfides interferes with the protective alumina scale. Diffusion-aluminized coatings of nominal composition Fe-(36-50) at% Al (with trace amounts of boron for improved ductility) have been developed to restore the protective alumina scale formation. Characterizations of coated microstructures and concentration profiles, and the results of cyclic oxidation tests, are presented.

13. R.A. Rapp, "Fundamental Aspects of High-Temperature Corrosion", J. Phys. IV, Colloque C9, **3**, Dec. (1993) pp. 1-15.

Despite the inherent difficulty to codeposit two or more elements with greatly differing stabilities for their halide species, cementation coating packs can be designed with selected combinations of powdered masteralloys and halide activator salts whereby the elements are codeposited to yield a desired surface composition. Selected examples for effective aluminizing/chromizing of Ni-base superalloys and for chromizing/siliconizing of steels are presented.

14. M.A. Harper and R.A. Rapp, "Codeposited Chromium and Silicon Diffusion Coatings for Fe-Base Alloys Via Pack Cementation", Oxid. Metals, Vol. 42, Nos. 3/4, (1994) pp. 303-333.

The simultaneous deposition of Cr and Si into plain carbon, low-alloy, and austenitic steels using a halide-activated pack-cementation process is described. Computer-assisted (STEPSOL) calculations indicate that NaCl-activated packs are chromizing, while NaF-activated packs deposit more Si and less Cr. The use of a "dual activator" (e.g. NaCl + NaF) allows for the deposition of both Cr and Si in desired amounts. A coated Fe-2.25Cr-1.0Mo-0.15 coupon with a surface composition of Fe-34 wt% Cr-3Si was cyclically oxidized in air at 700°C for over four months and 47 cycles. The weight gain was very low (<0.2

mg/cm^2) with no scale spalling detected. Such coated coupons have shown excellent oxidation-sulfidation resistance in reducing, sulfur-containing atmospheres at temperatures from 400 t0 700^{o}C and in erosion and erosion-oxidation testing in air at 650 and 850^{o}C.

15. R.A. Rapp, "The Codeposition of Elements in Diffusion Coatings by the Pack Cementation Method", Proceedings of International Workshop on Gasifiers", Petten, Netherlands, June 1993; Materials at High Temperatures, 11, (1993) pp. 181-18.

For a variety of ferritic and austenitic steels, codeposition of Cr plus Al, or Cr plus Si, has led to surface compositions with excellent oxidation resistance, and in some cases excellent sulfidation and aqueous corrosion resistance, and even hot erosion resistance. The principles for codeposition are discussed, along with some specific examples of particulariy effective coatings on steels.

16. F.D. Geib and R.A. Rapp, "Simultaneous Chromizing-Aluminizing Coating of Low Alloy Steels by a Halide-Activated Pack Cementation Process", Oxid. Metals, 40, (1993) pp.213-228

The simultaneous chromizing-aluminizing of low-alloy steels has achieved Kanthal-like surface compositions of 16-21Cr and 5-8 wt% Al by the use of cementation packs with a Cr-Al masteralloy and an NH_4Cl activator salt. An initial deposition of Al into the alloy induces the phase transformation of austenite to ferrite at the 1150^{o}C process temperature. The low solubility of carbon in ferrite results in the rejection of solute carbon into the ausenite core , thereby preventing the formation of an external Cr-carbide layer which would otherwise block aluminizing and chromizing. Parabolic cyclic-oxidation kinetics for alumina growth on the coated steels were observed over a wide range of relatively low temperatures (637-923^{o}C).

17. X. Wan, G. Wang and R.A. Rapp, "Resistance to Aqueous Corrosion of Steels Protected by a Cr-Si Diffusion Coating", Proceedings of International Corrosion Congress, Sept. 1993, Vol. 1, pp. 353-369, NACE, Houston, TX.

The simultaneous deposition of Cr and Si to form a diffusion coating on two steels (AISI 1045 and 4140) formed surface compositions approximating 30Cr-3 to 4 wt% Si. Coated coupons were corrosion tested in either 1N H_2SO_4 or 3.5wt% NaCl solution at room temperature. Coupons coated using the Cr-Si masteralloy had superior corrosion resistance in 1N H_2SO_4, while steels coated in packs containing elemental metal powders suffered pitting corrosion. The coated coupons were not adequately resistant to pitting corrosion in 3.5 wt% NaCl solution.

18. N. He, G. Wang and R.A. Rapp, "The Common Component Effect in Multiphase, Multicomponent Equilibria", High Temperature Science, vol. 34, (1994) pp. 117-125.

For the halide-activated pack cementation process, codeposition of Cr and Si into diffusion coatings on steel surfaces can be achieved by using two halide salts to optimize the partial pressures of $CrCl_2(v)$ and $SiF_2(v)$. The SOLGASMIX computer program was used to calculate the equilibrium vapor pressures of different metal halide species for different activator salt combinations. Two salts with the same cation develop low partial pressures for $CrCl_2(v)$ and $SiF_2(v)$, which are not high enough to codeposit Cr or Si into the coating. Two salts with different cations produce a different result. Some combinations, such as NaCl and CaF_2, have high and comparable partial pressures of $CrCl_2(v)$ and $SiF_2(v)$. The role of the partial pressure for the alkali metal is elucidated.

