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Nano-Structured Alloy and Composite Coatings for High Temperature Applications

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Nano-structured materials often possess special properties that materials with identical compositions but ordinary grain size do not have. This paper reports our work on the surface nano-crystallisation and nano-structured alloy and composite coatings. A number of processing methods including magnetron sputtering, thermal spray and pulse electro-spark deposition have been used to produce surface nano-crystalline structure. The compositions and microstructures can be well controlled by using different targets or electrodes, nano-structured composites and adjusting processing parameters. Surface nano-structured coatings can provide special chemical, mechanical and electronic properties such as high temperature corrosion and corrosive wear resistance. It has potential applications such as turbine blades, engine parts for petrochemical, aerospace and electronic device industries. This paper is focused on the study of the interrelations between processing, microstructure and properties. Physical models have been established to explain the effects of nano-crystalline structure on the properties.

Keywords: *Nano-materials, coating, high temperature corrosion, metal-oxide composite coatings, Ti and Ti-Al based materials*

1. Introduction

Nano- and micro-crystal materials often possess special properties that materials with identical compositions but ordinary crystal size do not have. These materials are finding wide applications especially as electronic, photonic, magnetic, and biomedical materials[1]. Nano- and micro-crystal materials are also known to have superior mechanical properties due to the extremely fine grain size[2]. However, it has not been well known that alloy and alloy-oxide composite coatings with nano- and micro-crystal grains have special properties for high temperatures corrosion properties. Nano structures promote selective oxidation, forming protective oxidation scales with superior adhesion to the substrate. Progress has been made in this area as nano- and micro-crystal alloy coatings, oxide dispersive alloy coatings and metal-oxide composite coatings show superior high-temperature corrosion resistance[3].

2. Processing of nano-crystal coatings

Nano-crystal and submicro-crystal alloy coatings or thin films can be produced in many ways including chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spray, electrochemical deposition, sol-gel methods, electro-spark deposition, and laser and electron beam surface treatment[4]. Processing parameters can be carefully controlled to obtain a fine grain size and processing temperature should be kept low. Magnetron sputter deposition (a PVD technique) has been used to produce alloy coatings with a wide range of alloy compositions[5]. When an alloy coating is deposited with an unbalanced magnetron sputter, the grain size and deposition rate are affected by the working Ar pressure, substrate bias voltage, target current and the distance between target and substrate[6-7]. When Ni-Cr-Al alloy coatings are deposited on alloy substrate, the coating grain size is mainly a function of the Ar pressure. Grain size as small as ~50 nm was obtained with a low Ar pressurez of 2-5 *mTorr*[7,8]. Doping can also change the grain size and shape of the deposited thin films. Figure 1 shows an example in which the Zn and ZnO thin films were deposited on a glass substrate by magnetron sputtering with DC or RF sources[9]. It can be seen that the Zn grains are much smaller toward the substrate surface (Fig. 1a); and the Al doping reduced the grain size

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to the level of ~50 nm (Fig. 1b). Zn oxide thin films can also be obtained by oxidation of thin Zn films under a controlled oxygen partial pressure. Nano-structured ZnO grains form clusters of ~100 nm size (Fig. 1c). When ZnO was directly deposited onto a substrate, the grain size was much smaller compared with metallic Zn (Fig. 1d). The microstructure, oxidation state, doping elements and doping levels have strong effects on the electronic properties

