Coating and near-surface modification design strategies for protective and functional surfaces

M.P. Brady*, P.F. Tortorelli, K.L. More, E.A. Payzant, B.L. Armstrong, H.-T. Lin, M.J. Lance, F. Huang, and M.L. Weaver

This paper discusses strategies for controlling the surface chemistry and microstructure of materials to form protective and functional surfaces through controlled gas-metal reactions. Potential applications range from oxidation, corrosion, and wear resistance to electrochemical devices such as fuel cells to catalysts. Phenomenological examples are presented for coatings designed to self-grade under oxidizing conditions, and for the growth of simple and complex (binary and ternary) nitride and carbide phase surface layers by nitridation and carburization reactions. Specific systems discussed include environmental barrier coatings (EBCs) for Si-based ceramics such as Si_3N_4 and SiC, the growth of continuous, protective CrN/Cr_2N, TiN, VN, NiNbVN, and related simple nitride layers on Fe- and Ni-base alloys, the possible formation of ternary nitride and carbide surface phases (e.g. Ti_3AlC_2 and related MAX-phases) on intermetallic surfaces to improve oxidation resistance, and the formation of composite near-surface structures in Ag-SiO_2 and Co(Mo)-$Co_6Mo_6C_2$ systems.

1 Introduction

Protective scale formation for low and high temperature environments remains a key materials challenge to the successful implementation and advancement of energy production and related technologies. In keeping with the theme of the 2004 European Federation of Corrosion conference on "Novel Approaches to the Improvement of High Temperature Corrosion Resistance," this paper will put forward some thoughts on how coatings or surface modification can alter near-surface composition and microstructure in potentially beneficial ways to achieve corrosion resistance using principles of gas-metal reactions. Extrapolation of these concepts to functional applications will also be discussed. This is the third in a series of related papers focusing on design strategies for oxidation/corrosion resistance and the control of surface chemistry for functional applications [1, 2]. These papers are not meant to be an exhaustive compilation of established approaches or a rigorous discussion of various oxidation mechanisms; rather, they speculate on some concepts and highlight some preliminary experimental phenomenological observations that show potential for possible future development.

In a simplistic sense, control of surface composition can generally be accomplished in one of two ways: 1) by deposition of coatings to modify surface composition relative to the substrate or 2) by application of internal and/or selective gas reactions (oxidation, nitridation, carburization, etc.) to precipitate new phases, modify existing phases, or preferentially segregate one or more elements from the substrate alloy to the surface. The latter phenomena encompass the basis for protective oxide scale formation, including the subsequent formation of scales on deposited coating alloys. However, it can also be extended to the formation of protective and/or functional nitride, carbide, etc. surface layers by elevated temperature gas reactions. These aspects will be discussed in the latter half of this paper.

2 Self-graded metallic precursor coating concepts

A key advantage to coatings is that the substrate alloy can be optimized for properties other than corrosion resistance (i.e. ductility, formability, creep strength, etc.). The key limitation is that the physical/chemical/mechanical differences between the substrate and the coating can lead to detrimental interactions, which can limit lifetime. Chief among these is interdiffusion between coating and substrate, which can result in the formation of brittle phases or the loss of protective scale-forming elements. For example, in thermal barrier coating (TBC)/superalloy systems, a major problem is the loss of Al from the bond coat to the substrate superalloy over time at temperature. This ultimately contributes to an inability to maintain Al_2O_3 growth and subsequent TBC failure [3, 4]. Design of coatings in consideration of the substrate, as well as substrate alloy design in consideration of the fact that it will be coated, has received increased attention in recent years [e.g. 5, 6]. For example, recent work by *Gleeson* et al. [4] has identified Ni-Al-Pt bond coat compositions for which Al diffuses from the superalloy substrate into the bond coat, helping to maintain a reservoir of Al for Al_2O_3 formation by the bond coat, rather than loss of Al from the bond coat into the substrate. Consideration of coating/substrate compatibility issues have also been extended to include a number of design and processing approaches, many of which utilize functionally graded structures to manage chemical and thermomechanical incompatibilities [7, 8].

