We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



12

Corrosion of Metal – Oxide Systems

Ramesh K. Guduru and Pravansu S. Mohanty
University of Michigan, Dearborn, Michigan
USA

1. Introduction

Corrosion of materials occurs because of several factors; for example the application environment, operational conditions, presence of non-equilibrium phases, failure of the protective phases or layers in the materials, etc. In addition to the electro-chemical phenomena occurring in the corrosion process, operational conditions, such as temperature could influence the corrosion rates to different degrees depending on the materials involved. The effect of temperature is known to be severe on the corrosion phenomenon due to the dependence of corrosion rates on diffusion of materials. From the materials perspective, presence of non-equilibrium phases or second phases and their thermodynamic stability, microstructures, properties, and protective layers could affect the corrosion rates. Usually oxide systems are known for their protective behavior because of their stability and hindrance to the diffusion of different ionic species. Understanding their stability and role in prevention or slowing down of corrosion rates is, therefore, very important for engineers to design new material systems with desired properties and structures for corrosion resistant applications. Although metallic alloys with oxide second phase are extensively used in high temperature applications for creep resistance, literature suggests that addition of different kinds of oxide particles could help control the corrosion properties. In this chapter, an overview will be given on the corrosion behavior of different oxide systems and their role in corrosion resistant applications of the oxide particle embedded metallic systems in different environments, including low and high temperature applications.

2. Corrosion process and inhibition

Corrosion is a continuous degradation process of a material. As shown in figure 1, the corrosion of a given material system can take place because of two external major components, namely the environment or the electrochemical system (eg: atmosphere, acid or corrosive media), and operating conditions shown by arrows (eg: stress or pressure, erosion and temperature etc.). The process of electrochemical corrosion occurs in multiple steps, where the ions are involved with a media for ionic motion, and at the same time the material involved should be conductive enough to participate in the electron transfer for a mutual charge transfer process due to the ionic motion. During the process of corrosion, the materials can undergo changes into a new form of the material which could be protective or reactive in further process. The driving force for the corrosion is usually the thermodynamic instability of a given material system in the superimposed surroundings and working conditions.

There are different types of corrosion that can take place on a material system and they could be uniform type or localized type. In uniform corrosion, as the name suggests, corrosion takes place all over the surface. On the other hand, localized corrosion can be several kinds, such as galvanic corrosion, pitting corrosion, selective attack, stray current corrosion, microbial corrosion, intergranular corrosion, crevice corrosion, thermo galvanic corrosion, corrosion due to fatigue, fretting corrosion, stress corrosion, hydrogen damage etc. (Jones, 1992). For more details on each process, the reader is suggested to refer to any review articles or books on corrosion science.

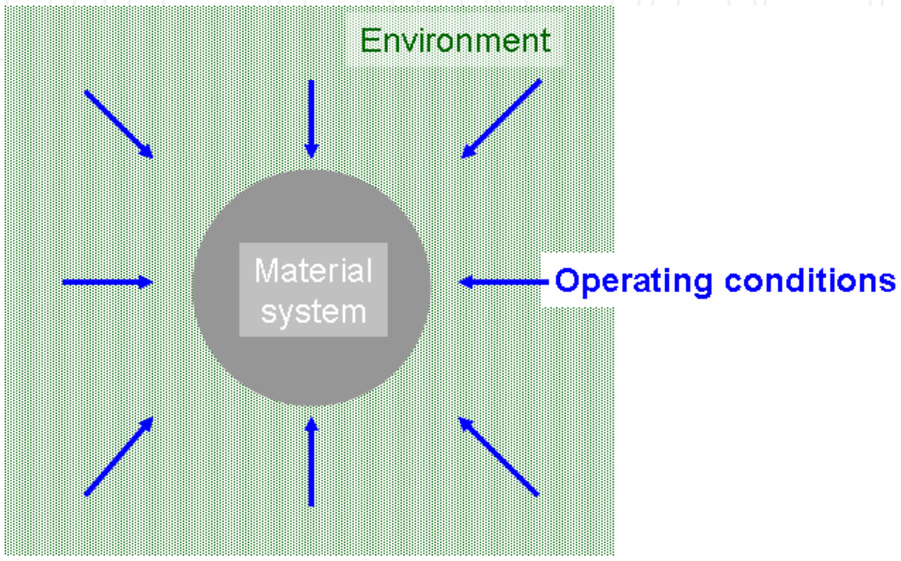


Fig. 1. Schematic for corrosion of a material system with the components involved in the corrosion process.

Different factors contribute to the corrosion under various situations during the service. For example, the components used in hot sections of gas turbine engines and hypersonic vehicles operate under extremely oxidizing, erosive and high temperature conditions, where a combination of high temperature mechanical strength along with excellent oxidation and corrosion resistance are required. In the applications related to marine and aircraft propulsion systems, quite corrosive and erosive environments exist around the components under different operational temperatures with cyclic nature. Therefore depending on the application, the surroundings and operational conditions vary; and usually high strength and high temperature protective coatings are used to meet the requirements of such harsh operating conditions.

There are different approaches adopted to reduce or slow down the corrosion of a material system depending on the type of application and corrosive environment. The simplest and preferred approach among all of the methods is through the application of protective or non-reactive phases over the material system in the form of coatings, which keeps the material from exposure to the surroundings. A classic example for an oxide layer assisted corrosion resistant alloy is stainless steel, in which the alloying element chromium (Cr) forms an impervious stable oxide layer (Cr_2O_3, also called chromia) along the grain boundaries and surface, as shown in the schematic in Fig. 2. Usually grain boundaries are

prone to corrosion attack because of defects and high energy sites unless they are protected via passivation. Although, chromia cannot be used alone because of brittleness, chromium enhances passivity when alloyed with other metals and alloying elements in stainless steel.

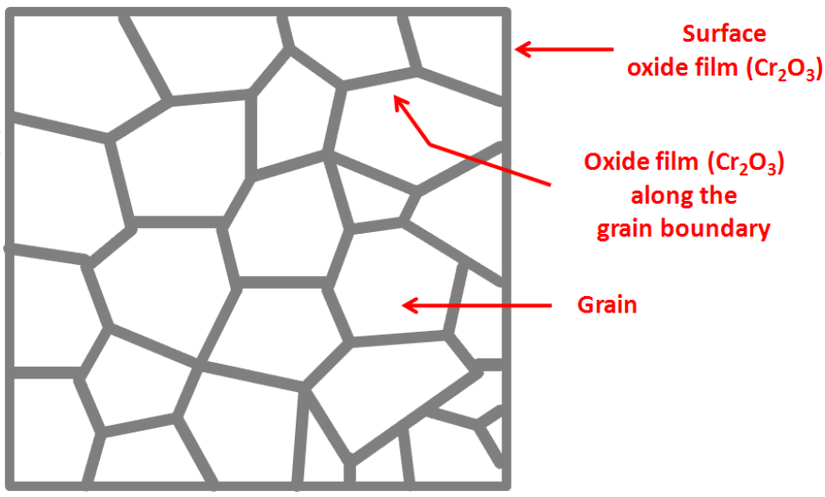


Fig. 2. Schematic for a thin passive layer of chromia (Cr_2O_3) along the grain boundaries as well as on the surface of stainless steel for corrosion protection.

As another example, Aluminum (Al) and Al – alloys could be discussed. However, the corrosion resistance of Al and its alloys can be attributed to the formation of passive oxide layer on their surfaces alone (Jones, 1992), as shown in the schematic in Fig. 3.

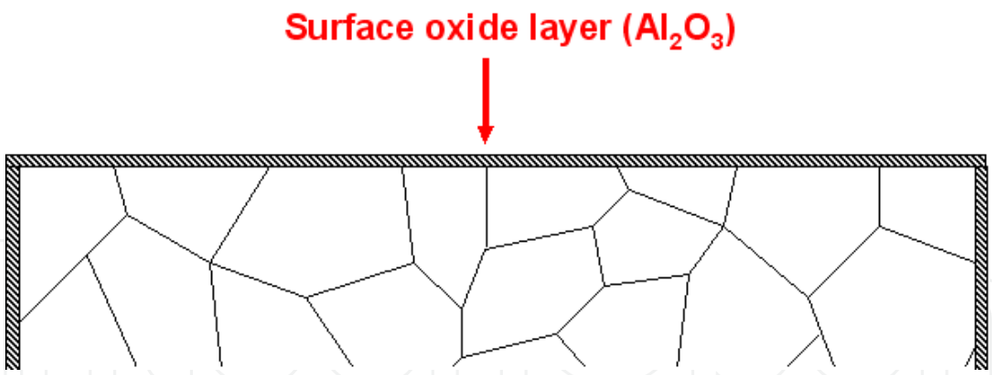


Fig. 3. Schematic for a thin passive layer of alumina (Al_2O_3) on the surface of the Aluminum and/or Aluminum alloys for corrosion protection.

There are a number of oxide systems as protective coatings, as well as dispersoids, demonstrating superior performance in terms of corrosion and other properties, which will be reviewed later in this chapter. However, in cyclic operating conditions with temperature fluctuations and wear conditions the oxide layers may not be suitable; as they can break down due to mismatch of the thermal coefficient of expansion (CTE) with underneath phases, or due to wear, or combination of both, and thereby lead to localized pitting, crevice corrosion, etc., of the underlying substrate. In addition, high temperatures can enhance the diffusion rates. To this end, protective coatings with oxide particle embedded systems are

found to be more useful. Most of the high temperature coatings and oxide dispersion strengthened (ODS) alloys are embedded with highly stable oxide phases, which can provide mechanical stability as well as enhance the corrosion and oxidation resistance. In addition to the oxide dispersoids, ODS alloys employ alloying elements (eg: Cr, Al etc.) in such a way that the oxide layers are formed on the surfaces as well as at the grain boundaries at high temperatures during the operation, which then act as protective layers from the corrosion point of view. The oxide dispersoids in the ODS alloys can provide mechanical stability with improved creep resistance.

Here, we will touch base on the corrosion phenomenon of oxide layer and oxide particle assisted corrosion behavior of metallic materials at low and high temperature applications with a brief review, and a case study will be presented on the corrosion phenomenon of oxide particle embedded high temperature composite coatings developed by thermal spray technique.