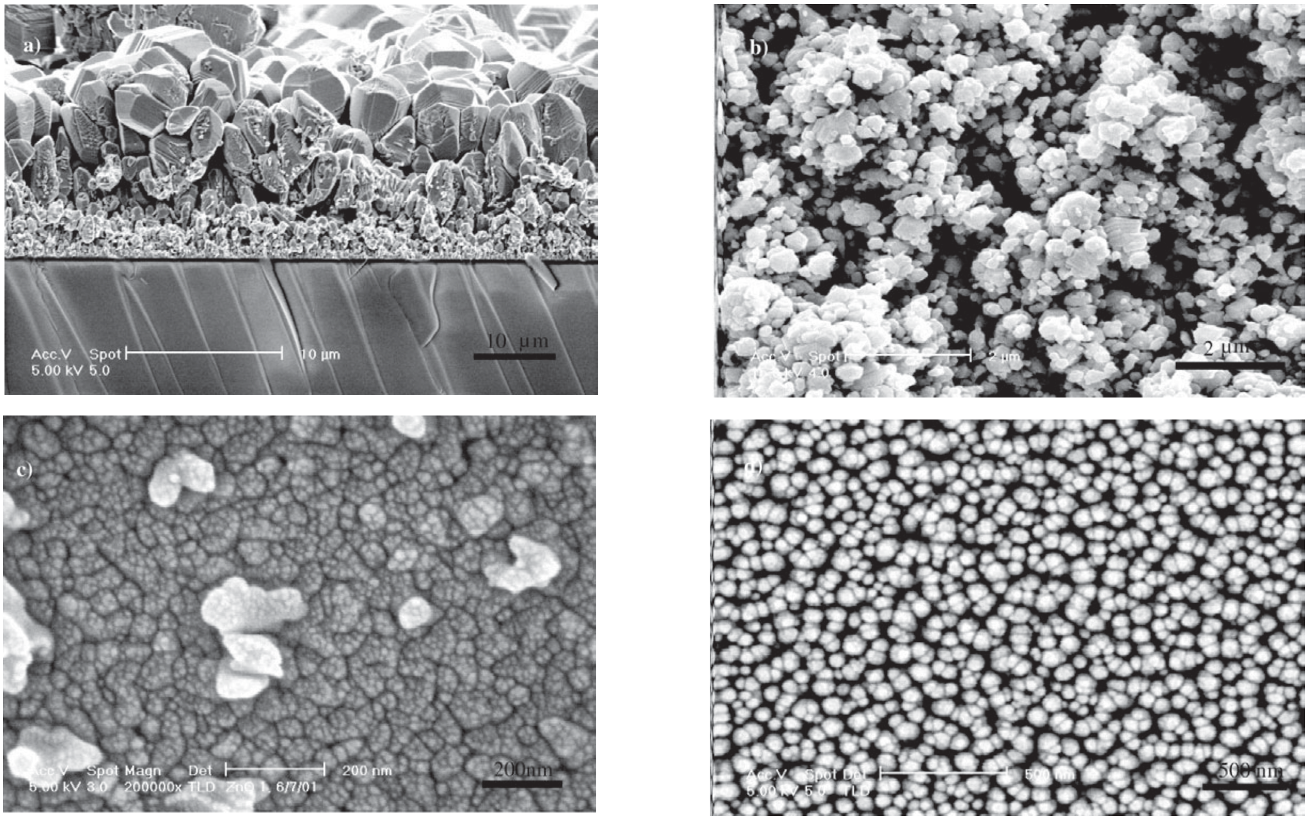

Figure 1. Zinc and ZnO thin films formed with direct oxidation and magnetron sputtering, a) Zn cross-section, b) Zn + 1.2at.%Al surface morphology showing the effect of Al doping on the microstructure, c) ZnO formed through oxidation of Zn under Po_2 @ 10^{-3}atm at 380°C for 24 hrs, and d) ZnO film with DC magnetron sputtering.

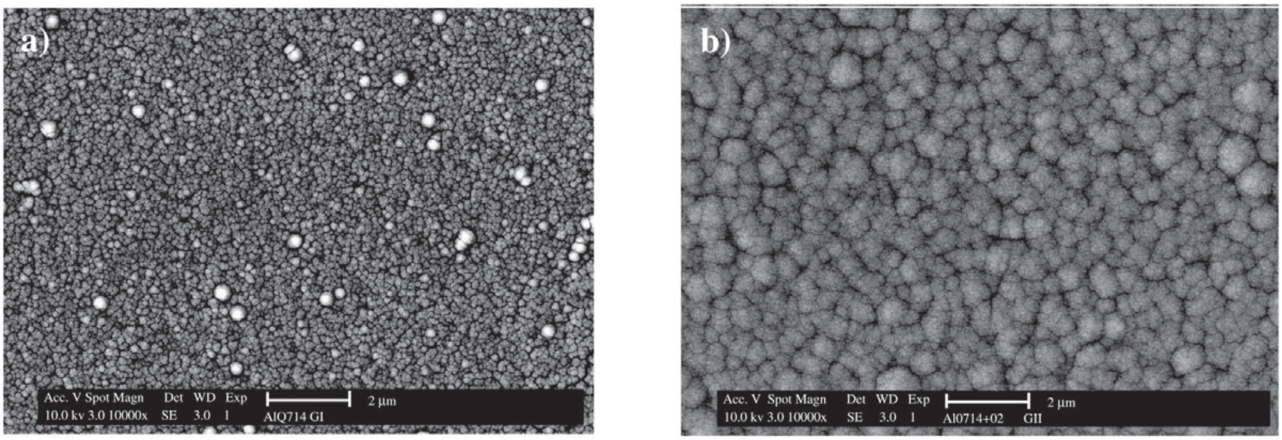

Figure 2. SEM surface morphologies of the coatings produced by a) co-deposition of 310 stainless steel and Al, and b) reactive deposition of Al with O_2.

of the oxide thin films, such as transparency, conductivity and photoluminescence (PL) properties[10].