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DOI: 10.1002/maco.200503875 © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

For applications utilizing oxide coatings, a potentially useful alternative to direct deposition of oxide compositions may be the deposition and subsequent complete oxidation of a thin metallic precursor alloy layer. The advantage is that the deposited metallic layer may self grade as it is converted to oxide, with the possibility of obtaining improved adherence and/or chemical compatibility with the substrate. For proof of principle exploration, a series of Al_2O_3-forming alloys based on Cr_2Al-Y (79.7Cr-20Al-0.3Y weight percent, wt.%), NiAl-Hf (69.6Ni-30Al-0.4Hf wt.%), NiCrAlY (79.7Ni-10Cr-10Al-0.3Y wt.%), and FeCrAlY (74.7Fe-20Cr-5Al-0.3Y wt.%) were sputtered deposited as thin layers (1–5 micron thick) onto Kyocera's SN282 and Honeywell Ceramic, Components NT154 Si_3N_4 and carborundum hot-pressed SiC (hexoloy) substrates. The technological driving force for such a coating was to explore the possibility of using Al_2O_3 as a volatility barrier for SiO_2-forming ceramics in high-temperature oxidizing environments containing water vapor. SiO_2 scales can be severely compromised due to volatilization and accelerated oxidation in the presence of water vapor, especially under the high pressure/high gas flow conditions encountered in gas turbines applications [9, 10]. Al_2O_3 scales are more resistant to water vapor [11], but also have a much higher coefficient of thermal expansion than do the Si_3N_4 and SiC substrates (~ 9 vs $\sim 3 \times 10^{-6}\,^{\circ}C$), which leads to cracking, spallation, and coating failure. This work was focused on trying to form a graded duplex scale, consisting of an outer Al_2O_3 layer overlying an inner graded oxide layer of the base metal(s) of the alloy (e.g. Cr, Ni, Fe), Si, and Al. Such grading may lead to enhanced chemical stability and, conceivably, reduce stress generation in the surface layers(s) during cooling because changes in CTE may occur more gradually throughout the volume of the modified material

The coated substrates were pre-oxidized at 1150–1250 °C for up to 1 h in pure O_2 to completely convert the deposited alloy layers to oxides. Representative cross-sections of the deposited coatings after the oxidation pretreatment are shown in Fig. 1. The microstructures of the oxidized coatings were qualitatively similar, and consisted of a 0.5 μm outer layer of Al_2O_3, overlying an inner Al-Si-O base layer 2–3 μm thick. The Al-Si-O layers also contained the base alloy components (Cr, Fe, Ni), and the levels of Si and Al varied across the layer, from more Si-rich near the substrate interface to more Al-rich at the interface with the outer Al_2O_3 layer. Little Al migrated into the ceramic. All the coatings were adherent after the oxidation pretreatment, although some surface cracking was observed, especially in the NiCrAlY and Cr_2AlY precursor samples. Photo-stimulated luminescence spectroscopy (PSLS) stress measurements [12, 13] of the Al_2O_3 scales (Fig. 2) indicated significant tensile stresses in the outer Al_2O_3 layers, suggesting that whatever grading that occurred was insufficient to greatly mitigate CTE mismatch issues (on the other hand, such high stresses do indicate good coating adhesion). A short term 1000 °C, 72 h oxidation exposure resulted in demixing of the oxide phases in the graded layer and/or significant spallation in the NiCrAlY and Cr_2Al-Y precursor coatings; however the NiAl-Hf and FeCrAlY precursor coatings remained adherent. Fig. 3 shows a cross-section of a NiAl-Hf precursor coating after a 1200 °C, 500 h exposure in air + 15% water vapor at 10 atm (details of typical exposure conditions provided in reference [14]). The coating did not act as a water vapor barrier, with significant accelerated/nonprotective SiO_2 growth evident below. Although these results indicate this approach is not promising for EBC applications, self-graded oxide coatings were successfully formed from the deposited metallic precursor alloys, and there may be other applications where such an approach may be of interest.

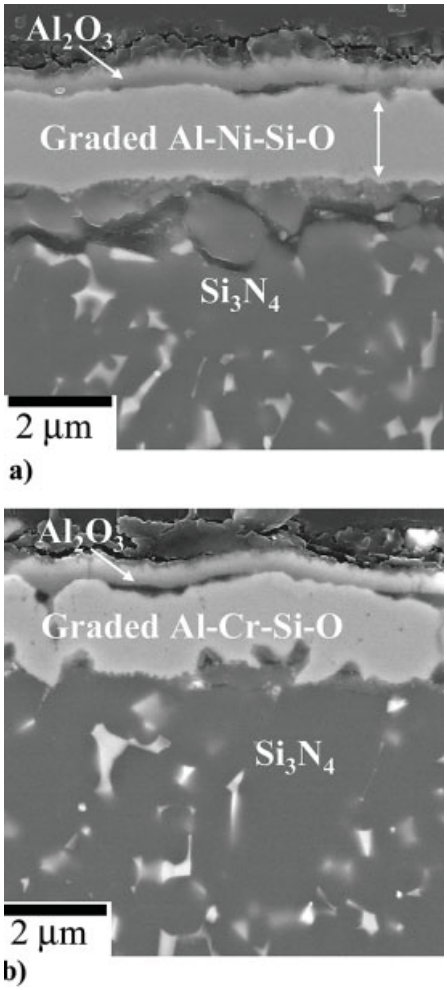

Fig. 1. Scanning electron cross-section images of sputtered deposited metallic precursor coatings on SN282 Si_3N_4 after a 30 min/1150 °C/O_2 exposure. a) NiAl-Hf, b) Cr_2Al-Y. Qualitatively similar microstructures were formed on all precursor metallic coating/substrate combinations studied