3. Oxide particle embedded metallic systems

Metal – oxide dispersed systems are well known for excellent mechanical properties because of high strength of the reinforcing ceramic oxide phases. Dispersion of hard oxide particles also enhances the surface properties, such as hardness and wear resistance, which are critical for tribological applications. The oxide particles also improve high temperature creep strength of the metallic materials by acting as obstacles to dislocations, reducing the deformation along the grain boundaries due to the diffusion processes or grain boundary rolling mechanism by pinning the grain boundaries. Thus the oxide particle embedded metallic systems have a vital role in many applications. Their processing is usually done in many routes depending on the type of application as well as the amount of material required. Here, we will briefly go through some of these techniques to introduce the reader to different processing routes. However, for more information one can refer to the literature and review articles on composite processing techniques. Following is the list of a few approaches usually employed to develop the metal – oxide composite systems (Kainer, 2006).

Powder processing route: In this approach, metal and oxide powders are blended together using different methods (eg: ball milling or mechanical alloying) and then compacted and sintered or consolidated into required shapes or bulk solids.

Melting route: There are different number of processes fall under this category that involve molten metals. This route is usually applied to low melting metal matrix composites, in which the metal ingots or pieces are melted and then the oxide particles are dispersed in the molten metal prior to solidification.

Electrodeposition: The oxide particles are suspended in an electrolyte which helps develop the matrix coating. Suspension of oxide particles along with continuous stirring in the electrolyte can embed the particles in the metal matrix during electrodeposition process.

Vapor deposition: Physical vapor deposition techniques (eg: electron beam evaporation, sputtering etc.) can be used to develop composite coatings using multiple targets in co-deposition approach with intermittent reactive deposition process.

Spray deposition: Different number of processes have evolved in this category in which a stream of molten metal droplets are deposited on a substrate to build the matrix layer; and for composites, the oxide particles are co-sprayed to embed them in the matrix layers.

Reactive formation: In this approach, selective oxidation of certain phases in the bulk structures with exothermic reactions results in the in-situ formation of composites.

As listed above there are several approaches available for processing metal – oxide systems, and their corrosion properties are going to be dependent on the processing technique employed too. For example, the processing defects like porosity, improper bonding between the matrix and the oxide dispersoids, and their interfacial properties can influence the corrosion behavior quite extensively. Wetting of the oxide particles becomes a critical factor in some of the processing approaches to deal with the particle - matrix bonding. Fig. 4 shows a schematic for interfacial bonding of the second phase particles with matrix along the grain boundaries and triple junctions. In addition, high temperatures in some of the processing techniques may cause an interfacial reaction between the metal matrix and the dispersed second phase particles, thereby the interfacial stability and its properties play an increasingly important role in the corrosion. It is also possible that the interfaces could become prone to corrosion attack by providing preferential sites. In spray deposition approach splat boundaries, porosity, and distribution of the oxide particles may play an important role in deciding the corrosion properties. Added to that, the microstructures of the composites could also vary from process to process. The effect of some of these parameters on the corrosion of different metal – oxide systems is discussed in brief in the following sections.

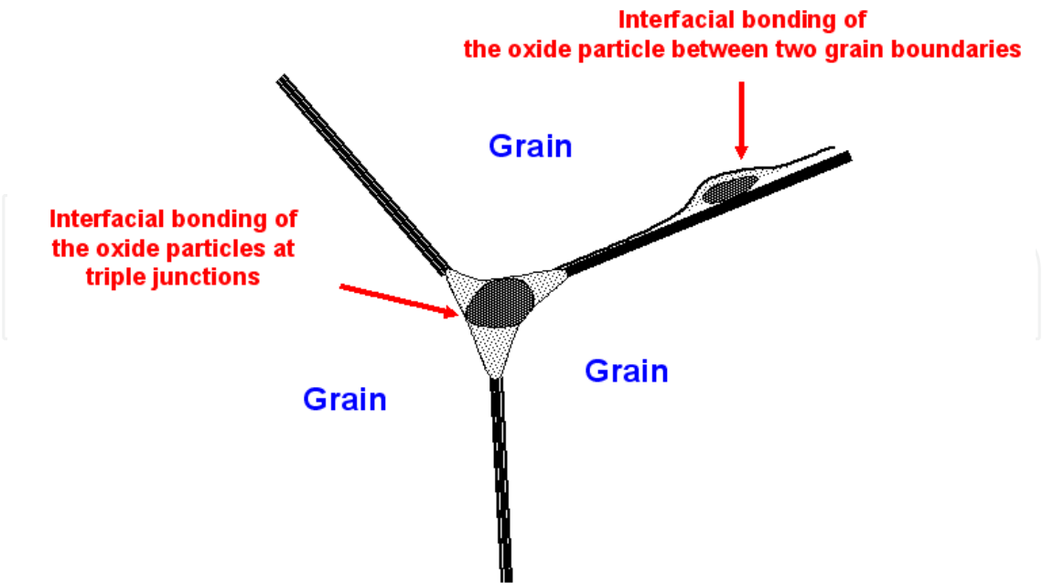


Fig. 4. Schematic for interfacial bonding of second phase particles at grain boundaries and triple junctions.

4. Overview of corrosion phenomena of metal – Oxide systems

Although, the metal matrix composites are well suited for mechanical, tribological and high temperature applications, it is to be clearly noted that their corrosion aspects could be considerably different, as well as complex, compared to the monolithic metallic systems. Corrosion of metal matrix composites could arise due to different reasons, such as electrochemical and chemical interaction between the constituent phases, microstructural effects, and possibly from processing related issues too (Cramer & Covino, 2005). Usually, composites have higher tendency to corrode because of the multiphase structure with metal matrix. If the second phase structure is conductive a galvanic cell can be formed within the system. For example, metallic composites reinforced with graphite or semi-conducting silicon carbide could undergo severe corrosion compared to the pure metals. Galvanic corrosion is not a problem if the second phase dispersoids are insulating, for example, oxide particles.

It is also very important that the second phase particles be uniformly distributed in the metal matrix. The effect of oxide particle size, volume fraction and their pretreatment can also influence the corrosion phenomenon. The other important factors that can contribute to the corrosion are surface morphology, porosity, stresses, bonding, defects at the matrix and dispersoid interfaces, crystallographic structure, and the type of oxide phase dispersed. For example, bonding between Al and Al_2O_3 (alumina) plays a crucial role in the corrosion of Al - Al_2O_3 composites. Usually the corrosion rate of the composites is measured by weight loss and the corrosion studies conducted on Al - Al_2O_3 composites in NaCl solution for prolonged periods showed considerable weight loss due to pits or microcrevice formation in the matrix near the particle-matrix interfaces, as well as from the particle dropout. The corrosion via pit initiation and propagation was determined to be due to the weak spots in the air-formed Al_2O_3 film because of the discontinuities and the second phase particles (Nunes & Ramanathan, 1995). In the case of 6061-T6 alloy mixed with 10 vol% Al_2O_3, poor corrosion resistance was reported to be due to poor bonding at the matrix and oxide particle interfaces (Bertolini et al., 1999). The Al alloys AA 6061 and AA 2014 embedded with Al_2O_3 particles exhibited stress-corrosion cracking when subjected to three-point beam bending along with alternate or continuous exposure to NaCl solution (Monticelli et al., 1997). Although addition of Al_2O_3 may seem to be detrimental in terms of corrosion resistance of Al alloys, with the combination of wear and corrosive conditions, the corrosion resistance of 6061 and 7075 Al alloys was observed to improve with the Al_2O_3 second phase dispersion (Fang et al., 1999; Varma & Vasquez, 2003) along with the enhancement of wear resistance. In marine biological applications, the microbial corrosion was also reported to occur in the Al - Al_2O_3 composites due to biofilm formation at the interfaces of Al and Al_2O_3 particles (Vaidya et al., 1997). In environmental and marine biological applications, the protective chromium oxides are not very benign because of their toxicity and as a result usage of chromia coatings is restricted. However, different rare earth oxides were proposed as alternatives for protection of Al alloys because of their cathodic inhibition properties (Aramaki, 2001; Hamdy et al., 2006; Hinton et al., 1986, 1987; Lin et al., 1992). Usually rare earth oxides are very useful for aerospace applications because of their high temperature oxidation resistance. According to Hamdy et al., (2006) CeO_2 (ceria) treated Al alloys exhibited improved corrosion resistance due to oxide layer thickening. Muhamed & Shibli (2007) also showed improved corrosion performance of Al – CeO_2 composites, but it was not in proportion to the amount of CeO_2 incorporated.

Presence of rare earth oxides was proved to enhance the corrosion resistance of Ni composites also. It was reported that the Ni matrix reinforced with micron CeO_2 particles possessed good corrosion resistance compared to Ni – ZrO_2, Ni – partially stabilized ZrO_2 (PSZ), and pure Ni coatings (Qu et al., 2006). Although the corrosion process usually proceeds along the grain boundaries, in the case of Ni – CeO_2 composites the corrosion path was observed to be preferentially along the Ni/CeO_2 interfaces, instead of Ni grain boundaries. Along with that, higher corrosion resistance of CeO_2 was also observed to enhance the corrosion resistance of Ni/CeO_2 interface. Also, codeposition of CeO_2 particles induced the formation of small equiaxed Ni grains, which resulted in the corrosion along less straight paths and thus lowering the corrosion rates in Ni - CeO_2 composites (Aruna et al., 2006). It is also considered that when CeO_2 nanosized particles are embedded in the nickel matrix, the corrosion path is more seriously distorted as compared to micro-sized particles, which is favorable for corrosion resistance. In fact, the fine grain structure arising from the co-electrodeposition of CeO_2 nanoparticles also promotes good corrosion resistance as compared to coarse grain structure (Qu et al., 2006).

Aruna et al. (2009) showed enhanced performance of wear and corrosion characteristics of Ni based composite coatings by embedding with alumina yttria doped cubic zirconia (AZY, $(1-x)Al_2O_3$–8 mol% yttria stabilized $xZrO_2$ (x = 10 wt%)) particles. The higher Warburg resistance of Ni - AZY and enhanced corrosion resistance was attributed to possible difference in mass transport phenomena in the Ni –AZY composites compared to the pure Ni with increased resistance of Ni grain boundaries in presence of AZY particles and thereby hindered the diffusion of chloride ions (Aruna et al., 2009).