Co-deposition and reactive deposition were also carried out using unbalanced magnetron sputter. Co-deposition is to sputter metals from two or more targets, or from a composite target[11-13]. Composite target is a plate made of several different materials. Coating compositions can be accurately controlled by adjusting the currents on the different targets, or the constitution of the composite target. Reactive deposition is performed by introducing certain amounts of reactive gases (e.g. O_2 or N_2) into the chamber [13]. Alloy-oxide or alloy-nitride coatings can be produced in this way. Fig.2 shows high-resolution SEM micrographs of co-deposited 310 stainless steel and Al, as well as reactive deposited Al coatings. The co-deposited coating has an average grain size of ~100 nm. The reactive deposited coating shows clusters of ~500 nm, each of which appeared to consist of many small grains. By careful control of the processing parameters, coatings with gradient compositions and microstructures can also be produced. These coatings have compositions gradually changing from interface to surface, resulting in higher concentrations of desirable components near the coating surface, and better interface connection between the coating and metal substrate. These coatings performed very well against high temperature corrosion[11-13].

Some novel but simple techniques were also developed to produce nano- and submicro- and micro-crystal coatings. Electro-spark deposition and high-energy, pulse plasma surface treatment are two of the recent developments[14-18]. These techniques use highly concentrated energy to melt the electrode and substrate surface, originally for producing hard and wear resistant coatings[19]. Nano- and submicro-crystal coatings with grain sizes of 50 - 500 nm are then formed due to the subsequent rapid-solidification. Nano-sized oxides such as Al_2O_3 and Y_2O_3 can be added into the coatings, resulting in oxide dispersive strengthening (ODS) alloy coatings. Fig. 3 is an atomic force microscopic (AFM) photo of the electro-spark treated surface, showing very fine crystal structure. Fig. 4 shows transmission electron micrographs (TEM) of oxide dispersion in Fe-Cr-Ni-Al-Y_2O_3 ODS coatings, showing spherical Y_2O_3 particles of ~15 nm size. These coating techniques

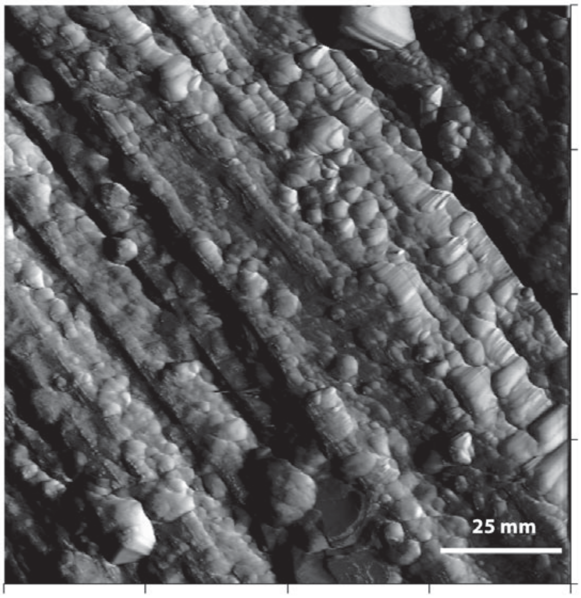

Figure 3. AFM image of electro-spark deposited coating surface on stainless steel, showing nano-crystal structure produced by rapid solidification.

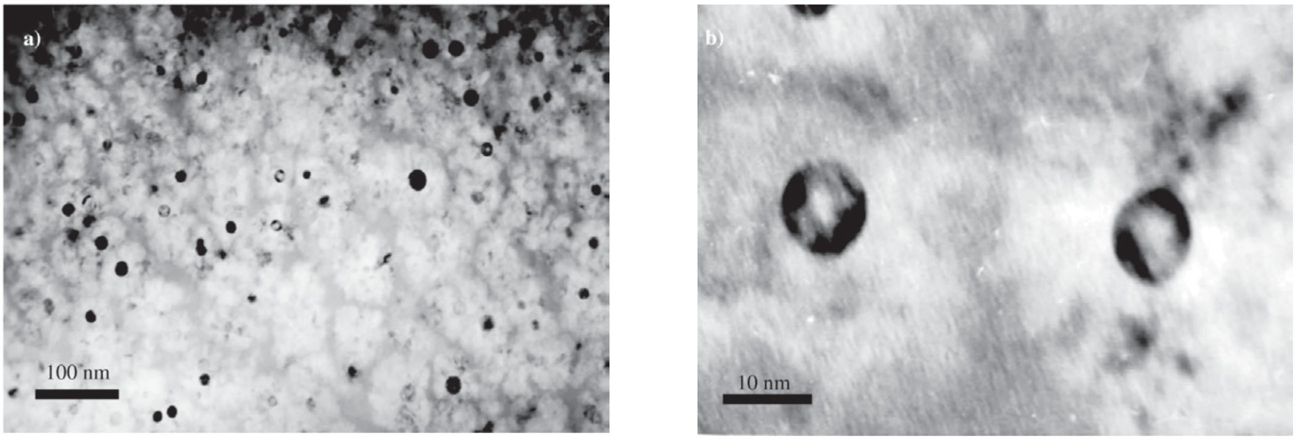

Figure 4. Dispersed oxide particles in the ODS coatings observed by TEM, showing nano-sized, spherical balls of Y_2O_3 dispersed inside Fe-Cr-Ni-Al-Y_2O_3 coating.