For the EBC application, a variation on conventional metallic coating strategy was subsequently investigated [13]. Alloy coatings are typically sufficiently thick such that they remain primarily metallic and can reform their protective oxide scale in the event of cracking or damage. Alumina-forming compositions based on Fe or Ni were not considered attractive options for Si-based ceramics because they may react with Si to form low melting point ($\sim \leq 1200\,^{\circ}C$) eutectics. In the case of Si_3N_4 substrates, Al/AlN is more stable than is Si/Si_3N_4 (at unit activities) and the loss of Al from the coating to the substrate would limit coating lifetime, as well as potentially degrade the mechanical properties of the Si_3N_4. In an attempt to manage this issue, an Al_2O_3-forming Ti-based alloy, Ti-51Al-12Cr atomic percent (at.%) was selected for evaluation [13, 15]. The nitrides of Ti are more stable than those of Al and Si and the lowest melting point eutectic in the Ti-Si system is around 1330 °C. The goal was for the TiAlCr coating to self grade, such that a Ti-N rich barrier layer is formed at the coating/substrate interface, leaving the Al to act as a reservoir for Al_2O_3 scale formation.

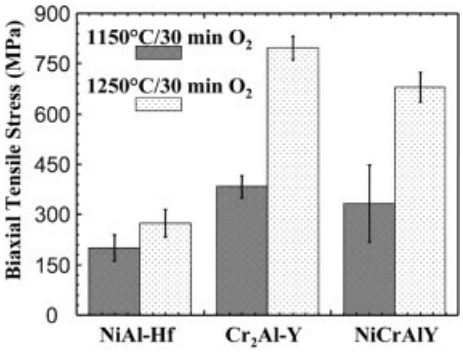

Fig. 2. Typical room-temperature PSLS stress measurements of the Al_2O_3 scales formed on oxidized metallic precursor coatings on SN282 SI_3N_4. Tensile stresses were observed for all precursor metallic coating/substrate combinations studied, with the exception of one NiAl-Hf/SiC sample, which showed a biaxial compressive stress of $\sim$ 200 MPa

Fig. 4 shows an oxidized cross-section of an initially 8–10 μm thick TiAlCr (Ti-51Al-12Cr at.%) [13] sputtered deposited metallic bond coat on SN282 Si_3N_4. The coating self graded in the desired manner. At the onset of oxidation, Al was selectively oxidized from the TiAlCr coating to form Al_2O_3. Concurrently, Ti reacted with the substrate Si_3N_4 to form a Ti-rich nitride. The movement of the Ti to the

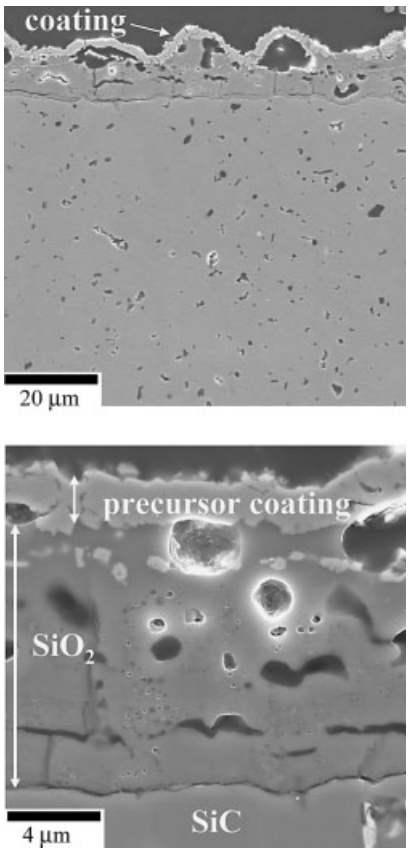

Fig. 3. Scanning electron cross-section image of a sputter deposited/oxidized NiAl-Hf precursor coating on SiC after 500 h at 1200 °C in air + 15% water vapor at 10 atm. Penetration of water vapor through the coatings resulted in rapid, non protective SiO_2 formation on the SiC substrate. a) low magnification overview, b) remaining coating on oxidized substrate (SiC)