In other examples, Li et al. (2005) demonstrated the effect of the type of oxide particles dispersed on the corrosion behavior of Ni composites. Li et al. (2005) developed nanocomposite coatings consisting of TiO_2 in the form of anatase and rutile in Ni matrix via electrochemical deposition technique, and showed improved corrosion properties of Ni – TiO_2 composites compared to the pure Ni; however, the improvement in corrosion resistance was predominant in the case of anatase dispersed Ni composites. Improved corrosion resistance of Ni – TiO_2 composites was attributed to the inhabitant behavior of TiO_2 particles at the grain boundaries and triple junctions, which are the usual sites for corrosion attack. With an increase in the amount of TiO_2, a decrease in the corrosion rates was also demonstrated because of the increased number of inhabited sites, which reduce penetration of the corrosive solution into the composite coatings. On the other hand, Ni - Al_2O_3 composite coatings (Erler et al., 2003) reported to show poor corrosion resistance compared to the monolithic Ni. Szczygieł and Kołodziej (2005) indicated that the lower corrosion resistance of Ni - Al_2O_3 could be due to poor bonding between the oxide particles and the matrix, which can increase the possibility of dissolution of loosely held Al_2O_3 (alumina) particles at high potentials and result in more nickel exposure to the electrolyte for corrosion attack. In another study by Aruna et al. (2011) the corrosion properties of Al_2O_3 embedded Ni composites showed the oxide phase dependent corrosion performance. Their studies indicated that the corrosion resistance of Ni - α Al_2O_3 was better than the corrosion resistance of Ni – γ Al_2O_3 as well as the Ni – α and γ Al_2O_3 mixture; however, the reason for such behavior was not explained.

At high-temperatures the corrosion failure of a material system results from failure of its protective oxide scale. Different researchers have proved that addition of a small amount of

reactive elements (such as Y, Ce, La, and Hf), or their oxides, improves the oxidation resistance of some high temperature alloys by decreasing the growth rate of the oxide and increasing the adherence of the oxide scale to the underlying alloys (Peng et al., 1995). Addition of Y_2O_3, CeO_2, ThO_2, La_2O_3 and AI_2O_3 to Ni - Cr alloys, and Y_2O_3, HfO_2, ZrO_2 and TiO_2 to Co - Cr alloys may promote the formation of Cr_2O_3 protective oxide scale as well as increase its adherence to the ODS alloy system very effectively (Michels, 1976; Stringer & Wright 1972; Stringer et al., 1972; Whittle et al., 1977; Wright et al., 1975). In Ni - 20Cr - Y_2O_3 ODS alloy coatings, presence of Y_2O_3 was observed to promote the formation of Cr_2O_3 scale and thereby the improvement in scale spallation (Lianga et al., 2004). Stringer et al. (1972) proposed that the dispersed oxide particles act as heterogeneous nucleation sites for Cr_2O_3 grains and reduce the internuclear distance for the Cr_2O_3 scale formation, which will allow rapid formation of a continuous Cr oxide film with a finer grain size. The oxide layer with fine grain size can then easily release the thermal stress and therefore prevent crack propagation. Extensive experimental results and detailed mechanistic studies have indicated that the effects of dispersed oxides seem to be independent of the choice of the oxides, as long as they are not less stable than Cr_2O_3 (Lang et al., 1991). According to this mechanism, dispersion of above mentioned oxides expected to be most effective in enhancing Cr_2O_3 scale formation and thus lead to improved resistance to hot corrosion most effectively. According to He and Stott (1996) a short-circuited diffusion of Cr reduced the concentration of Cr in the alloy and thereby facilitated formation of Cr_2O_3 in Ni - 10Cr alloy with presence of Al_2O_3 and Y_2O_3 particles. Quadakkers et al. (1989) reported that Y_2O_3 incorporation in ODS alloys retarded the diffusion of Cr because of prevailing anionic diffusion over cationic diffusion. This mechanism was also supported by Ikeda et al. (1993), who also confirmed that the adhesion of Al_2O_3 could be promoted by the dispersed Y_2O_3 phase in ODS alloys.

According to Carl Lowell et al. (1982), the oxidation and corrosion resistance of ODS alloys was superior compared to the superalloys. However, different corrosion behavior among different ODS alloys, for example Ni based (NiCrAl) and Fe based (FeCrAl) ODS alloys, was attributed to the CTE mismatch and therefore the spallation resistance. Usually lower CTE mismatch between the ferritic ODS alloys and protective alumina film helps reduce the amount of stresses in the oxide during thermal cycling and thereby considerably less, or no, spalling. In contrast, the high CTE of Ni - based ODS alloys directly leads to spalling during cycling from 1100 ^{0}C to room temperature. Similarly, better oxidation and hot salt corrosion behavior is expected for Fe - based ODS alloys compared to the Ni - based ODS alloys. Therefore, it is apparent that the corrosion behavior of ODS alloys is highly dependent on the protective oxide layers formed during the high temperatures compared to the oxide particles embedded within the alloys, unlike the metal – oxide composites; however, formation of a uniform protective oxide scale could be dependent on the embedded oxide particles in the metal matrix. Thus, presence of oxide particles in a metal matrix can directly, as well as indirectly, help enhance the corrosion properties of different alloys and composite systems.

5. Case study on high temperature coatings developed by spray deposition

This case study presents synthesis and characterization of oxide particle embedded high temperature coatings developed by thermal spray technique, which is one of the processing routes discussed in the Section - 3, for boiler coating applications.

As discussed in the earlier sections, high temperature coatings are ubiquitous to industrial power generation, marine applications, and aircraft propulsion systems. Most high temperature coatings operate under extremely harsh conditions with conflicting operational requirements. For instance, coatings used in power plant boilers need to ensure an effective protection against high temperature corrosion under oxidizing, sulfidizing, carburizing environments and erosion from fly ash, as well as having a high thermal conductivity to exchange heat in order to provide an effective and economical maintenance. Further, to avoid premature failure, as discussed in the previously discussed overview section, the high temperature coatings also require good adhesion to the substrate, minimal mismatch in CTE between the coating and the substrate material, good thermal fatigue, and creep resistance (Bose, 2007; Patnaik, 1989; Uusitalo et al., 2004; Yoshiba, 1993; Yu et al., 2002).

Most commercial coating systems do not meet all the required attributes for a given environment. For example, NiCr (55/45 wt.%) alloy is usually recommended for erosion–corrosion protection for boiler tubes in power generation applications (Higuera, 1997; Martinez-Villafan et al., 1998; Meadowcroft, 1987; Stack et al., 1995). Weld overlay coatings of Alloy 625(Ni-21Cr-9Mo-3.5Nb) have also been used for this application. When nickel is alloyed with chromium (>15wt%), Cr oxidizes to Cr_2O_3, which could make it suitable for use up to about 1200°C (Goward, 1986), although in practice its use is limited to temperatures below about 800°C. The efficacy of NiCr coatings deteriorates severely when molten ash deposits consisting of sodium-potassium-iron tri-sulfates $(Na,K)_3Fe(SO_4)_3$ are present. Further, higher Cr content also reduces the creep resistance of NiCr alloys. Particularly, this issue becomes magnified in the case of thermal spray coatings. In addition to the grain boundaries, presence of splat boundaries, an inherent feature in thermal sprayed coatings also contributes to poor corrosion and creep performance at very high temperatures (Soltani et al., 2008; Zhu & Miller, 1997). Thus, from the materials perspective, the corrosion is influenced by several parameters, for example surface and bulk microstructures, thermodynamic stability of the phases, microstructural constituents, electrochemical potentials, protective phases and residual stresses etc. Thereby, it becomes user's responsibility to select an appropriate material system for a given operating condition either to avoid or slow down the deterioration during the service period.

The continued pursuit for increased efficiency in power generation and propulsion systems led to the development of functionally engineered coatings with multiple attributes. For example, an alternative method of combating the effects of coal ash corrosion is to install a material that contains sufficient amount of oxide stabilizing elements such as aluminum or silicon (NiCrAl, NiCrBSi NiCrMoBSi and NiCrBSiFe) to resist the dissolution of the oxide film when the molten ash is deposited. Similarly, functionally gradient materials (FGM) were proposed (Niino & Maeda, 1990) to obtain multifunctional properties with a combination of different metallic and ceramic systems in an engineered fashion. These materials were found to be very promising candidates for high temperature applications because of the reduced thermal stresses between the interfaces, resulting in enhanced thermal fatigue life (Bahr et al., 2003). The high temperature creep strength of metals is also greatly improved by the addition of high temperature stable dispersoid phases, due to grain boundary pinning such as the oxide dispersion strengthened super alloys (Ni-ThO_2 and NiCr-ThO_2) (Clauer & Wilcox, 1972).

Various approaches have been adopted to disperse the second phase particles into bulk matrix phase, such as mechanical alloying/powder metallurgy (Kang & Chan, 2004), in situ formation of dispersoids via a chemical reaction within the matrix phase (Cui et al., 2000), spray synthesis (Chawla, 1998), casting techniques (Rohatgi et al., 1986) and elecrodeposition (Clark et al., 1997). Processing methods, such as powder metallurgy (Heian et al., 2004; Kawasaki & Watanabe, 1997, 2002) and thermal spraying (Hamatani et al., 2003; Khor et al., 2001, 2003; Polat et al., 2002; Prchlik et al., 2001), cannot easily tailor the composition in a functional manner. Typically, thermal sprayed composite coatings are made using premixed powders with a given ratio of the constituent phases. This limits the production as well as the design flexibility. Further, a spray deposition approach involving direct spraying of nano-sized powders, has a number of limitations (Rao et al., 1997; Skandan et al., 2001). The primary issue is the introduction of nano-sized powders into the high velocity thermal spray jet and their impingement on the substrate. Nano-sized powders tend to agglomerate, resulting in plugged particle feed line, and the extremely small particles do not readily penetrate the jet. Also, impingement on to the substrate is difficult as the small powders follow the gas streamlines. An alternative methodology is to introduce a liquid or gaseous precursor, which reacts in flight to form nanosized particles (Rao et al., 1997; Xie et al., 2004). This approach is very promising, and has worked well for several material systems. Combustion synthesis using liquid precursors has been used to deposit a number of different high temperature oxide coatings, including Al_2O_3, Cr_2O_3, SiO_2, CeO_2, some spinel oxides ($MgAl_2O_4$, $NiAl_2O_4$), and yttria stabilized zirconia (YSZ) (Hampikian & Carter 1999). For example, using a solution of aluminum acetylacetonate in ethanol, alumina was deposited at temperatures of approximately 850, 1050, and 1250°C (Hendrick et al., 1998). Similarly, SiO_2 has been deposited by combustion synthesis of ethanol containing tetrathyloxysilicate precursor.