19. C. McVay and R.A. Rapp, "Diffusion Aluminizing Coatings to Produce Ni_3Al Alloy Welding Rods", Scripta Met. & Mater. Vol. 33, (1994) pp.201-204.

A pack chemistry of 40 wt% Ni-Al powder (30 at% Ni-70 Al), 1.75 wt% AlF_3, and balance Al_2O_3 was used to produce Ni_2Al_3 coatings on alloyed Ni coupons that contained the required amount of Al for the average composition of a Ni_3Al alloy welding rod. The coating time was 7.8 hr. at a temperature of 1000°C. Coating produced at shorter times showed slower kinetics and a lower Al surface concentration due to an adherent layer of sintered pack powder that was not present for long coating times.

20. Y-R. He, R. A. Rapp and P.F. Tortorelli, "Oxidation-Resistant Ge-Doped Silicide Coating on $Cr-Cr_2Nb$ Alloys by Pack Cementation" Materials Sci. & Eng., vol. A222, (1996) pp.109-117.

The halide-activated pack cementation process was modified to produce a Ge-doped silicide diffusion coating on $Cr-Cr_2Nb$ alloys in a single processing step. Higher Ge content in the pack suppressed the formation of $CrSi_2$ and reduced the growth kinetics of the coating. Under cyclic and isothermal oxidation conditions, the Ge-doped silicide coating protected the Cr-Nb alloys from significant oxidation and from pesting by forming a Ge-doped silica film.

21. M. Zheng and R.A. Rapp, "Simultaneous Aluminizing and Chromizing of Steels to Form (Fe,Cr)$_3$Al Coatings", Oxid. Metals, vol. 49, Nos.1/2 (1998) pp. 19-30.

A cementation pack involving halide activators and elemental Al and Cr powders has been used to achieve the codeposition and diffusion of Al and Cr into low-alloy steels. A two-step treatment at 925°C and 1150°C yields dense and uniform ferrite coatings of about 400 microns thickness, with surface compositions of approximately Fe$_3$Al plus several percent Cr. Upon cyclic oxidation in air at 700°C, the coated steel exhibits a negligible 0.085 mg/cm^2 weight gain for 1900 one-hour cycles. Virtually no attack was observed on coated steels tested in a simulated boiler atmosphere at 500°C for 500 hr. But coatings with a surface composition of only 8 wt% Cr suffered limited sulfidation attack in the simulated boiler atmosphere at temperatures higher that 500°C for 1000 hr.

22. G. Wang and R. A. Rapp, "Codeposition of Chromium with Silicon or Aluminum into Low-Alloy Steels", Heat Resistant Materials II, K. Natesan, P Ganesan, and G. Lai, Eds., ASM Internat., (1995) pp.471-476.

Pack cementation diffusion coatings can inexpensively modify the surface chemistry of plain-carbon or low-alloy steels. Excellent adherence of the coating to the substrate is one of the most distinct advantages of this process. Significant variations in the surface composition can be achieved by a codeposition process. The resistance of ferritic Fe-Cr-Si and Fe-Cr-Al coatings to isothermal and long-term cyclic oxidation at elevated temperatures and to aqueous corrosion is reported.

PATENTS

R.A. Rapp and M.A. Harper, "Codeposition of Chromium and Silicon Diffusion Coating on Fe-Base Alloys using Pack Cementation", U.S. Patent No. 5,364,659, Nov. 1994.

R.A. Rapp, G. Wang and E. Pangestuti, "Method of Depositing Chromium and Silicon on a Metal to Form a Diffusion Coating", U.S. Patent No. 5,492,727, Feb. 1996.

R.A. Rapp, G. Wang and E. Pangestuti, "Method of Depositing Chromium and Silicon on a Metal to Form a Diffusion Coating", U. S. Patent No. 5,589,220, Dec. 1996.

HONORS AND AWARDS

During this project, a number of Honors and Awards were received by project participants:

Mark Harper:

TMS Graduate Student Paper Award

BFGoodrich Collegiate Inventor's Award (one of 3 in USA), 1992

Fulbright Scholarship to University of NS Wales, Australia 1992

Morris Cohen Outstanding Graduate Student Award of Corrosion Division of the Electrochemical Society, 1992

SAMPE Outstanding Graduate Student Award, 1991

Robert A. Rapp:

Distinguished Engineering Alumnus, Purdue University, 1988

National Academy of Engineering 1988

Distinguished University Professor, Ohio State University, 1989

Outstanding Achievement Award, High Temperature Materials Div., The Electrochemical Soc., (1990)

Membe d'Honneur, Societe Francaise de Metallurgie et de Materiaux, 1990

Acta/Scripta Metallurgica Lecturer, 1991-93

Lumley Research Award, OSU College of Engineering 1991

BFGoodrich Collegiate Inventor's Awards (one of three annual awards in USA), with student Robert Bianco, 1991; with Mark Harper, 1992.

Ulrick R. Evans Award, British Corrosion Institute, 1992

Chevalier dans l'ordre des Palmes academiques, Ministere de l'Education et de la Culture Francaise, 1993

Fellow, The Electrochemical Soc. 1993

Fellow, NACE International, 1994

Honorary Doctorate Degree, Institute Polytechnique de Toulouse, France, 1995.

Henry B. Linford Award for Distinguished Teaching, The

Electrochemical Soc., May 1998.

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