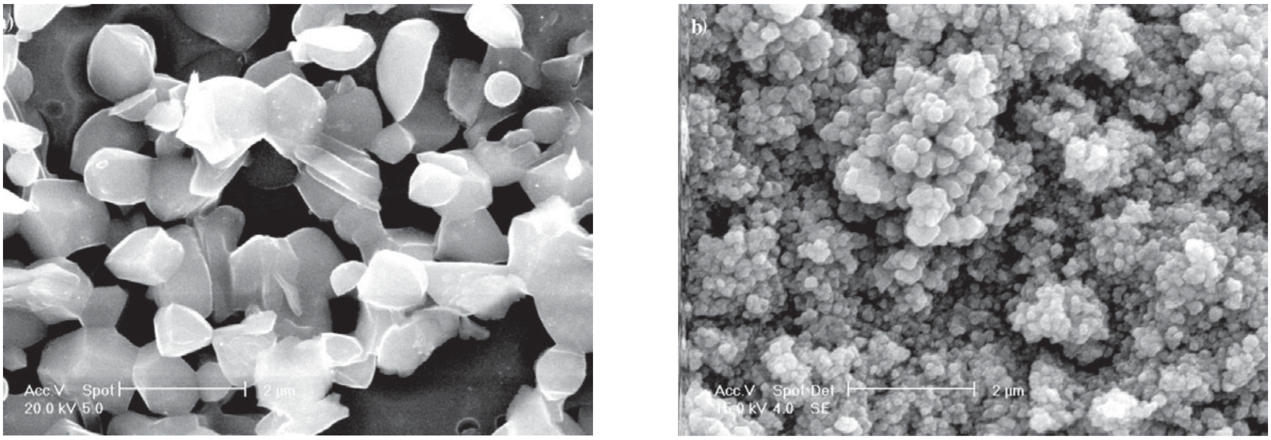

Figure 5. Ti_3Al-TiC composite fabricated through MA and HIPing: a) etched, shows the TiC particles; b) shows the formation of fine oxides.

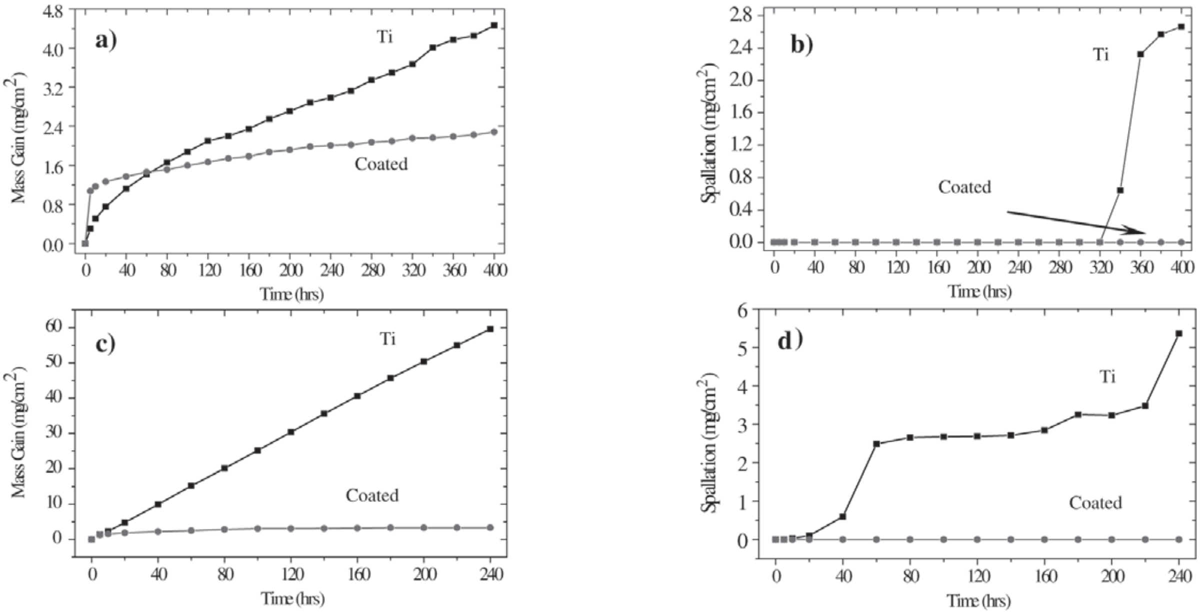

Figure 6. Oxidation kinetics and scale spallation of Ti with and without composite coating: a-b) 700 °C; c-d) 800 °C.