As for the production of nanoparticle dispersed microcrystalline coating by thermal spray technique, different approaches have been adopted, such as agglomeration of nano-sized particles with a binder used in the Co-WC cermet (Skandan et al., 2001) or premixing of dispersoid phase with the matrix powder (Laha et al., 2004, 2007; Bakshi et al., 2008). However, these approaches also suffer from the same design inflexibility mentioned above. This case study presents an innovative approach to synthesize ultrafine/nano particulate dispersed (Al_2O_3, SiO_2) NiCr alloy coatings. A novel process called "Hybrid Spray Technique" (Kosikowski et al., 2005) has been employed to fabricate these functionally engineered coatings in a single step. The rationale behind the selection of the dispersoid phases, their liquid precursors and the particulate distribution layout is presented. The influence of these dispersoid phases on the functional characteristics of the resulting coatings is discussed.

5.1 Processing and testing of high temperature coatings

The "hybrid spray" process utilized in this study was conceptualized in our laboratory at the University of Michigan (Kosikowski et al., 2005). This process combines the arc and high velocity oxy fuel (HVOF) spray techniques; molten metal at the arcing tip is atomized and rapidly propelled to the substrate by a HVOF jet. This so called "hybrid" concept shown in Fig. 5 offers many advantages.

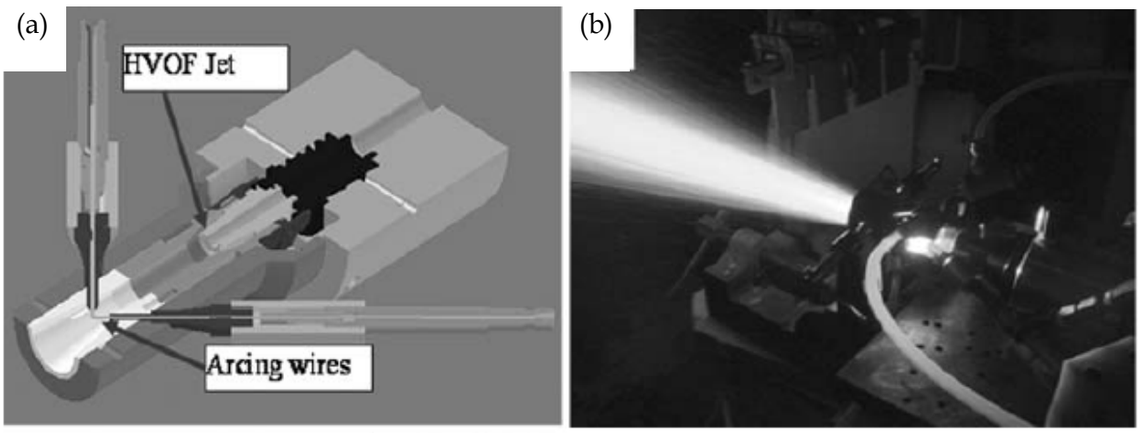


Fig. 5. (a) Schematic of hybrid gun and (b) hybrid gun in operation.

The hybrid process offers all benefits of wire stock and productivity of electric arc spraying combined with noticeably improved coating density of HVOF. In addition to introducing material through arcing mechanism, if desired, powder/liquid/gas precursors can also be fed through the HVOF coaxial feed line (Fig. 5a). This enables us to tailor the composition inflight by introducing particles into the HVOF jet, to cater to specific property requirements of a composite coating. This unique capability completely eliminates the necessity of processing and handling of the ultrafine particulates prior to feeding them into the hybrid gun. Synthesizing and introducing ultrafine and nano dispersoids inflight in a functional manner to produce composite coatings by the hybrid technique is quite unique in terms of simplicity compared to any other processes. A comparative picture of the steps involved in processing of particulate reinforced composites by conventional routes versus our approach is presented in Table 1.

Target Material	**Precursor Materials**	**Percentage**
NiCr-Matrix	NiCr wire	(55/45 wt. %)
Al_2O_3 particulate	Aluminum nitrate -$Al(NO_3)_3 \cdot 9H_2O$	1:1 by weight in isopropyl alcohol (70%)
Cr_2O_3 Stabilizer	Chromium nitrate -$Cr(NO_3)_3 \cdot 9H_2O$	Up to 50% by weight of aluminum nitrate
SiO_2 particulate	Tetraethoxysilane	100 %

Table 1. List of precursors used.

Following the above mentioned approach of inflight synthesis, different oxide ceramic particles were introduced into the NiCr (55/45 wt.%) alloy coating. The following coatings were deposited onto mild steel coupons for characterization: (a) NiCr only, (b) NiCr + Cr_2O_3, (c) NiCr + Al_2O_3, and (d) NiCr + SiO_2. Along with these coatings, NiCr coatings using a twin wire arc spray process (TAFA 3830, Praxair Surface Technologies, Indianapolis, IN) were also deposited for comparison purposes. The arc current and voltage for both the processes were kept at 100 amps and 36 volts, respectively. The HVOF gas pressures were

maintained at 50/65/80 psi of propylene/oxygen/air, respectively. The Aluminum nitrate and Tetraethoxysilane precursors were fed from separate reservoirs, however, they were mixed together prior to the injection into the combustion jet. The atomization of the liquid was achieved by a two fluid injector. Liquid precursors up to 100 cc/min were fed to the HVOF jet coaxially.

Table 1 lists the liquid precursors employed for the synthesis of the dispersoid phase particles. The rationale behind the selection of the dispersoids (SiO_2, and Al_2O_3,) and their influence on the properties is as follows.

- The silica particles are expected to provide both creep and crack resistance. It has also been demonstrated that the presence of SiO_2 enhances the high temperature resistance of chromia scale (Carter et al., 1995; Liu et al., 2004).
- The presence of alumina is expected to provide enhanced high temperature corrosion resistance. Also, the introduction of SiO_2 into alumina based coatings has been found to form mullite and reduce the cracking within the coating (Marple et al., 2001). Mullite is known for its excellent creep resistance (Dokko et al., 1977; Lessing et al., 1975).
- It has also been found that the presence of chromia aids in α - alumina formation, as well as limits the phase transformations during heating to temperatures below 1200 ^{0}C (Marple et al., 2001; Chraska et al., 1997). Therefore, chromium nitrate was added to the aluminum nitrate precursor to stabilize the α - alumina phase.

Microstructural analysis of the coatings was done using electron microscopy (SEM/TEM). The oxidation characteristics of the coatings were characterized on a TA instruments SDT Q600 model for thermogravimetric analysis (TGA). For functional property characterization, coatings were tested for hot erosion, wet corrosion and hot corrosion; and compared with 304 stainless steel, as well as alloy 625 overlay cladding. The hot erosion test setup consisted of a grip for holding and rotating (80 rpm) the coated samples while heating with a heat source (HVOF flame), and an alumina grit (250 mesh) delivering system at a fixed angle (45^0) as shown in Fig. 6a. The flow rate of the grit was 60 gm/min and the applied grit carrier air pressure was 15 psi at a rate of 42 SCFM. Testing was done at 750 ^{0}C for 3 minutes on spray-coated cylinders. Wet corrosion tests were done at room temperature in a dilute 0.1% NaCl solution. NiCr coatings sprayed by the hybrid and arc techniques were tested using an electrochemical cell shown in Fig 6b. Electrochemical experiments were performed using a Solartron (Hampshire, England) SI 1287 potentiostat at the open circuit potential for two different time periods (0hrs and 24 hrs). Hot corrosion tests were carried out by applying film of sulfates and chlorides (potassium, sodium and iron) on to the surface of coated samples (304 stainless steel caps) as shown in Fig. 6c. Samples were initially weighed, and then their surfaces were coated with a solution of sulfate/chloride mixed with water in a weight ratio of 1:1. The samples were carefully masked to ensure salt solution only covered the sprayed coating and the area coated with salt solution was also measured. The solution was dried to leave a film of salt on the surface of the sample. The masking material was removed and the sample was weighed again. Samples were then placed in an oven at 900^0 C for 24 hours. This test also included samples of bare 304 stainless steel cap as well as alloy 625 overlay cladding. After the hot corrosion test, weight loss/gain of the samples was measured to evaluate the corrosion resistance.

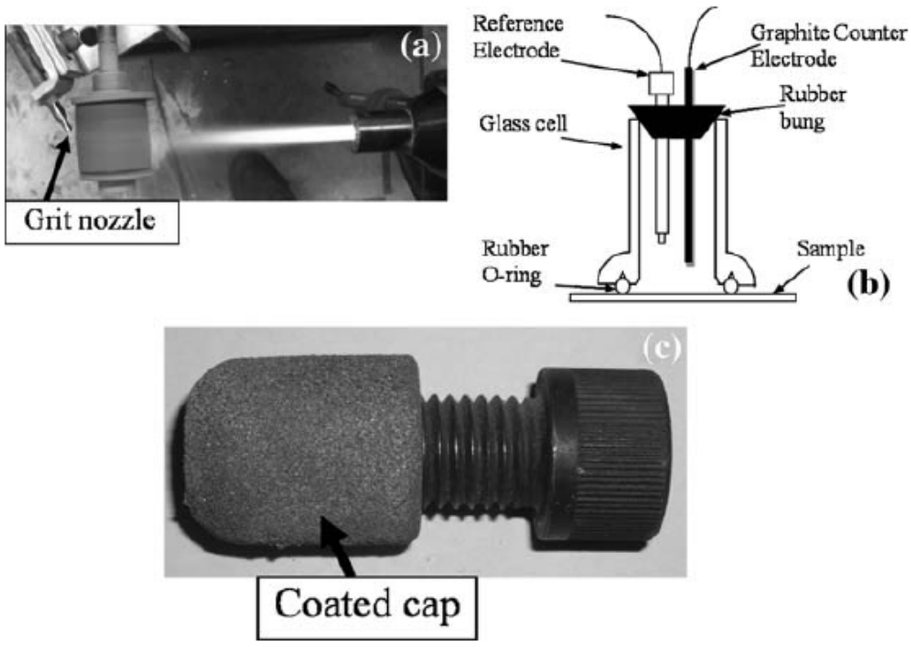


Fig. 6. (a) Hot erosion test set up, (b) corrosion cell, and (c) sample for hot corrosion test.