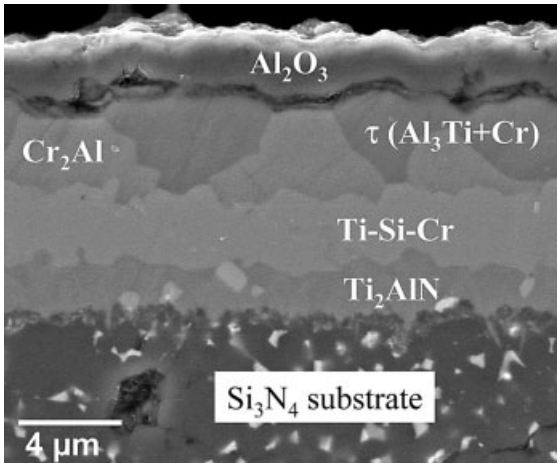

Fig. 4. Scanning electron image of a sputter deposited Ti-51Al-12Cr at.% coating on SN 282 Si_3N_4 after three 100 h cycles at 1000 °C in air [13]. The τ region underneath the scale contained $\sim$ 65 at.% Al, and the Ti_2AlN region at the interface with the Si_3N_4 contained $\sim$ 60 at.% Ti (phase identification based on composition)

Si_3N_4 was sufficiently more rapid than the consumption of Al to form Al_2O_3 such that the unusual and beneficial situation of Al-enrichment (relative to the initial coating composition) underneath the Al_2O_3 scale resulted. The Cr rejected from the oxidation front and Si moving out from the Si_3N_4 reacted with Ti to form a Ti-Si-Cr rich phase as an intermediate layer between the Al-rich outer layer and the Ti-rich inner layer. Effectively, the coating alloy formed a Ti-N rich barrier in-situ at the substrate/coating interface, which prevented loss of Al, at least under the short-term exposure conducted. Significantly more work for the EBC application will be necessary to determine if this approach is feasible for long lifetimes. The growth rate of Al_2O_3 would likely also limit this type of coating to no higher than 1100–1150 °C for the 40,000 h lifetimes needed. (Details are provided in reference [13]). However, the observed pattern of behavior does demonstrate the potential of this form of self grading to manage coating/substrate interdiffusion.

3 Surface modification approaches

3.1 Continuous protective nitride and carbide surface layer formation

Protective oxide scale forming alloy design principles can readily be extended to the formation of continuous layers of nitrides, carbides, borides, sulfides, etc. Under high-temperature conditions in the presence of oxygen, these phases will subsequently form oxides. However, there are low and high temperature situations where such initial dense (nitride, carbide, etc.) layer formation may be desirable.

One such example is the formation of protective layers for metallic bipolar plates in proton exchange membrane fuel cells (PEMFCs). Bipolar plates serve to electrically connect the anode of one cell to the cathode of the next in a fuel cell stack to achieve a useful voltage. Metallic alloys would be ideal as bipolar plates because they are amenable to low-cost/high-volume manufacturing, offer high thermal and electrical conductivities, and can be made into thin sheet or foil form (0.1–1 mm thick) to achieve high power densities [16–

18]. However, most metals exhibit inadequate corrosion behavior in PEMFC environments (aqueous/acidic in the 60–80 °C temperature range) due to formation of passive oxide layer(s), which increase cell resistance, and contamination of the polymer membrane by metallic ion dissolution (as little as 10 ppm can degrade behavior) [19–21]. Metal nitrides are of interest as protective coatings because they offer an attractive combination of high electrical conductivity and corrosion resistance [21]. However, conventional coating methods tend to leave pin-hole defects [22], which result in local corrosion and unacceptable behavior. A potential solution is the use of thermal nitridation reactions to form the protective nitride surface layer [23, 24]. Pinhole defects are not expected because at elevated temperatures thermodynamic and kinetic factors favor reaction of all exposed metal surfaces. Rather, the key issues are nitride layer composition, morphology, and adherence, which can potentially be controlled through proper selection of alloy composition/microstructure and nitridation conditions. Thermal nitridation is also a relatively inexpensive, industrially viable technique (usually used to impart wear resistance) and is viable for covering complex surface geometries such as bipolar plate flow field features.

Fig. 5 shows a cross-section of a model Ni-50Cr alloy that was nitrided at 1100 °C for 2 h in N_2 [24]. A dense, continuous CrN/Cr_2N surface layer was formed, overlying an extensive internally nitrided zone. This material exhibited excellent behavior during a 4000 h corrosion exposure under simulated anodic and cathodic PEMFC conditions and 1000 h of single-cell fuel cell testing, with no evidence of significant pin-hole defects, no increase in surface contact resistance, and virtually no metal ion dissolution [24]. This result provides strong proof of principle evidence that thermal nitridation can be used to form dense, pin-hole free nitride layers to provide protection under aqueous corrosion conditions. Current work for this application is focused on forming such nitride layers on lower cost Fe-Cr base alloys for PEMFC bipolar plates [25, 26].