produce nano-crystal coatings with strong metallurgical bonding, exhibiting remarkably improved high-temperature oxidation and hot-corrosion resistance[14,16,17]. These techniques also have the advantages of simple/portable equipment and fast/easy operation. Vacuum or protective atmospheres can be applied but are not necessary. These features make the techniques very attractive for industrial applications such as parts repairing and *in situ* treatment[20].

3. Nano-composites and coatings for Ti and Ti alloys

Ti alloys and Ti-Al intermetallics have the advantages of high strength, light-weight and high melting point. They have great potential applications in aerospace and automotive industries due to their excellent mechanical properties at high temperatures and corrosion resistance. However, their oxidation resistance at elevated temperatures is poor. The formation of TiO_2 does not provide good protection against further oxidation. As a result, Ti, Ti alloys and Ti_3Al based materials can only be ed up to ~650 °C without excessive oxidation. Great efforts have been made to improve their oxidation resistance. Expensive alloying additions (e.g. Nb) were used to improve the oxidation resistance. The results are not satisfactory.

SiC and TiC particulate reinforced Ti_3Al intermetallic matrix composites were fabricated using mechanical alloying and hot pressing or HIPing methods. Fig.5 shows the microstructure of a Ti_3Al-20vol.%TiC composite after etching. It was found that the oxidation resistance of the composites is significantly improved compared to Ti, Ti alloys and Ti_3Al intermetallics. Ti_3Al-SiC showed a rather low mass gain due to the formation of Ti-Si compounds and discontinuous SiO_2 particles. However, the most significant improvement is that all composite samples exhibited excellent scale spallation resistance. While the cast Ti_3Al suffered severe spallation, no scale spallation could be found on the composites during oxidation tests. It is believed that the small oxide grain size relieves the stresses in the scale effectively, and the complex oxide-metal interface results in strong adherence between the scale and the substrate[21,22].

A special type of composite, $Ti_3Al(O)$-Al_2O_3, was prepared by ball milling of TiO_2 with Al and consolidation[23]. It was applied on pure Ti substrate as a coating through thermal spraying. The coatings show superior oxidation and scale spallation resistance at 700 and 800°C up to 400 h exposure, Fig. 6. The enhanced resistance is attributed to the incorporation of Al_2O_3 into the coating, which plays a multiple role during oxidation. Thick TiO_2 scale with a layered structure formed on Ti metal during oxidation. Cracks tend to develop along the scale, causing detachment (Figs. 7a and 7c). On the other hand, the coated material showed very different morphology. The alumina particles served as a diffusion barrier, an inhibitor to crack propagation in the oxide scale, and the connectors between the coating and oxide scale, Figs. 7b and 7d. As a result, the coating can increase the application temperature of Ti, Ti and Ti_3Al alloys from ~650 °C to ~800 °C[24].

Electro-spark deposition technique was also applied to produce aluminide coatings on Ti_3Al and TiAl