5.2 Microstructural analysis of high temperature coatings

Fig. 7a, presents the general cross section microstructure of a NiCr coatings with embedded alumina particles produced by the hybrid spray process. The coating is very dense and exhibits the characteristics of an HVOF coating rather than of an arc sprayed coating. The hybrid spray process is unique in the sense that while it yields comparable density to that of the HVOF process, the deposition rate is closer to that of an arc spray process. The observed density is advantageous for high temperature corrosion and erosion performance of the coatings. Details on the corrosion and erosion performance of the coatings are discussed in the forthcoming sections. The dispersion of the alumina particles (dark phase) in the NiCr matrix is shown in Fig. 7b.

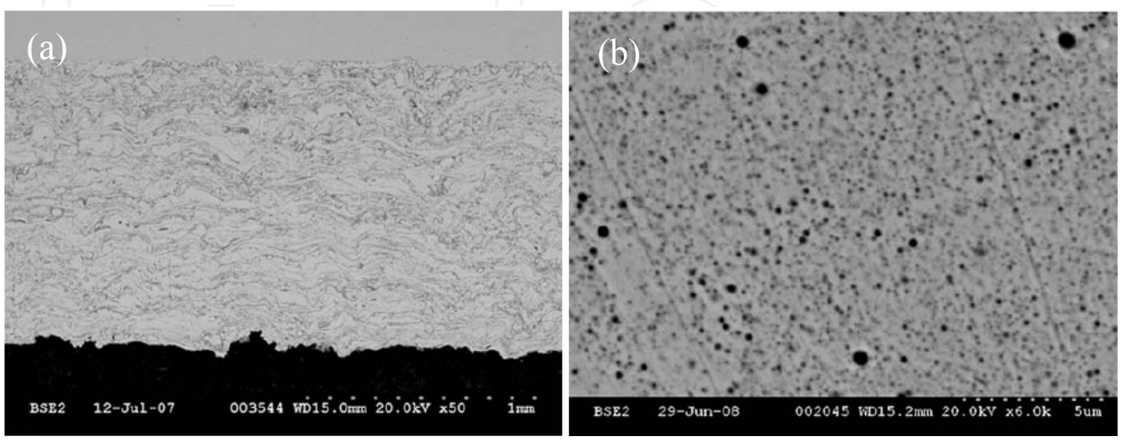


Fig. 7. (a) SEM picture of NiCr coating with dispersed Al_2O_3 particulates and (b) higher magnification SEM picture of NiCr coating with dispersed Al_2O_3 particulates.

The atomization of the liquid precursor (for oxide particles) prior to the injection into the combustion jet plays an important role on the size as well as on the distribution of the particles in the final coating. The requirements for the atomization system include: controlled and uniform flow, ability to operate against a back pressure of 30 psi pressure that exists in HVOF flame at the point of injection and the ability to generate mono-dispersed micron sized droplets. Details on the atomization and optimization of parameters could be found elsewhere (Mohanty et al., 2010). From Fig. 7(b), it is apparent that the distribution of the particles was uniform across the cross section. Similar observations were made in the case of NiCr + Cr_2O_3 and NiCr + SiO_2 systems also. It is to be noted that composites made from premixed powders commonly exhibit large clusters of nanoparticles. Fig. 8 presents the TEM picture of a NiCr coating with embedded silica particles. Many fine particles are observed in the matrix, as well as along the grain boundaries. For enhanced creep resistance resulting from grain boundary pinning, the particles must be small and coherent with the matrix. Especially alloys with very high chrome content can substantially benefit from such ultrafine particle embedment as observed in Fig. 8.

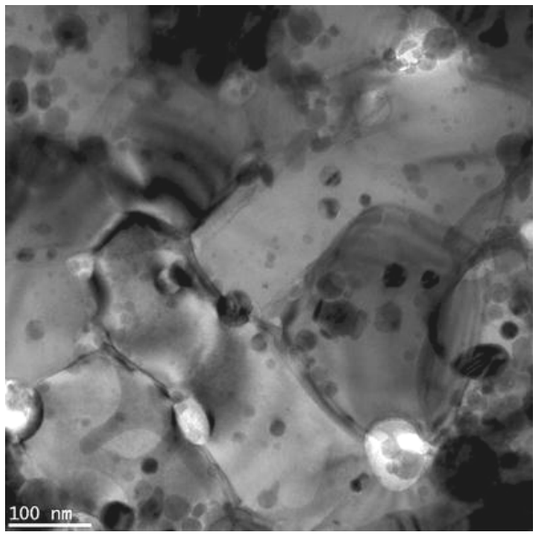


Fig. 8. TEM picture of NiCr coating with dispersed SiO_2 particulates.

5.3 Characterization of high temperature coatings

5.3.1 Oxidation studies

The oxidation characteristics of all the coatings (a), (b), (c) and (d) (refer to page 9) including the arc sprayed NiCr coating, were investigated by TGA studies in air after removing them from the substrate. The TGA curves shown in Fig. 9 indicate an overall weight gain for all the coatings while heating, although there was an initial weight loss for most samples.

The weight gain can be attributed to the oxidation of Cr in the NiCr matrix, as well as the changing oxidation state of the existing oxides. The later phenomenon can also lead to a weight loss in the initial stages because of the changing stoichiometry. Literature (Eschnauer et al., 2008; Hermansson et al., 1986; Richard et al., 1995; Schutz et al., 1991; Vippola et al., 2002) suggests that the oxidation of chromium during thermal spray processes could lead to nonstoichiometric compounds or metastable oxides (CrO_2, CrO and Cr_3O_4) which can

undergo changes upon reheating. If CrO_2, which has higher oxygen content compared to Cr_2O_3, forms during the spray process; it can undergo stoichiometric changes to a stable oxide (Cr_2O_3) upon reheating and this could lead to an initial weight loss in the coatings. However, part of the initial weight loss could also be attributed to the evaporation of moisture absorbed by porosity in the coatings. According to Lars Mikkelsen (2003), the specimens may also lose weight due to vaporization of chromium containing species from the chromia scale. Whereas the oxidation of pure Cr to Cr_2O_3 and also the transformation of CrO and Cr_3O_4 to Cr_2O_3 will lead to weight gain because of increasing oxygen content in the coatings.

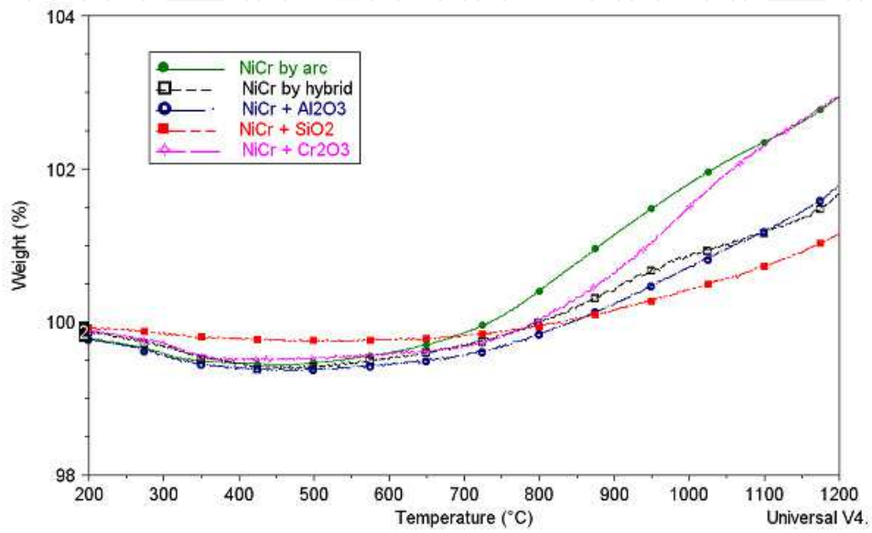


Fig. 9. Weight gain measured using TGA for oxidation studies.

The weight gain for arc sprayed NiCr coating was the highest compared to all other coatings and this could be due to the inherent porosity in the arc spray coatings. The pores in the coatings enhance the oxidation rate. The weight gain in the hybrid NiCr coatings (without any particulate) was much lower than the arc sprayed coating because of their dense splat structure. NiCr + SiO_2 showed the lowest weight gain. The weight gain by NiCr + Al_2O_3 was comparable to that of the plain hybrid NiCr coatings. A large weight gain by the NiCr + Cr_2O_3 could be due to the changes associated in the chromium oxide composition. It is to be noted that there is no need to add Cr_2O_3 particles into NiCr coating using a precursor. The role of chromium nitrate precursor here is to stabilize the α -alumina phase. However, excess addition could lead to undesirable consequence as observed in the case of the NiCr + Cr_2O_3 sample. Determining the appropriate level of chromium nitrate is beyond the scope of this study. From these studies we conclude that addition of SiO_2 has the most remarkable effect on the oxidation behavior of NiCr coatings. It has been demonstrated that the presence of SiO_2 enhances the high temperature resistance of the chromia scale, which helps to improve the oxidation and corrosion resistance of the coatings (Carter et al., 1995).

5.3.2 Hot erosion test

The setup utilized for evaluating the hot erosion behavior was shown in Fig. 6a. The weight of cylinders was measured before and after the hot erosion test. Also, the amount of grit used for each test was measured. The measured weight loss of each sample was based on

200 gm of grit being used. Samples tested included arc sprayed coatings, plain hybrid coatings, and hybrid coatings with alumina, chromia and silica, respectively. The results of the tests, shown in Fig. 10, indicate that the hybrid coatings are up to 30% more resistant to erosion than the arc sprayed coatings at 750^0C and this is thought to be due to the higher density of the hybrid coatings. However, the weight loss was slightly higher in the case of oxide particulate embedded coatings. This is contrary to the observation of Jiang Xu et al. (Xu et al., 2008), who have reported improved erosion resistance with the addition of nanoparticles in Ni based alloys. Especially, in the case of chromia embedment, the difference was evident. This may be linked to the large bubble shaped features with internal voids that were observed in chromia particles (which are not shown here).