Other continuous nitride layers can also readily be formed by this approach. Fig. 6 shows typical cross-sections for Fe-(5-15)Ti, Ni-(5-15)Ti, and Ni-10Nb-5V alloys which formed continuous, external layers of binary TiN, and a Ni-Nb-V nitride by thermal nitridation. Note that a wide range of nitride microstructures, from fine, equiaxed TiN grains to coarse, columnar Ni-Nb-V nitride base phase grains are possible. Again, the potential advantage of this approach is the growth of pinhole free layers on components with complex surface geometries to provide corrosion protection in aqueous environments.

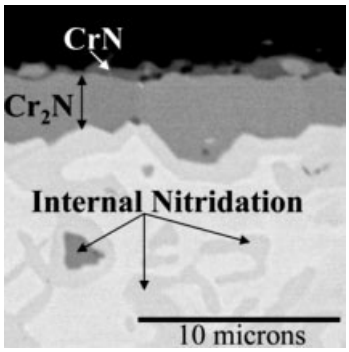

Fig. 5. Scanning electron image of continuous, external Cr-nitride formed on Ni-50Cr after nitridation at 1100 °C for 2 h in N2 [23–25]

As discussed by *Rubly* and *Douglass* [27], much higher levels of Cr are needed in Ni-Cr alloys to form an external Cr-nitride layer on nitridation, as compared to the level of Cr needed to form an external Cr-oxide layer on oxidation. Other than a possible improvement in wear resistance due to the high hardness of the Cr-nitride surface layer, there would be no advantage to pre-nitriding Ni-Cr alloys to improve high temperature oxidation resistance. However, some situations may exist where it may be possible to preferentially segregate a protective oxide scale forming element to the surface by a nitridation, carburization, etc. reaction, at a lower alloying level than is needed for oxidation. It is interesting to note that the TiN and related surface layers shown in Fig. 6 were formed on Ni and Fe base alloys at relatively low levels of additions, much lower than that needed with Cr/Cr-nitrides.

Following the above reasoning, the level of Al needed to form a continuous AlN scale on nitridation may (hypothetically) be lower for a particular alloy than the level needed to form an Al_2O_3 scale in oxygen/air. On exposure to a high temperature oxidizing environment, the AlN layer could then subsequently form a protective Al_2O_3 scale. The advantage of this approach over a conventional pre-oxidation treatment to form Al_2O_3 directly is that the nitride layer could heal the Al_2O_3 scale if it became cracked or otherwise damaged, whereas a scale formed on pre-oxidation may not be able to reform the Al_2O_3. This speculated protection scheme clearly is not viable for all applications, and there would certainly be limitations based on the thickness of the initial AlN layer that could be formed, and CTE and related issues with AlN.

3.2 Ternary nitride and carbide protective surface layer formation

Nitridation, carburization, etc. surface treatments to improve high temperature oxidation resistance are an area of increasing interest, especially for intermetallic phases such as TiAl which are borderline for protective oxide scale formation [28–31]. Results to date for nitridation and related surface treatments have been mixed, with true protective Al_2O_3 scale formation by such surface treated TiAl alloys generally not reported. (Some success has been achieved by the introduction of Cl to the surface of TiAl alloys, see reference [32] for further details). At the same time, there has been great recent interest in layered ternary nitride and carbide phases, due to a unique combination of properties, including their ability to be easily machined [33, 34]. This class of materials is referred to as MAX phases, and follow a general formula of $M_{n+1}AX_n$, where n = 1,2, or 3, M is an early transition metal, A is an A group element, and X is carbon or nitrogen [33, 34]. Some of these phases, notably Ti_3AlC_2 and Ti_2AlC, also form continuous protective Al_2O_3 scales on exposure in air, despite their low Al content (comparable to or less than that of Ti_3Al, which does not form Al_2O_3) [35–37]. Reduced oxygen permeability in these structures compared with the corresponding binary Ti_3Al phases of equivalent Al content is likely a key contributor to their ability to form protective Al_2O_3. A number of these ternary phases with transition/refractory metals exist and are potentially capable of protective scale formation.

These MAX phase observations suggest the possibility of a carburization pretreatment to improve the oxidation resistance of related intermetallic phases [2]. For example, one could envision surface treatment of a Ti_3Al alloy under carburization conditions to form a case layer of Ti_3AlC_2, which would then be capable of forming protective Al_2O_3 [2]. An interesting