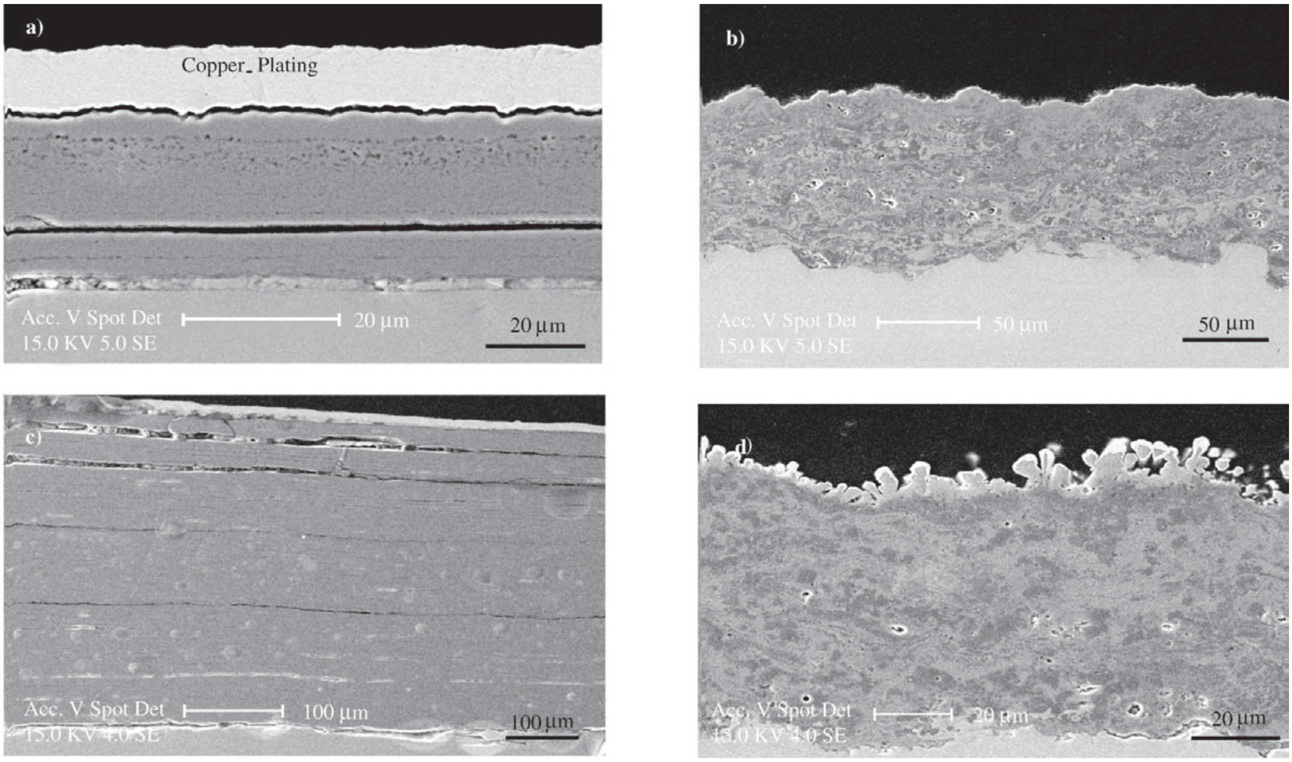

Figure 7. Cross-sections of Ti with and without composite coating: a) 700 °C, 400 h; Ti, b) 700 °C, 400 h, coated Ti; c) 800 °C, 240 h, Ti; d) 800 °C, 240 h, coated Ti.

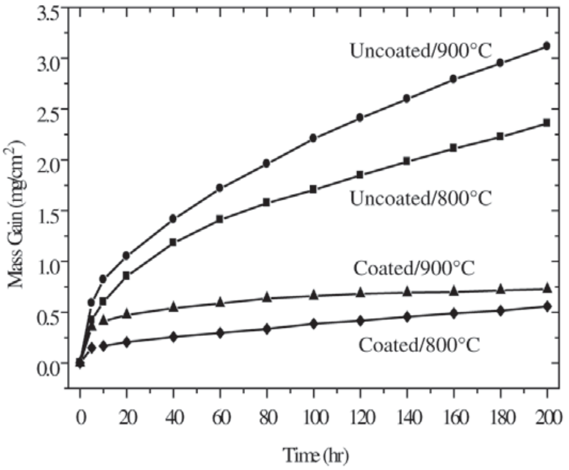

Figure 8. Oxidation of coated and uncoated Ti_3Al-Nb with ESD aluminide coating

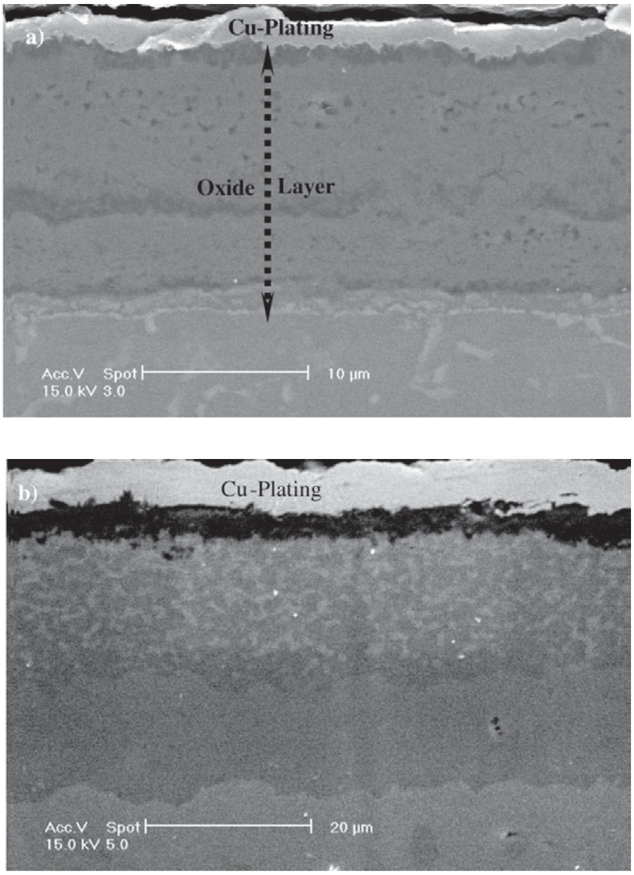

Figure 9. Cross-section morphology showing oxide layers on Ti-Al intermetallics: a) uncoated, thick layer mainly composed of rutile; b) coated, thin and dense alpha-alumina layer (900 °C).

intermetallics[25-26]. Isothermal oxidation tests showed that the coated specimens exhibited much lower oxidation rates than uncoated specimens (Fig. 8). The formation of TiO_2 was largely suppressed; and Al_2O_3 then became the main oxidation product. Furthermore, oxide scale spallation resistance was greatly improved by the nano-structure. No scale cracking or spallation could be observed on the coated specimens during the oxidation tests (Fig. 9). Nano- or submicro-alloy coatings produced by electro-spark deposition, therefore, provide another powerful tool for Ti-Al intermetallics to be used as high temperature structural materials.

4. Selective oxidation of nano-crystal coatings

One of the most important advantages of nano-crystal coatings is the ability to promote selective oxidation. Engineering alloys rely on the formation of protective oxide films such as Al_2O_3 and Cr_2O_3 to resist high-temperature and corrosive environments. Unfortunately, relatively large concentrations of Al or Cr are needed to form a complete Al_2O_3 or Cr_2O_3 scale. In the Ni-20Cr-Al alloy system, for instance, > 6 wt.%Al is required to form a complete Al_2O_3 scale[27]. High Al contents, however, often degrade the mechanical properties of alloys. If the Al content is lower than 6wt.%, complex oxides consisting of Cr_2O_3, $NiCr_2O_4$ and internal Al_2O_3 may form, resulting in high reaction rates and poor oxidation resistance.

With nano-crystal alloy coatings, the Al content that is required to form a complete protective oxide scale can be substantially reduced. Experimental results indicated that when the grain size of Ni-20Cr-Al coatings was in the level of ~60 nm, alloys containing ~2 wt.%Al could form a complete α-Al_2O_3 scale at 1000 °C in air. This concentration is only 1/3 of the required %Al for the Ni-20Cr alloy with normal grain size! Fig.10 shows the cross-section SEM micrographs of oxidised samples, exhibiting very different oxide scales that formed on the Ni-20Cr-2Al coatings with different grain sizes.

Due to the formation of highly protective α-Al_2O_3, the oxidation rate of the nano-crystal coatings is much lower than the coatings with the same composition but a larger grain size. A detailed study showed that the composition and microstructure of the oxide scales are a function of coating grain size. Fig. 11 shows the relationship between the oxide products, coating grain size and Al content, indicating that the selective oxidation of Al is greatly promoted by nano-crystal structure[7]. The promotion effect of nano-crystal grains on selective oxidation is attributed to short-circuit diffusion of Al through the grain boundaries.

Mathematical models based on simultaneous diffusion through the crystal lattice and grain boundaries have been established to predict selective oxidation and to describe

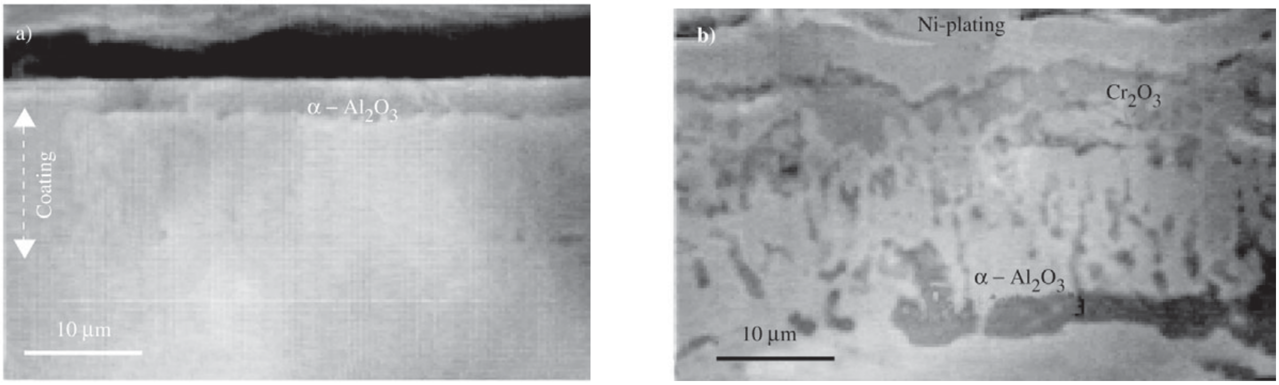

Figure 10. Cross-section of Ni-20Cr-2Al coating samples after oxidation at 1000 °C for 100 h: a) coating grain size ~60 nm; b) coating grain size ~370 nm.