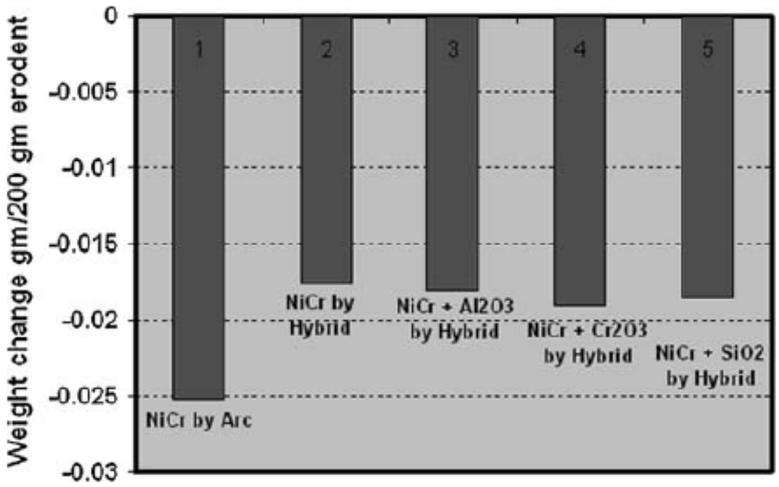


Fig. 10. Weight loss measured in hot erosion test.

5.3.3 Wet corrosion test

The corrosion currents measured from the electrochemical tests are shown in Fig. 11. At zero hours, although the hybrid coating showed less current compared to the arc sprayed coating;

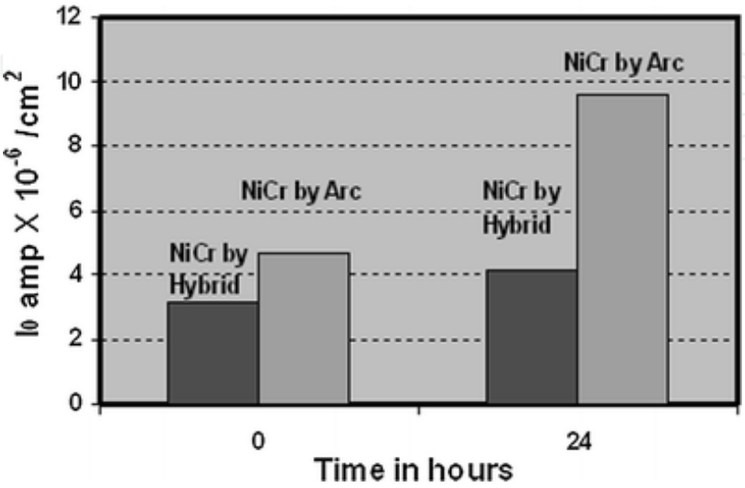


Fig. 11. Wet corrosion of thermally sprayed NiCr coatings in NaCl solution at room temperature.

the difference was not that significant. After 24 hours of immersion, the current values significantly differed between the coatings. The arc spray coating measured two times greater current, Io, after 24 hours. Io is a measure of the corrosion resistance of a material and higher current values indicate lower corrosion resistance. These results confirm that the hybrid coating being denser than the arc spray coating restricts the migration of the corrosive solution/ions to the substrate interface and, therefore, provides more protection to the substrate. Although aqueous corrosion is not an issue for these high temperature coatings, this test has some significance in terms of molten deposit (sulfates) migration through the coating in a coal fired boiler environment.

5.3.4 Hot corrosion test

The hot corrosion test results are shown in Fig. 12. This chart compares the weight loss data obtained on weld overlay coating (with and without salt), 304 stainless steel (304 SS) sample and the coatings – NiCr by arc spray, NiCr and NiCr + SiO_2 by hybrid gun . The chromia stabilized alumina embedded coatings were not included in the test due to their unfavorable oxidation results presented in Fig. 9. NiCr + SiO_2 coatings showed the lowest weight loss compared to all the other samples. Plain NiCr coating by hybrid spray also exhibited lesser weight loss compared to the arc spray coating and this could be attributed to the improved density of the hybrid spray coatings. The superior corrosion resistance of the NiCr + SiO_2 coating is possibly due to the enhanced stability of the chromia scale and the improved oxidation resistance caused by SiO_2. Weld overlay coating showed least weight loss in the absence of the salt; however, when salt was present, it showed poor corrosion resistance compared to the hybrid spray coatings.

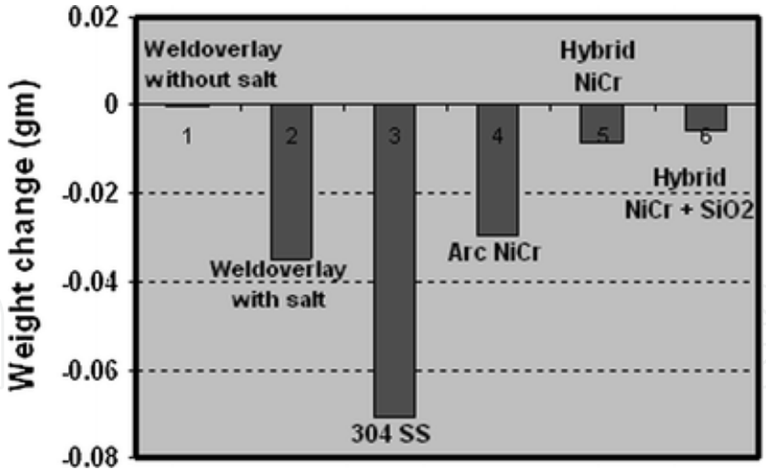


Fig. 12. Weight loss measured in hot corrosion test.

The case study demonstrates that even the base NiCr hybrid spray coatings outperformed the alloy 625 coatings in the presence of corrosive salts. The presence of second phase particles, especially SiO_2, showed improved oxidation and corrosion characteristics. Incorporation of ultrafine and nano sized oxide particles is expected to improve the creep properties by pinning the splat boundaries and reduce the oxidation rate. Chromia addition by itself did not help improve the properties significantly. However, it could act as a

stabilizer for alumina and limit the phase transformations up to 1200^0C (Marple et al., 2001; Chraska et al., 1997). Combination of SiO_2 and Al_2O_3 can help improve high temperature creep and corrosion resistance (Carter et al., 1995; Liu et al., 2004; Stollberg et al., 2003).

6. Summary

It is apparent from the brief review and case study that oxide systems could be quite helpful to reduce or slow down the corrosion phenomenon of metallic systems. However, it could be dependent on the oxide system employed. Importantly the stability of oxide phases is very vital as it could undergo several changes during the operation depending on the temperatures of application environment. Dispersion of SiO_2 showed marked enhancement in the oxidation and corrosion resistance of the hybrid coatings at high temperatures.

7. References

Aramaki, K. (2001). The inhibition effects of chromate-free, anion inhibitors on corrosion of zinc in aerated 0.5 M NaCl. *Corrosion Science,* Vol. 43, No. 3, pp. 591-604, ISSN 0010938X

Aruna, S. T.; Bindu, C. N.; Ezhil Selvi, V.; William Grips, V. K. & Rajam, K. S. (2006). Synthesis and properties of electrodeposited Niceria nanocomposite coatings. *Surface & Coatings Technology*, Vol. 200, No. 24, pp. 6871–6880, ISSN 2578972

Aruna, S. T.; William Grips, V. K. & Rajam, K. S. (2009). Ni-based electrodeposited composite coating exhibiting improved microhardness, corrosion and wear resistance properties**.** *Journal of Alloys and Compounds,* Vol. 468, No. 1-2, pp. 546–552, ISSN 09258388

Aruna, S. T.; Ezhil Selvi, V. ; William Grips, V. K. & Rajam, K. S. (2011). Corrosion- and wear-resistant properties of Ni–Al2O3 composite coatings containing various forms of alumina. *Journal of Applied Electrochemistry*, Vol. 41, pp. 461-468, ISSN 15728838

Bahr, H. A.; Balke, H.; Fett, T.; Hoffinger, I.; Kirchhoff, G.; Munz, D.; Neubrand, A.; Semenov, A. S.; Weiss, H. J. & Yang, Y. Y. (2003). Cracks in Functionally Graded Materials. *Materials Science and Engineering A*, Vol. 362, No. 1-2, pp. 2-16, ISSN 09215093

Bakshi, S. R.; Singh, V.; Balani, K.; Graham McCartney, D.; Seal, S. & Agarwal, A. (2008). Carbon Nanotube Reinforced Aluminum Composite Coating via Cold Spraying, *Surface & Coatings and Technology*, Vol. 202, No. 21, pp. 5162-5169, ISSN 2578972

Bertolini, L.; Brunella, M. F. & Candiani, S. (1999). Corrosion Behavior of a Particulate Metal-Matrix Composite. *Corrosion*, Vol. 55, No. 4, pp. 422-431, ISSN 00109312

Bose, S. (2007). *High Temperature Coatings*, Butterworth-Heinemann Publishers, ISBN 0750682523, Boston, MA, USA

Carter, W. B.; Hampikian, J. M.; Godfrey, S. H. & Polley, T. A. (1995). Thermal Aging of Combustion Chemical Vapor Deposited Oxide Coatings. *Materials Manufacturing Processes*, Vol. 10, No. 5, pp. 1007-1020, ISSN 15322475

Chawla, K. K. (1998). *Composite Materials – Science and Engineering*, Springer-Verlag Inc., ISBN 0387984097, New York, USA

Chraska, P.; Dubsky, J.; Neufuss, K. & Pisacka, J. (1997). Alumina Based Plasma Sprayed Materials, Part I: Phase Stability of Alumina and Alumina-Chromia. *Journal of Thermal Spray Technology*, Vol. 6, No. 3, pp. 320-326, ISSN 15441016

Clark, D.; Wood, D. & Erb, V. (1997). Industrial Applications of Electrodeposited Nanocrystals. *Nanostructured Materials*, Vol. 9, No. 1-8, pp. 755-758, ISSN 09659773

Clauer, A. H. & Wilcox, B. A. (1972). The Role of Grain Size and Shape in Strengthening of Dispersion Hardened Nickel Alloys. *Acta Metallurgica*, Vol. 20, No. 5, pp. 743-757, ISSN 00016160

Cramer, S. D & Covino, B. S. Jr. (2005). *ASM Handbook Vol. 13 B, Corrosion: Materials,* ASM International, ISBN 0871707071, Materials Park, OH, USA

Cui, C., Shen, Y. & Meng, F. (2000). Review of Fabrication Methods of In Situ Metal Matrix Composites. *Journal of Materials Science and Technology*, Vol. 16, No. 6, pp. 619-642, ISSN 10050302

Dokko, P. C.; Pask, J. A. & Mazdiyasni, K. S. (1977). High-Temperature Mechanical Properties of Mullite under Compression. *Journal of the American Ceramic Society*, Vol. 60, No. 3-4, pp. 150-155, ISSN 15512916

Eschnauer, H. (2008). Hard Material Powders and Hard Alloy Powders for Plasma Surface Coating. *Thin Solid Films*, Vol. 73, No. 1, pp. 1-17, ISSN 0040-6090