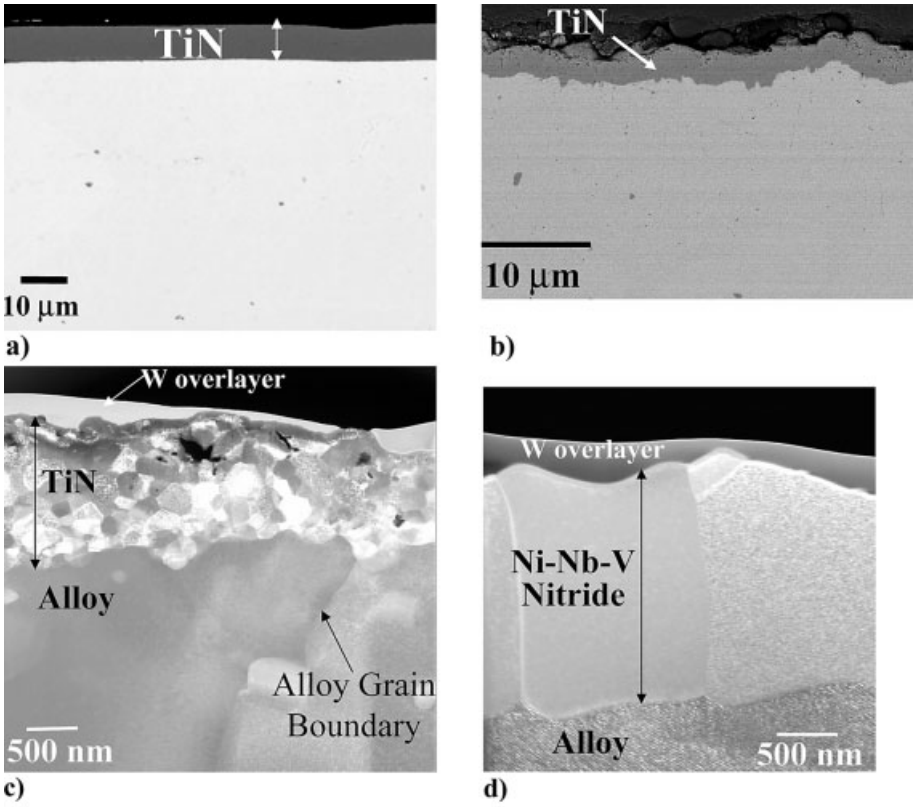

Fig. 6. Cross-section scanning electron (a,b) and scanning transmission electron (c, d) images illustrating a range of microstructures in continuous nitride layers. a) continuous TiN layer on Ni-10Ti-2.5W-0.15Zr wt.%, 1100 °C/24 h/N_2, b) continuous TiN layer on Fe-15Ti wt.%, 1100 °C/36 h/N_2, c) nanoscale equiaxed TiN on Ni-10Ti-0.15Zr wt.%, 1100 °C, 24 h, N_2, d) coarse, columnar structure of a ternary Ni-Nb-V nitride on Ni-10Nb-5V wt.%, 1100 °C/24 h/N_2. The W overlayer in (c, d) was for sample preparation purposes

question is whether such ternary phases can be formed directly as continuous surface layers by gas reactions. For direct ternary interstitial analogs of intermetallic phases, such ternary phase formation may occur readily. However, phases such as Ti_3AlC_2 are not simply carbon interstitial analogs of Ti_3Al and would require atomic/rearrangement during the gas reaction to form. The formation of anti-perovskite Cr_3PtN by nitridation of Cr_3Pt intermetallic was recently demonstrated and it was speculated that structural and bonding aspects of intermetallic compounds may favor formation of related ternary carbide and nitride phases on gas reaction [2, 38]. The formation of Cr_3PtN also depended greatly on the stoichiometry of the Cr_3Pt, such that a nearly single phase continuous external Cr_3PtN layer formed on Cr-25Pt at.%, but a complex internal lamellar structure formed on Cr-17Pt at.% (Fig. 7) [38]. *Inoue* et al. recently reported the plasma nitridation of TiAl to form Ti_2AlN, and by quantum chemical simulation found evidence that formation of the ternary nitride was influenced primarily by chemical interaction of the N with the Ti sublattice [39, 40]. The formation of Ti_2AlC was also reported by plasma carburization of TiAl [41], although oxidation resistance of the carburized surface was apparently not studied.

Fig. 8 shows the cross-section of an initial attempt to carburize a Ti_3Al alloy to form a ternary carbide surface to improve oxidation resistance. An outer layer of TiC was formed, overlying an inner region consisting of Ti, Al, and C. X-ray diffraction data suggested that the inner layer may have contained Ti_3AlC_2 and/or Ti_2AlC, however, the data was not definitive and cross-section transmission electron microscopy will be needed for positive phase identification. A simple air oxidation screening at 900 °C showed no evidence of improved oxidation resistance via the carburization treatment. A close examination of the as-carburized structure indicated that fingers of TiC penetrated well into the inner layer, i.e. the inner Ti-Al-C containing layer was not continuous and unlikely to be able to form a protective Al_2O_3 layer. Further work will clearly be needed, however, it is believed that the potential at

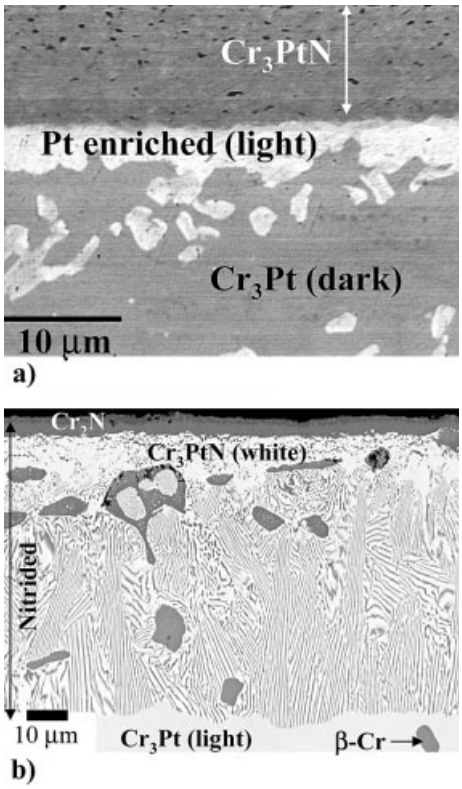

Fig. 7. Scanning electron cross-section images of nitrided Cr_3Pt alloys showing effect of Cr:Pt stoichiometry [38]. a) 75Cr-25Pt at.%, 24 h/950 °C/N_2, b) 83Cr-17Pt, 24 h/1000 °C/N_2

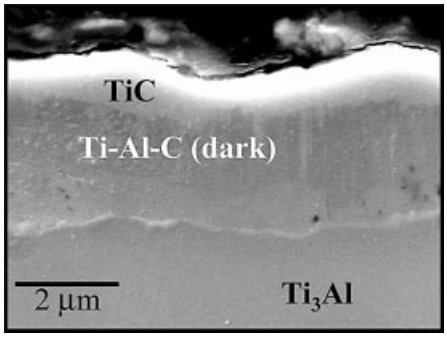

Fig. 8. Scanning electron cross-section image of Ti-25Al at.% after carburization at 950 °C for 24 h in ~ 0.1 atm CH_4

least exists to improve oxidation resistance by formation of surface layers of MAX and related phases via carburization pretreatments.

4 Functional surface formation by gas reactions

A possible extension of the aforementioned phenomena is the use of gas reactions as a synthesis approach to functional near-surface structures [2, 38, 42]. Two reaction schemes are of particular interest: 1) the use of multi-phase alloys as templates to form composite surfaces and 2) exploiting the atomic level mixing and structure of intermetallics as precursors to form complex ceramic phases. The potential technological utility of these phenomena as a synthesis route is yet to be determined, however, early results appear to show some promise.

Fig. 9 shows the surface of a vapor deposited Ag-Si thin film on a single crystal MgO substrate after oxidation. The Ag-Si system was selected as a model system because these elements are immiscible, Si readily forms an oxide in air while Ag is relatively noble, and Ag-SiO_2 composite structures are of general interest for functional applications such as nonlinear optical devices [43]. The film was adherent after the oxidation treatment, and went from mirror-like as deposited to tinted/transparent after oxidation. Preliminary EDS analysis in the SEM suggested the formation of regions containing 75 – 100 nm size range "spheres" of Ag dispersed in SiO_2 (note that TEM analysis to confirm this structure has not yet been performed). The original intention was to form this type of structure by in-place internal oxidation, however, Ag has a tendency for surface migration and the structure may have resulted from surface diffusion of the Ag rather than an internal oxidation process.

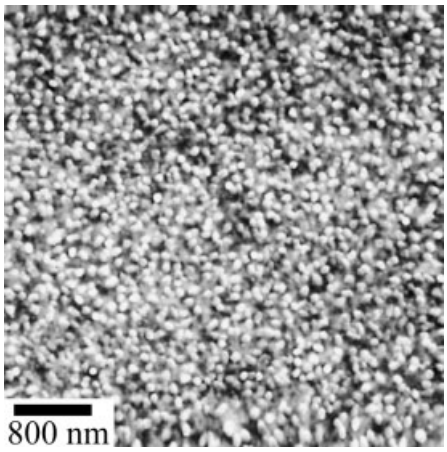

Fig. 9. Scanning electron surface image of a ~ 250 nm Si-Ag layer vapor deposited on single-crystal MgO after oxidation at 725 °C for 10 min in air. Preliminary analysis suggested that the bright phase is Ag-base and the dark phase is SiO_2. Note that regions of coarse, micron sized Ag-base "spheres" were also observed

Fig. 10 shows surface micrographs of CoMo intermetallic alloys after carburization in an attempt to synthesize a bimetallic (ternary) carbide. Such phases are of increasing interest as catalysts for a variety of industrial processes, including hydrotreating to remove S, N, and O impurities from fossil fuels, ammonia synthesis, water gas shift reaction to produce hydrogen, and fuel cell catalysts [44 – 47]. They are typically formed by gas reactions of complex oxide precursors or by molecular precursor or chemical synthesis [48 – 50] routes. The use of intermetallic precursors offers the potential to leverage a different set of precursor stoichiometries and structures to form new complex carbide and nitride phases not attainable by currently used synthesis routes [2, 38, 42]. It also offers the opportunity to leverage the initial metallic phase equilbria of the precursor alloy to control the morphology and structure of the phases that are formed; for example, to synthesize a near-surface composite structure based on an initial two-phase alloy precursor microstructure [2, 38, 42]. Preliminary analysis of the surface of several carburized CoMo alloys in an attempt to form the $Co_6Mo_6C_2$ phase [44] suggests that both single-phase $Co_6Mo_6C_2$ and composite mixtures of

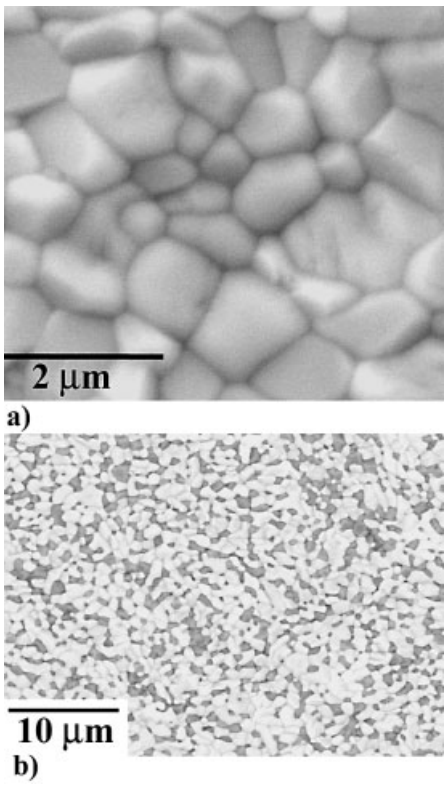

Fig. 10. Surfaces of CoMo intermetallic alloys after carburization illustrating range of surface features possible [51]. a) secondary electron image of Co-45Mo consistent with single phase $Co_6Mo_6C_2$ formed on CoMo, b) Back scatter electron image of a two-phase Co(Mo) + CoMo alloy Co-25Mo showing $Co_6Mo_6C_2$-light and Co(Mo)-dark phase formation (preliminary identification)

$Co_6Mo_6C_2$ with Co(Mo) could be formed, depending on the initial precursor alloy composition (Fig. 10) [51]. Detailed microstructural characterization of the surfaces and evaluation of catalytic properties to test this approach are currently in progress.

5 Concluding remarks

This paper combined speculation regarding new approaches to mitigating oxidation/corrosion with preliminary results in order to highlight oxidation phenomena of potential interest for future development. Many of these approaches appear to show promise for controlling surface chemistry. However, the key to their ultimate technological utility for applications as protective scales lies in the ability to form these phases as dense, continuous surface layers. This appears to be possible, particularly for the growth of protective nitride layers on Ni- and Fe-base alloys. Of scientific interest will be to study the similarities and differences that arise from the growth of surface nitride, carbide etc. layers on multi-component/multi-phase alloys, compared to the more well studied oxide phase formation. For functional applications, gas reactions of complex multi-component/multi-phase alloys to form complex near-surface surface structures appear to be of both scientific and technological interest. Such efforts are an extension of the surface modification strategies currently employed in semiconductor and related industries, as well as for catalysts, sensors, etc, generally for the formation of simple (binary) oxide phases by gas reactions of pure metals [52, 53]. The driving force is the potential gain possible through improved control of the resultant surface via the manipulation of the precursor alloy composition and microstructure (i.e. leveraging the metallurgical variables of the precursor alloy), as well as the possibility to form new phases based on here-to-fore untapped precursor metallic and intermetallic structures.

6 Acknowledgements

The authors gratefully acknowledge ongoing discussions with *T. Besmann, B. Gleeson, J.A. Haynes, B.A. Pint, R.A. Rapp, J.L Smialek*, and *I.G. Wright* in the area of high temperature oxidation reactions, and *T. Brummett, C.A. Carmichael, L.D. Chitwood, K. Cooley, G. W. Garner, M. Howell, P. Sachenko*, and *L.R. Walker* for assistance with much of the experimental work presented in this paper. The authors also thank *J.H. Schneibel* and *M. Radovic* for reviewing this manuscript. This research was sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research Materials (ARM) Program, the Assistant Secretary for Energy Efficiency and Renewable Energy For Distributed Energy Programs, and the Hydrogen, Fuel Cells, and Infrastructure program. Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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(Received: April 29, 2005) W 3875