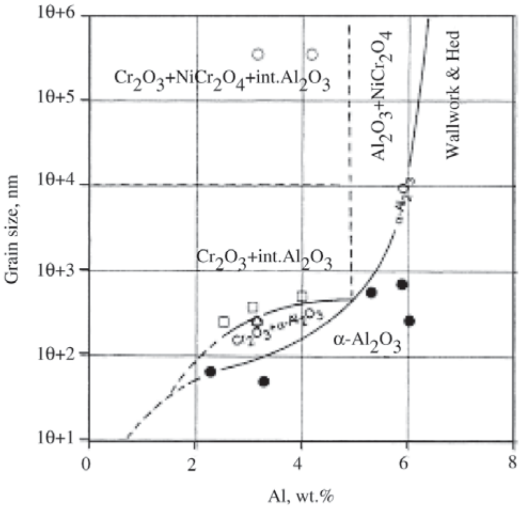

Figure 11. A diagram showing the relationship of grain size, Al content, and oxidation products for Ni-20Cr-xAl at 1000 °C in air.

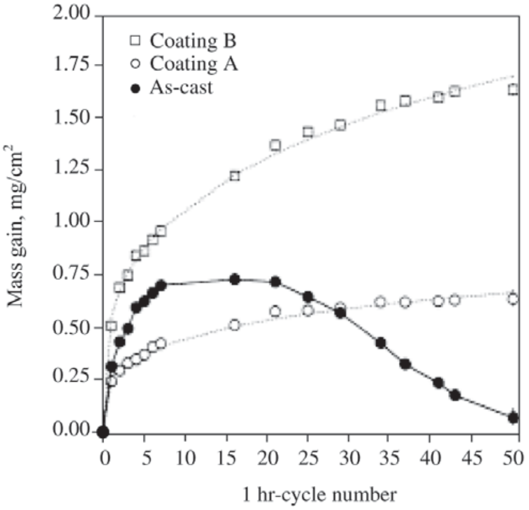

Figure 12. Oxidation mass gains versus time for Ni-20Cr-3Al, as-cast alloy (grain size ~0.4 mm), coating A (~50 nm) and coating B (~0.5 μm).

oxidation kinetics. These models showed a good agreement with the experimental results obtained by the authors in other materials and reported in the literatures[7,28].

5. Improve oxide scale spallation resistance

Parts working at high-temperatures and corrosive environments rely on the formation of an oxide scale to protect the materials from further oxidation. This oxide scale should be strong, tough and possess good adherence to the metal substrate. A problem many alloys have is that the protective oxide scales do not last long. Scale cracking and spallation take place after certain time at high-temperatures, or during thermal cycles, contaminating the equipment and substantially reducing the service life of the parts. The oxide scales formed on nano- and micro-crystal coatings show a superior resistance to cracking and spallation. Cyclic and long-time oxidation resistance was significantly improved by applying nano-crystal coatings of *AISI 310* stainless steel[11], Ni-Cr-Al[29-30], FeAl intermetallic compounds[31], and Ti-Al intermetallic composites[21,23,32]. Fig. 12 compares the cyclic oxidation behaviours of Ni-20Cr-3.5Al as a cast alloy (average grain size 0.4 mm), a submicro-crystal coating (~0.5 μm) and a nano-crystal coating (~50 nm). Both nano- and micro-crystal coatings show good oxide spallation resistance compared to the as-cast alloy. The nano-crystal coating also showed a lower oxidation rate.

Scale spallation is a complex process influenced by many mechanical and chemical factors. The mechanisms by which nano-crystal structures improve scale spallation resistance are also complex. Several mechanisms can be suggested based on the experimental results. Firstly, nanocrystal structures promote selective oxidation to form more protective oxides. Secondly, the fine-grained coatings and/or the fine-grained oxide scales often show a fast creep rate at high-temperatures, which can release the stresses accumulated in the scales, and therefore reducing the scale spallation tendency. Thirdly, the oxides formed on nano- and submicro-crystal coatings are pegged onto the grain boundaries to form a complex interface. The so-called "micro-pegging" effect of the inward-grown oxides results in better scale adhesion to the metal substrate.

6. Summary

This paper demonstrated that nano- and submicro-structured coatings possess superior high-temperature oxidation and corrosion resistance. The high-density of grain boundaries provide fast diffusion paths, promoting the selective oxidation of protective oxide scales. Scale adhesion and spallation resistance are also improved by stress release and micro-pegging effects. Nano- and micro-crystal alloy and alloy-oxide composite coatings have been proven to be a powerful technique to combat high-temperature corrosion. The theories and models developed from this research can be used to design coatings and alloys for high-temperature, energy related applications.

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