Erler, F.; Jakob, C.; Romanus, H.; Spiess, L.; Wielage, B.; Lampke, T. & Steinhouser, S. (2003). Interface behaviour in nickel composite coatings with nano-particles of oxidic ceramic. *Electrochimica Acta*, Vol. 48, No. 20-22, pp. 3063-3070, ISSN 00134686

Fang, C.; Huang, C. & Chuang, T. (1999). Synergistic effects of wear and corrosion for Al_2O_3 particulate-reinforced 6061 aluminum matrix composites. *Metallurgical and Materials Transactions A*, Vol. 30, No. 3, pp. 643-651, ISSN 10735623

Goward, G. W. (1986). Protective Coatings Purpose, Role and Design. *Materials Science and Technology*, Vol. 2, No. 3, pp. 194-200, ISSN 17432847

Hamatani, H., Shimoda, N. & Kitaguchi, S. (2003). Effect of the Composition Profile and Density of LPPS Sprayed Functionally Graded Coating on the Thermal Shock Resistance. *Science and Technology of Advanced Materials*, Vol. 4, No. 2, pp. 197-203, ISSN 1878-5514

Hamdy, A. S.; Beccaria, A. M. & Traverso, P. (2005). Effect of surface preparation prior to cerium pre-treatment on the corrosion protection performance of aluminum composites. *Journal of Applied Electrochemistry*, Vol. 35, No. 5, pp. 473-478, ISSN 15728838

Hamdy, A. S. (2006). Advanced nano-particles anti-corrosion ceria based sol gel coatings for aluminum alloys. *Materials Letters*, Vol. 60, No. 21-22, pp. 2633–2637, ISSN 0167577X

Hampikian, J. M. & Carter, W. B. (1999). The Fabrication, Properties and Microstructure of Cu–Ag and Cu–Nb Composite Conductors. *Materials Science and Engineering A*, Vol. 267, No. 1, pp. 7-18, ISSN 09215093

He, Y. & Stott, F. H. (1996). The effects of thin surface-applied oxide coating films on the selective oxidation of alloys. *Corrosion Science*, Vol. 38, No. 11, pp. 1853-1868, ISSN 0010938X

Heian, E. M.; Gibeling, J. C. & Munir, Z. A. (2004). Synthesis and Characterization of Nb5Si3/Nb Functionally Graded Composites. *Materials Science and Engineering A*, Vol. 368, No. 1-2, pp. 168-174, ISSN 09215093

Hendrick, M. R.; Hampikian, J. M. & Carter, W. B. (1998). Combustion CVD-Applied Alumina Coatings and Their Effects on the Oxidation of a Ni-Base Chromia Former. *Journal of the Electrochemical Society*, Vol. 145, No. 11, pp. 3986-3994, ISSN 00134651

Hermansson, L.; Eklund, L.; Askengren, L. & Carlsson, R. (1986). On the Microstructure of Plasma Sprayed Chromium Oxide. *Journal De Physique*, Vol. 47, pp. 165-169, ISSN 1155-4304

Higuera, V., Belzunce, F. J. & Ferna´ndez Rico, E. (1997). Erosion Wear and Mechanical Properties of Plasma-Sprayed Nickel- and Iron-Based Coatings Subjected to Service Conditions in Boilers. *Tribological International*, Vol. 30, No. 9, pp. 641-649, ISSN 0301679X

Hinton, B. R. W.; Arnott, D. R. & Ryan, N. E. (1987). Cationic film-forming inhibitors for the corrosion protection of AA 7075 Aluminum alloy in chloride solutions. *Materials Performance*, Vol. 8, No. 8, pp. 42-47, ISSN 00941492

Hinton, B. R. W.; Arnott, D. R. & Ryan, N. E. (1986). Cerium conversion coatings for the corrosion protection of aluminum. *Materials Forum*, Vol. 9, pp. 162-173, ISSN 0883-2900

Ikeda, Y.; Nii, K. & Yata, M. (1993). Y_2O_3 Dispersion Effect on Al_2O_3 Protective Coating Examined on the Basis of Five Models. *ISIJ International*, Vol. 33, No. 2, pp. 298-306, ISSN 09151559

Jones, Denny A. (1992). *Principles and Prevention of Corrosion*, Prentice Hall Inc., ISBN 0133599930, Upper Saddle River, NJ, USA

Kainer, Karl U. (2006). *Metal Matrix Composites: Custom-made Materials for Automotive and Aerospace Engineering*, John Wiley & Sons, ISBN 9783527608270, Betz-Druck GmbH, Darmstadt, Germany

Kang, Y. C. & Chan, S. L. (2004). Tensile Properties of Nanometric Al_2O_3 Particulate-Reinforced Aluminum Matrix Composites. *Materials Chemistry and Physics*, Vol. 85, No. 2-3, pp. 438-443, ISSN 02540584

Kawasaki, A. & Watanabe, R. (1997). Concept and P/M Fabrication of Functionally Graded Materials. *Ceramics International*, Vol. 23, No. 1, pp. 73-83, ISSN 02728842

Kawasaki, A. & Watanabe, R. (2002). Thermal Fracture Behavior of Metal/Ceramic Functionally Graded Materials. *Engineering Fracture Mechanics*, Vol. 69, No. 14-16, pp. 1713-1728, ISSN 00137944

Khor, K. A.; Gu, Y. W. & Dong, Z. L. (2001). Mechanical Behavior of Plasma Sprayed Functionally Graded YSZ/NiCoCrAlY Composite Coatings. *Surface and Coatings Technology*, Vol. 139, No. 2-3, pp. 200-206, ISSN 2578972

Khor, K. A.; Gu, Y. W.; Quek, C. H. & Cheang, P. (2003). Tensile Deformation Behavior of Plasma-Sprayed Ni–45Cr Coatings. *Surface and Coatings Technology*, Vol. 168, No. 2, pp. 195-201, ISSN 2578972

Kosikowski, D.; Batalov, M. & Mohanty, P. S. (2005). Functionally Graded Coatings by HVOF-Arc Hybrid Spray Gun, *Proceedings of the International Thermal Spray Conference*, ISSN 10599630, Basel, Switzerland, May 2-4, , pp. 444-449

Laha, T.; Agarwal, A.; McKechnie, T. & Seal, S. (2004). Synthesis and Characterization of Plasma Spray Formed Carbon Nanotube Reinforced Aluminum Composite. *Materials Science and Engineering A*, Vol. 381, No. 1-2, pp. 249-258, ISSN 09215093

Laha, T.; Kuchibhatla, S.; Seal, S.; Li, W. & Agarwal, A. (2007). Interfacial Phenomena in Thermally Sprayed Multiwalled Carbon Nanotube Reinforced Aluminum Nanocomposite. *Acta Materialia*, Vol. 55, No. 3, pp. 1059-1066, ISSN 13596454

Lang, Zhou; Ruizeng, Ye; Shouhua, Zhang & Lian, Gao. (1991). The behaviour of a sputtered chromia dispersed Co-Cr coating. *Corrosion Science,* Vol. 32, No. 3, pp. 337-346, ISSN 0010938X

Lessing, P. A.; Gordon, R. S. & Mazdiyasni, K. S. (1975). Creep of Polycrystalline Mullite. *Journal of the American Ceramic Society*, Vol. 58, No. 3-4, pp. 149- 150, ISSN 15512916

Lianga, J.; Gaoa, W.; Lia, Z. & He, Y. (2004). Hot corrosion resistance of electrospark-deposited Al and Ni Cr coatings containing dispersed Y_2O_3 particles. *Materials Letters*, Vol. 58, No. 26, pp. 3280-3284, ISSN 0167577X

Li, J.; Sun, Y.; Sun, X. & Qiao, J. (2005). Mechanical and corrosion-resistance performance of electrodeposited titania-nickel nanocomposite coatings. *Surface & Coatings Technology,* Vol. 192, No. 2-3, pp. 331– 335, ISSN 2578972

Lin, S.; Shih, H. & Mansfeld, F. (1992). Corrosion Protection of Metal Matrix Composites by Polymer Coatings. *Corrosion Science*, Vol. 33, No. 9, pp. 1331-1349, ISSN 0010938X

Liu, Y.; Zha, S. & Liu, M. (2004). Novel Nanostructured Electrodes for Solid Oxide Fuel Cells Fabricated by Combustion Chemical Vapor Deposition. *Advanced Materials*, Vol. 16, No. 3, pp. 256-260, ISSN 15214095

Liu, Y.; Compson, C. & Liu, M. (2004). Nanostructured and Functionally Graded Cathodes for Intermediate Temperature Solid Oxide Fuel Cells. *Journal of Power Sources*, Vol. 138, No. 1-2, pp. 194-198, ISSN 03787753

Lowell, Carl E.; Deadmore, Daniel L. & Whittenberger, Daniel, J. (1982). Long-term high-velocity oxidation and hot corrosion testing of several NiCrAl and FeCrAl base oxide dispersion strengthened alloys. *Oxidation of Metals,* Vol. 17, Nos. 3-4, pp. 205-221, ISSN 15734889

Marple, B. R.; Voyer, J. & Becharde, P. (2001). Sol Infiltration and Heat Treatment of Alumina–Chromia Plasma-Sprayed Coatings. *Journal of the European Ceramic Society*, Vol. 21, pp. 861-868, ISSN 09552219

Martinez-Villafan, A.; Almeyara, M. F.; Gaona, C.; Gonzalez, J. C. & Porcayo, J. (1998). High-Temperature Degradation and Protection of Ferritic and Austenitic Steels in Steam Generators. *Journal of Materials Engineering and Performance*, Vol. 7, No. 1, pp. 108-113, ISSN 15441024

Meadowcroft, D.B. (1987). High Temperature Corrosion of Alloys and Coatings in Oil- and Coal-Fired Boilers. *Materials Science and Engineering*, Vol. 88, pp. 313-320, ISSN 09215093

Michels, H. T. (1976). The effect of dispersed reactive metal oxides on the oxidation resistance of nickel-20 Wt pct chromium alloys. *Metallurgical Transactions,* Vol. 7, No. 3, pp. 379-388, ISSN 03602133

Mikkelsen, L. (2003). High Temperature Oxidation of Iron-Chromium Alloys, (Ph.D. Thesis, Riso National Laboratory Roskilde, Denmark, Date of access: 20th of August 2011, Available at http://130.226.56.153/rispubl/reports/ris-phd-2.pdf

Mohanty, P. S.; Roche, A. D.; Guduru, R. K. & Varadaraajan, V. (2010). Ultrafine Particulate Dispersed High-Temperature Coatings by Hybrid Spray Process. *Journal of Thermal Spray Technology*, Vol. 19, No. 1-2, pp. 484-494, ISSN 15441016

Monticelli, C.; Zucchi, F.; Brunoro, G. & Trabanelli, G. (1997). Stress corrosion cracking behaviour of some aluminium-based metal matrix composites. *Corrosion Science*, Vol. 39, No. 10-11, pp. 1949-1963, ISSN 0010938X

Muhamed Ashraf, P. & Shibli, S. M. A. (2007). Reinforcing aluminium with cerium oxide: A new and effective technique to prevent corrosion in marine environments. *Electrochemistry Communications,* Vol. 9, No. 3, pp. 443–448, ISSN 13882481

Niino, M. & Maeda, S. (1990). Recent Development Status of Functionally Gradient Materials. *ISIJ International*, Vol. 30, No. 9, pp. 699-703, ISSN 09151559

Nunes, P. C. R. & Ramanathan, L. V. (1995). Corrosion behavior of alumina-aluminium and silicon carbide-aluminium metal-matrix composites. *Corrosion*, Vol. 51, No. 8, pp. 610-617, ISSN 00109312

Patnaik, P. C. (1989). Intermetallic Coatings for High Temperature Applications—A Review. *Materials Manufacturing Processes*, Vol. 4, No. 4, pp. 133-152, ISSN 1532-2475

Peng, X.; Ping, D. H.; Li, T. F. & Wu, W. F. (1998). Oxidation Behavior of a Ni-La_2O_3 Codeposited Film on Nickel. *Journal of the Electrochemical Society*, Vol. 145, No. 2, pp. 389-398, ISSN 00134651

Polat, A.; Sarikaya, O. & Celik, E. (2002). Effects of Porosity on Thermal Loadings of Functionally Graded Y_2O_3 ZrO_2/NiCoCrAlY Coatings. *Materials and Design*, Vol. 23, No. 7, pp. 641-644, ISSN 02613069

Prchlik, L.; Sampath, S.; Gutleber, J.; Bancke, G. & Ruff, A. W. (2001). Friction and Wear Properties of WC-Co and Mo-Mo_2C Based Functionally Graded Materials. *Wear*, Vol. 249, No. 12, pp. 1103-1115, ISSN 00431648

Qu, N. S.; Zhu, D. & Chan, K. C. (2006). Fabrication of Ni–CeO_2 nanocomposite by electrodeposition. *Scripta Materialia*, Vol. 54, No. 7, pp. 1421-1425, ISSN 13596462

Quadakkers, W. J.; Halzbrechen, H.; Brief, K. G. & Beske, H. (1989). Differences in growth mechanisms of oxide scales formed on ODS and conventional wrought alloys. *Oxidation of Metals*, Vol. 32, No. 1-2, pp. 67-88, ISSN 15734889

Rao, N. P.; Lee, H. J.; Kelkar, M.; Hansen, D. J.; Heberline, J. V. R.; McMurry, P. H. & Girshick, S. L. (1997). Nanostructured Materials Production by Hypersonic Plasma Particle Deposition. *Nanostructured Materials*, Vol. 9, No. 1-8, pp. 129-132, ISSN 09659773

Richard, C.; Lu, J.; Be´ranger, G. & Decomps, F. (1995). Study of Cr_2O_3 Coatings Part I: Microstructures and Modulus. *Journal of Thermal Spray Technology*, Vol. 4, No. 4, pp. 342-346, ISSN 15441016

Rohatgi, P. K.; Asthana, R. & Das, S. (1986). Solidification, Structure and Properties of Metal-Ceramic Particle Composites. *International Metals Reviews*, Vol. 31, No. 3, pp. 115-139, ISSN 03084590

Schutz, H.; Gossmann, T.; Stover, D.; Buchkremer, H. & Jager, D. (1991). Manufacture and Properties of Plasma Sprayed Cr_2O_3. *Materials and Manufacturing Processes*, Vol. 6, No. 4, pp. 649-669, ISSN 10426914

Skandan, G.; Yao, R.; Kear, B.; Qiao, Y.; Liu, L. & Fischer, T. (2001). Multimodal Powders: A New Class of Feedstock Material for Thermal Spraying of Hard Coatings. *Scripta Materialia*, Vol. 44, No. 8-9, pp. 1699-1702, ISSN 13596462

Soltani, R.; Coyle, T. W. & Mostaghimi, J. (2008). Microstructure and Creep Behavior of Plasma-Sprayed Yttria Stabilized Zirconia Thermal Barrier Coatings. *Journal of Thermal Spray and Technology*, Vol. 17, No. 2, pp. 244-253, ISSN 15441016

Stack, M. M.; Chacon-Nava, J. & Stott, F. H. (1995). Relationship between the Effects of Velocity and Alloy Corrosion Resistance in Erosion-Corrosion Environments at Elevated Temperatures. *Wear*, Vol. 180, No. 1-2, pp. 91-99, ISSN 00431648

Stollberg, D. W.; Hampikian, J. M.; Riester, L. & Carter, W.B. (2003). Nanoindentation Measurements of Combustion CVD Al_2O_3 and YSZ Films. *Materials Science and Engineering A*, Vol. 359, No. 1-2, pp. 112-118, ISSN 09215093

Stringer, J. & Wright, I. G. (1972). The high-temperature oxidation of cobalt-21 wt.% chromium-3 vol.% Y_2O_3 alloys. *Oxidation of Metals*, Vol. 5, No. 1, pp. 59-84, ISSN 15734889

Stringer, J.; Wilcox, B. A. & Jafee, R. A. (1972). The high-temperature oxidation of nickel-20 wt. % chromium alloys containing dispersed oxide phases. *Oxidation of Metals,* Vol. 5, No. 1, pp. 11 – 47, ISSN 15734889

Szczygieł, Bogdan & Kołodziej, Małgorzata. (2005). Composite Ni/Al2O3 coatings and their corrosion resistance. *Electrochimica Acta*, Vol. 50, pp. 4188-4195, ISSN 00134686

Uusitalo, M. A.; J. Vuoristo, P. M. & Mantyla, T. A. (2004). High-Temperature Corrosion of Coatings and Boiler Steels Below Chlorine-Containing Salt Deposits. *Corrosion Science*, Vol. 46, No. 6, pp. 1311-1331, ISSN 0010938X

Vaidya, R. U.; Butt, D. P.; Hersman, L. E. & Zurek, A. K. (1997). Effect of Microbial Corrosion on the Tensile Stress-Strain Response of Aluminum and Al_2O_3-Particle Reinforced Aluminum Composite. *Corrosion*, Vol. 53, No. 2, pp. 136-141, ISSN 00109312

Varma, S. K. & Vasquez, G. (2003) Corrosive wear behavior of 7075 aluminum alloy and its composite containing Al_2O_3 particles. *Journal of Materials Engineering and Performance*, Vol. 12, No. 1, pp. 99-105, ISSN 15441024

Vippola, M. ; Vuorinen, J.; Vuoristo, P.; Lepisto, T. & Mantyla, T. (2002). Thermal Analysis of Aluminum Phosphate Sealed Plasma Sprayed Oxide Coatings. *Journal of the European Ceramic Society*, Vol. 22, No. 12, pp. 1937-1946, ISSN 09552219

Whittle, D. P.; El-Dahshan, M. E. & Stringer, J. (1977). The oxidation behavior of cobalt-base alloys containing dispersed oxides formed by internal oxidation. C*orrosion Science,* Vol. 17, No. 11. pp. 879-891, ISSN 0010938X

Wright, I. G.; Wilcox, B. A. & Jafee, R. A. (1975). The high-temperature oxidation of Ni-20%Cr alloys containing various oxide dispersions. *Oxidation of Metals,* Vol. 9, No. 3, pp. 275-305, ISSN 15734889

Xie, L.; Jordan, E. H.; Padture, N. P. & Gell, M. (2004). Phase and Microstructural Stability of Solution Precursor Plasma Sprayed Thermal Barrier Coatings. *Materials Science and Engineering A*, Vol. 381, No. 1-2, pp. 189-195, ISSN 09215093

Xu, J.; Tao, J.; Jiang, S. & Xu, Z. (2008). Investigation on Corrosion and Wear Behaviors of Nanoparticles Reinforced Ni-Based Composite Alloying Layer. *Applied Surface Science*, Vol. 254, No. 13, pp. 4036-4043, ISSN 0169-4332

Yoshiba, M. (2003). Effect of Hot Corrosion on the Mechanical Performances of Superalloys and Coating Systems. *Corrosion Science*, Vol. 35, No. 5-8, pp. 1115-1121, ISSN 0010938X

Yu, X. Q.; Fan, M. & Sun, Y. S. (2002). The Erosion–Corrosion Behavior of Some Fe_3Al-Based Alloys at High Temperatures. *Wear*, Vol. 253, No. 5-6, pp. 604-609, ISSN 00431648

Zhu, D. & Miller, R. A. (1997). Determination of Creep Behavior of Thermal Barrier Coatings Under Laser Imposed Temperature and Stress Gradients, NASA Technical Memorandum 113169, Report Number ARL-TR-1565, Date of access: 15th of August 2011, Available at http://gltrs.grc.nasa.gov/reports/1997/TM-113169.pdf

IntechOpen

IntechOpen



Corrosion Resistance

Edited by Dr Shih

ISBN 978-953-51-0467-4
Hard cover, 472 pages
Publisher InTech
Published online 30, March, 2012
Published in print edition March, 2012

The book has covered the state-of-the-art technologies, development, and research progress of corrosion studies in a wide range of research and application fields. The authors have contributed their chapters on corrosion characterization and corrosion resistance. The applications of corrosion resistance materials will also bring great values to reader's work at different fields. In addition to traditional corrosion study, the book also contains chapters dealing with energy, fuel cell, daily life materials, corrosion study in green materials, and in semiconductor industry.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Ramesh K. Guduru and Pravansu S. Mohanty (2012). Corrosion of Metal - Oxide Systems, Corrosion Resistance, Dr Shih (Ed.), ISBN: 978-953-51-0467-4, InTech, Available from: http://www.intechopen.com/books/corrosion-resistance/corrosion-of-oxide-layers-and-oxide-dispersed-metallic-systems

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the Creative Commons Attribution 3.0 License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen