

DEVELOPMENT OF OXIDATION PROTECTION COATINGS FOR GAMMA TITANIUM ALUMINIDE ALLOYS

T. A. Wallace and R. K. Bird
NASA Langley Research Center
Hampton, VA

S. N. Sankaran
Lockheed Martin Space Operations
Hampton, VA

ABSTRACT

Metallic material systems play a key role in meeting the stringent weight and durability requirements for reusable launch vehicle (RLV) airframe hot structures. Gamma titanium aluminides (γ -TiAl) have been identified as high-payoff materials for high-temperature applications. The low density and good elevated temperature mechanical properties of γ -TiAl alloys make them attractive candidates for durable lightweight hot structure and thermal protection systems at temperatures as high as 871°C. However, oxidation significantly degrades γ -TiAl alloys under the high-temperature service conditions associated with the RLV operating environment.

This paper discusses ongoing efforts at NASA Langley Research Center to develop durable ultrathin coatings for protecting γ -TiAl alloys from high-temperature oxidation environments. In addition to offering oxidation protection, these multifunctional coatings are being engineered to provide thermal control features to help minimize heat input into the hot structures. This paper describes the coating development effort and discusses the effects of long-term high-temperature exposures on the microstructure of coated and uncoated γ -TiAl alloys. The alloy of primary consideration was the Plansee alloy γ -Met, but limited studies of the newer alloy γ -Met-PX were also included. The oxidation behavior of the uncoated materials was evaluated over the temperature range of 704°C to 871°C. Sol-gel-based coatings were applied to the γ -TiAl samples by dipping and spraying, and the performance evaluated at 871°C. Results showed that the coatings improve the oxidation resistance, but that further development is necessary.

INTRODUCTION

γ -TiAl intermetallic alloys are candidate materials for many high-temperature structural applications because of their high specific strengths and excellent high-temperature properties. These applications include airframe hot structures and thermal protection systems for reusable hypersonic flight vehicles which re-enter the earth's atmosphere under extreme temperature and environmental conditions hundreds of times during the vehicle's life. However, these alloys are prone to both oxidation and oxygen embrittlement when exposed to these severe service conditions. Therefore, development of coatings to prevent environmental damage is critical, especially for thin-gage sheet and foil products where a significant portion of the material cross-section can be severely affected.

Many challenges exist in the development of a useful coating. It must be thin and lightweight in order to minimize structural weight. Ease of application is important because the coating process must allow coverage of large acreage material and be compatible with in-field repair. The coating process must not adversely impact the mechanical properties of the alloy, and the coating must be chemically compatible with the alloy throughout the service life. In addition, the coating can also be used to modify the surface of the structure to enhance its thermal control characteristics. For many applications, a high emittance coating can significantly reduce the amount of heat that is absorbed by the structure. Also, in hot flowing-air environments where gaseous species (such as oxygen and nitrogen) have been dissociated into their atomic form, the recombination of these atoms at the surface can cause significant increases in heat input into the structure. Catalytic efficiency, or recombination efficiency, is a measure of the propensity of a material to promote this recombination and can vary significantly for different materials. Generally metallic materials have a relatively high catalytic efficiency, and coatings that reduce the efficiency of this recombination can greatly reduce the structural temperature.

Multifunctional, multilayer coatings are being developed at NASA Langley Research Center (LaRC) to meet the oxidation protection and thermal control requirements for γ -TiAl hot structures. One technique that is attractive for applying these coatings is a sol-gel process because of its ability to produce very thin, lightweight coatings, and the wide range of coating chemistries that can be produced. In addition, sol-gel coatings are simple to apply, offering the potential for easy scale-up and field repair.

This paper discusses the work at NASA LaRC to develop ultrathin, lightweight, sol-gel based coatings that offer environmental protection and thermal control for candidate titanium aluminide alloys. Testing was performed on a γ -TiAl based alloy with elemental additions to increase room temperature ductility. Oxidation performance was evaluated using thermogravimetric analysis (TGA), and the oxidation products formed were evaluated using scanning electron microscopy (SEM), wavelength dispersive spectroscopy (WDS) and X-ray diffraction (XRD). The oxidation performance of the uncoated γ -Met was evaluated over the temperature range 704°C to 871°C. Several methods for applying the sol-gel coatings were investigated, and coating performance was evaluated at 871°C.

COATING TECHNOLOGY

Sol-gels are colloidal aggregates produced by destabilizing and drying metal-hydroxide and metal-salt solutions. When heated they decompose into oxides, densify, and at sufficiently high temperatures crystallize. Decomposition temperatures are generally below 500°C, and full densification temperatures are generally before 1000°C. The sol-gel process is a promising route for the fabrication of ceramic oxide coatings. Sol-gels have major advantages for practical applications: (a) relatively low processing temperatures, (b) potential for coating large and complex areas, and (c) good homogeneity and high purity. In principle, an oxide coating of almost any composition can be prepared from sol-gels provided that the appropriate starting materials are chosen.

In the sol-gel process, a precursor coating is formed from a metal-organic solution that is applied as a liquid at room temperature. Gel formation will then occur at room temperature and is accelerated through heating. The final step is curing during which the precursors decompose into oxides and densify. The final product is environmentally inert and stable.

A variety of methods like dipping, brushing or spraying can be used to apply precursor sol-gel coatings to the substrate. For uniform, thin coatings, dipping has been proven to produce good results on a range of metallic materials.¹ The set-up for application is typically simple and inexpensive and primarily consists of a container to hold the sol and mechanism to dip and withdraw the part at a specific rate. The coating thickness, uniformity and integrity are controlled by the sol chemistry, viscosity of the sol, and by the rate of withdrawal of the specimen from the sol. However, a technique such as spraying would be more amenable to coating large structure and field repair.

A multiplayer coating design has been adopted for meeting the oxidation, emittance, and low catalysis characteristics needed in hypersonic structures. This coating design consists of up to five types of layers and is shown schematically in Figure 1. The outermost layer is designed for low catalysis efficiency to minimize aerothermodynamic heating and is based on borosilicate or borophosphate glasses. The high emittance layer consists of various constituents that provide emittance enhancement

to the total system. It is shown as the second layer from the outer surface, but its location may be changed to optimize the combination of oxidation resistance and emittance. The third layer is an oxygen diffusion barrier. This layer is composed of a two-phase glass and may consist of two sublayers: the base, and an outer sealant which is similar in content to the base but with a higher proportion of a low melting temperature constituent to promote fluidity and sealing effectiveness in the coating. A reaction barrier layer is required in most alloys to prevent reaction between the coatings and the substrate alloy.

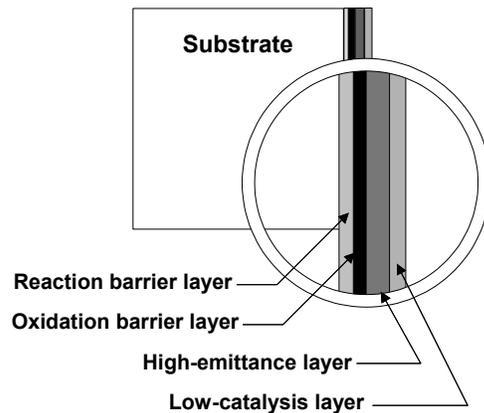


Figure 1. Schematic of coating

EXPERIMENTAL PROCEDURE

MATERIALS

The material used in this study was 1-mm thick hot-rolled γ -Met sheet in the primary annealed condition produced by Plansee. This alloy has a nominal composition of Ti – 46.5 Al – 4 (Cr, Nb, Ta, B) in atomic percent. For comparative purposes, a limited amount of oxidation evaluation was performed on 1-mm thick γ -Met-PX alloy with a composition proprietary to Plansee. This alloy was developed to offer improved strength, creep resistance, and oxidation resistance.

SPECIMENS

Two types of specimens were used for coating and oxidation behavior evaluation: thermogravimetric analysis (TGA) specimens and tensile blanks from which tensile specimens were machined following oxidation exposures. The TGA specimens measured approximately 10 mm by 15 mm. The tensile blanks measured approximately 140 mm by 50 mm. These tensile blanks were wide enough to allow three tensile specimens to be machined from them. The TGA specimens and the tensile blanks had a 1.5-mm diameter hole drilled through one end to allow suspension of the specimens during the dip coating process.

The tensile specimen configuration was based on ASTM E8. The specimen design was modified to incorporate a more gradual transition between the test section and the grip section due to the limited ductility of the alloy. The specimen length was 120 mm and the width was 8.4 mm in the grip areas. The test section had length of 32 mm and width of 6.4 mm. Filets with radius of 305 mm were used to transition from the test section to the grip section. The edges of the specimen were polished prior to testing to remove scratches from the machining process.

COATING

Prior to application of the various layers, the specimens were detergent cleaned, rinsed with acetone followed by methanol, and blotted dry. The specimens were also further cleaned in a HF/HNO₃/water solution to remove residual oxides from the surface.

Two layers of coatings were applied to the specimens. The first layer was an Al₂O₃ reaction barrier to prevent the oxidation barrier layer from reacting with the base alloy. The second layer was the SiO₂-based two-phase glass (TPG) oxidation barrier layer. Both layers were applied through sol gel processing via one of two techniques: dip coating and spray coating. In the dip coating process, the specimen was immersed in the sol and withdrawn at a constant rate. The viscosity of the sol and the rate of specimen withdrawal dictate the thickness of the sol film on the specimen. The spray process, which is more amenable to coating large pieces of structure and for field repair, involved introducing the sol into an aerosol can and hand spraying the sol onto the specimen. Visual inspection is used to confirm uniform coverage. Once a sol film had been applied to a specimen, the sol was allowed to air dry at room temperature to form a gel, then cured at 650°C for 5 minutes to form the dense oxide coating. This process was repeated for each coating layer. The final thickness for each coating layer (reaction barrier and oxidation barrier) was approximately 1-2 μm.

It was also desired to investigate TiAl₃ as a reaction barrier. However, TiAl₃ cannot be applied using the sol-gel process. Therefore, this coating layer was applied by vapor depositing a 1-μm layer of aluminum onto the specimen and reacting it with the base alloy at 620°C for 8 hours under vacuum to form a layer of TiAl₃.

OXIDATION EXPOSURES

Oxidation tests were conducted from 704°C to 871°C for times up to 100 hours using a TGA. The sample weight was recorded continuously during exposure using a Cahn C2000 microbalance with an accuracy of 1 μg. Samples were suspended in a mullite tube inside a vertical tubular furnace, and the temperature was monitored continuously using a R-type thermocouple located just below the suspended specimen. A low flow of the test gas (1 cc/s) through the tube was maintained throughout the test. Most tests were conducted using commercially available high purity air with a hydrocarbon content of less than 0.1 ppm that was also passed through a cold trap maintained at -70°C to remove residual moisture and hydrocarbons prior to introduction into the test chamber. Selected tests were also conducted using a mixture of argon and 10% high purity air to simulate the lower oxygen partial pressures expected in a re-entry flight environment.

METALLURGICAL ANALYSIS

Metallography was performed on the surfaces and mounted cross sections of selected specimens after oxidation exposure. These studies were performed on both coated and uncoated specimens. Scanning electron microscopy was used as the main technique for metallography, using a JEOL JSM 840 scanning electron microscope (SEM). Wavelength dispersive spectroscopy (WDS) was used to perform elemental analysis and distribution maps in both coated and uncoated specimens while in the SEM. All the data were recorded in digital format. For cross-sectional examination, the specimens were in the unetched condition and viewed using back scattered electrons (BSE).

TENSILE TESTS

Room temperature tensile properties were measured before and after coating in accordance with ASTM E8 [2]. Tests were conducted in a closed-loop hydraulic test system with hydraulic grips. Strain was monitored with back-to-back extensometers with 25.4-mm gage length. Specimens were loaded at a stroke rate of 0.25 mm/minute.

RESULTS AND DISCUSSION

OXIDATION BEHAVIOR OF γ -TiAl

Figure 2 shows a summary of the weight gain data for the uncoated γ -Met alloy over the temperature range 704°C to 871°C in 100% air, and at 871°C in 10% air. These results show that the weight gains decreased with decreasing exposure temperature until at 704°C less than 1 mg/cm² was gained after 100 hours. This may indicate that below 704°C the oxidation is small enough to allow usage of the γ -Met alloy without a coating; but further evaluation is still required. However, the γ -Met alloy had only a small reduction in weight gain at 871°C when exposed to the 10% air test gas mixture as compared to 100% air.

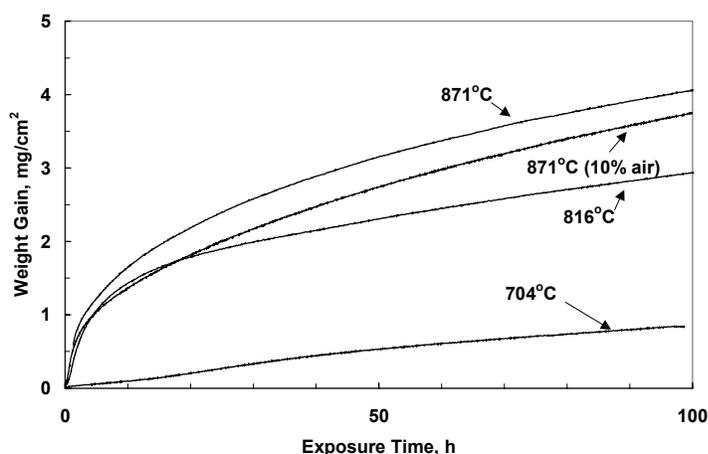


Figure 2. Oxidation data for γ -Met exposed at 871°C, 816°C, and 704°C in 100% air, and 871°C in 10% air

Metallurgical analysis was performed on unexposed samples and after exposure at all test temperatures. Using XRD analysis, only peaks of γ -TiAl were identified in the unexposed sample, while peaks corresponding to TiO₂ and Al₂O₃ were also identified in all oxidized samples. Peaks corresponding to Ti₂AlN were also identified in the samples exposed at 871°C. These results are consistent with previous studies of other γ -TiAl alloys which showed that they react with air to form both oxides and nitrides [3,4].

SEM and WDS examination was also conducted on mounted and cross-sectioned oxidized samples, and the results are presented in Figures 3-5. Figure 3 compares the microstructure of an unexposed sample to that of samples oxidized for 20 and 100 hours. Examination of the as-received microstructure showed it to be consistent with the primary annealed condition of γ -Met; described by LeHolm et al [5] as a fine grained, globular γ microstructure, with a small amount of α_2 and β . This structure appears to be retained after the oxidation exposures except for the formation of an oxide layer at the surface. After 20 hours the oxide appears dense and adherent. However, the oxides formed after 100 hours exposure spalled during cool-down making further analysis of the oxide products difficult.

Figures 4 and 5 present higher magnification SEM micrographs and results of WDS analysis for samples exposed for 20 and 100 hours at 871°C. Analysis of the sample exposed 20 hours showed that there is a top layer of Ti and O, and thin layer below that of Al and O, a thick layer consisted of Ti, Al, O, and a thin bottom layer enriched in N. Cr is also present throughout the oxide layer and N layer. The remaining oxide on the sample exposed for 100 hours shows comparable elemental segregation, consisting of an oxide of both Ti and Al, and a bottom layer enriched in Ti, Cr, and N. These results are consistent with the XRD results that showed that the primary oxide products were TiO₂, Al₂O₃ and Ti₂AlN.

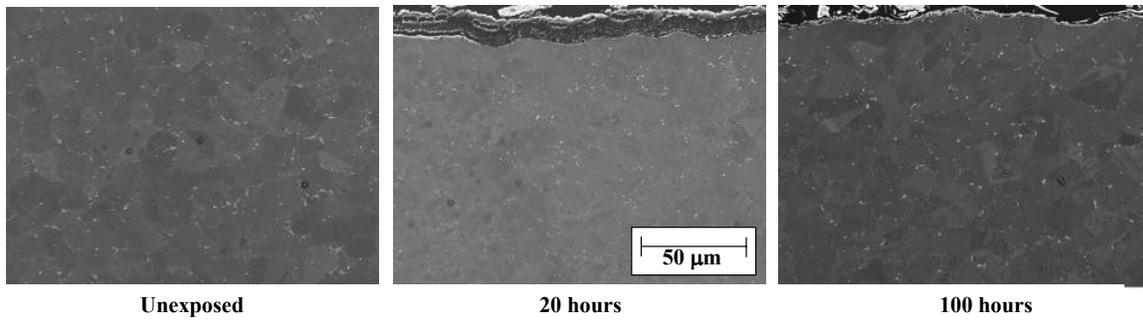


Figure 3. SEM Micrographs of uncoated γ -Met before exposure, and after 20 and 100 hours exposure at 871°C.

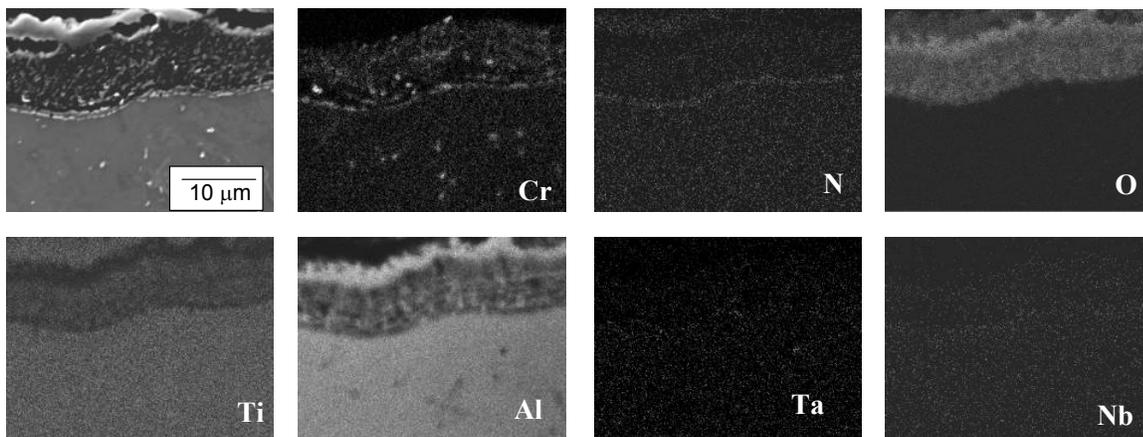


Figure 4. SEM micrographs and WDS elemental dot maps of uncoated γ -Met exposed 20 hours at 871°C.

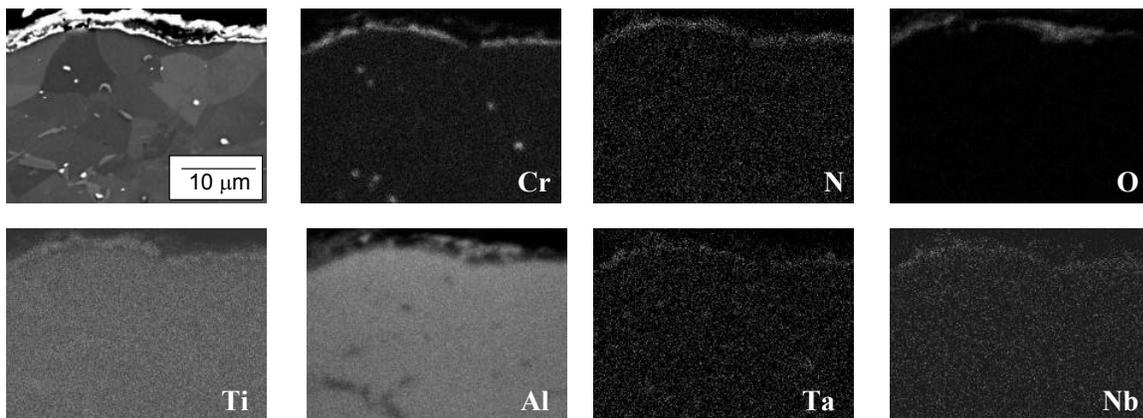


Figure 5. SEM micrographs and WDS elemental dot maps of uncoated γ -Met exposed 100 hours at 871°C.

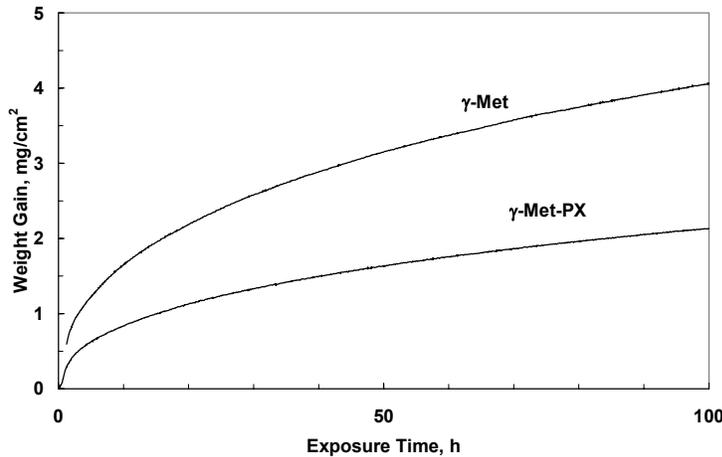


Figure 6. Comparison of the weight behavior of γ -Met and γ -Met-PX when exposed at 871°C.

Oxidation exposures were also conducted on the γ -Met-PX alloy in air at 871°C, and the weight gain results are presented in Figure 6. These data show a substantial improvement in the weight gain resistance of the γ -Met-PX alloy compared to the γ -Met.

COATING PERFORMANCE

Tensile tests were conducted at room temperature on spray-coated and uncoated γ -Met sheet without oxidation exposure to isolate the effect of the coating process alone on the mechanical properties of the alloy. Table 1 shows the ultimate tensile strength (UTS), yield strength (YS), modulus (E), total strain to failure (e_{tot}), and ductility as measured by plastic strain to failure (e_p). Duplicate specimens were tested in the coated and uncoated conditions. The data indicate that the coating process had minimal effects on the tensile properties of the γ -Met sheet.

Table 1. Room temperature tensile data for coated and uncoated γ -Met sheet specimens.

Specimen Condition	Spec. No.	UTS, MPa	YS, MPa	E, GPa	e_{tot} , %	e_p , %	Notes
Uncoated, No Exposure	NC-1	465	437	155	0.86	0.55	(a)
	NC-2	475	444	158	0.73	0.44	(a)
	Avg.	470	440	156	0.80	0.50	
Coated, No Exposure	224-1	452	427	154	0.77	0.48	(a)
	224-2	474	439	155	0.93	0.62	(a)
	Avg.	463	433	155	0.85	0.55	

(a) Specimens broke outside gage-length

The oxidation performance of coating applied by both dipping and spraying were evaluated and the results presented in Figure 7. Two samples were prepared by each technique and exposed for 100 hours at 871°C. These results show that while both coatings improve the weight gain performance, the spray coating appears to be slightly more effective.

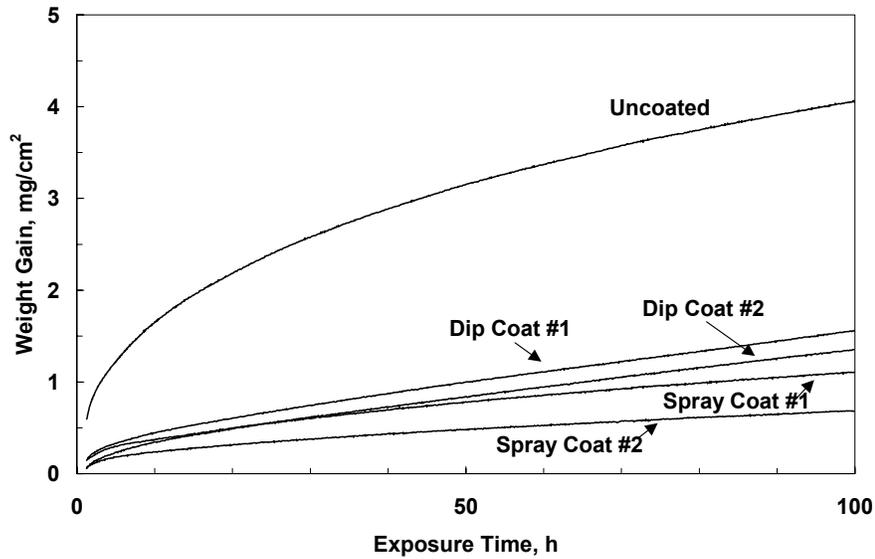


Figure 7. Weight change of coated and uncoated γ -Met exposed at 871°C.

Cross-sectional SEM images and WDS analysis of the oxidized coated samples are presented in Figure 8 for both the spray and dip coatings. Results presented consist of the SEM images, and maps for O and Si to show the location of oxide products and the original coatings respectively. The results show that both coatings allowed oxygen penetration into the base material and oxide formation, which XRD analysis showed to consist of both TiO_2 and Al_2O_3 .

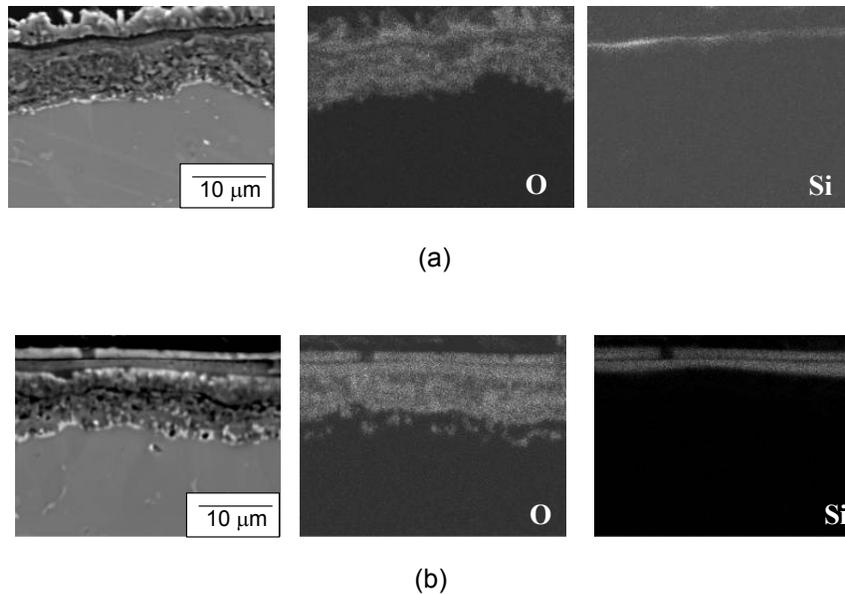


Figure 8. SEM micrograph and WDS elemental dot maps for (a) dip coated and (b) spray coated γ -Met after 100 hours exposure at 871°C.

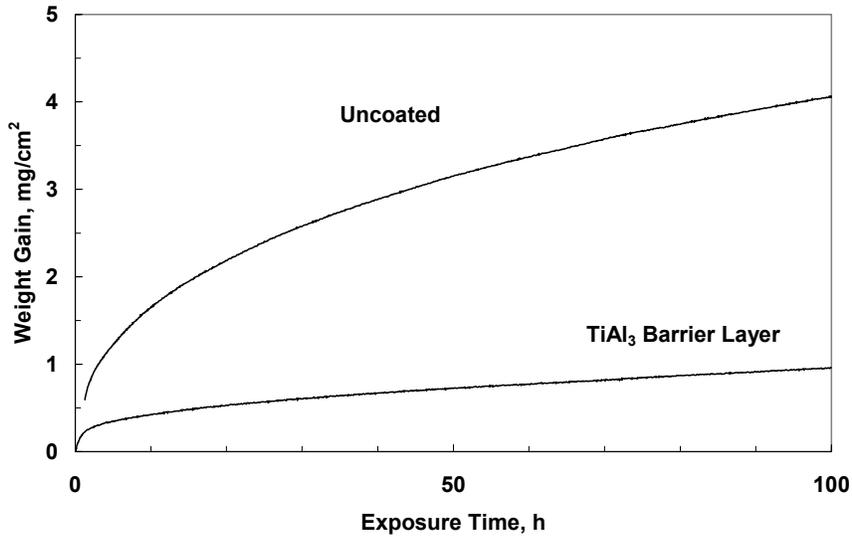


Figure 9. Effect of TiAl₃ barrier layer on oxidation of γ -Met at 871°C.

In order to improve the oxidation behavior of these coatings, TiAl₃ was investigated as a reaction barrier by applying a layer of TiAl₃ (as described previously) onto the γ -Met and then evaluating the oxidation behavior. Samples with the TiAl₃ reaction barrier were then exposed at 871°C for 100 hours, and the resulting weight gain data are presented in Figure 9. SEM examination was also performed on samples with the TiAl₃ barrier layer before and after exposure, and micrographs and elemental maps of Al, Ti, and O are presented in Figure 10. These results show that the TiAl₃ layer improves the oxidation performance of the γ -Met alloy and reduces the amount of oxidation products formed as compared to either the dip or spray coatings alone. This suggests that the application of a TiAl₃ layer as a barrier layer underneath the sol-gel layers would improve the performance of the final coating system.

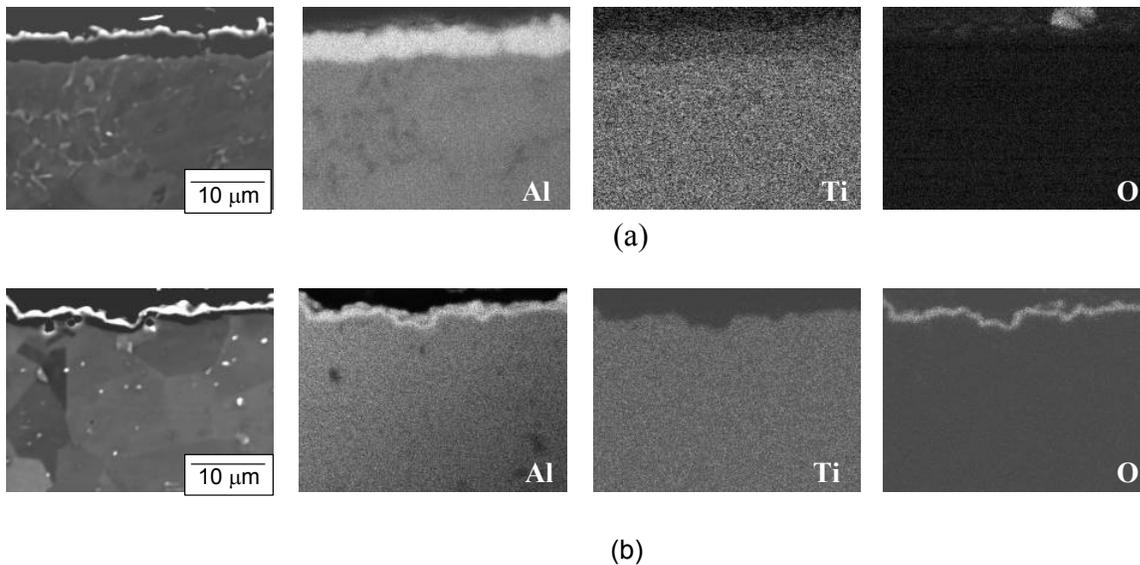


Figure 10. SEM micrographs and WDS elemental dot maps for γ -Met TiAl₃ barrier layer (a) before oxidation exposure and (b) after 100-hour exposure at 871°C.

SUMMARY AND CONCLUSIONS

Ultrathin lightweight sol-gel coatings were developed for environmental protection of γ -TiAl based alloys. Tests of the uncoated Plansee alloy γ -Met were conducted over the temperature range of 704°C to 871°C, and revealed a significant amount of oxidation damage. Sol-gel based coatings were applied by two techniques, dipping and spraying. Tensile tests of the coated materials showed that the coating techniques did not degrade the substrate properties. The coatings greatly reduced oxidation weight gain; but microstructural analysis showed that they still allowed oxidation of the substrate. A reaction barrier layer of TiAl₃ was investigated to prevent this interaction. This layer was applied by vapor depositing Al on the γ -Met and then reacting to form TiAl₃. Preliminary tests showed this layer successfully reduced oxidation rates and prevented oxidation damage to the base metal.

FUTURE WORK

Further work is still needed to evaluate the effectiveness of the present reaction barrier and oxidation protection coating layer formulations. This work includes completing oxidation exposures on coated and uncoated specimens, conducting detailed microscopy on exposed samples, and evaluating the tensile properties following exposure. Based on these results the chemistries and application techniques for these coating layers will be optimized to meet the requirements for γ -TiAl hot structure. In addition, coating layers with high emittance and low catalytic efficiency will be developed and incorporated into the coating system to enhance its thermal control characteristics.

ACKNOWLEDGMENTS

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REFERENCES

1. Bird, R. K; Wallace, T.A.; and Sankaran, S.N., "Development of Protective Coatings for High-Temperature Metallic Materials", Elevated Temperature Coatings: Science and Technology IV, New Orleans, LA, USA, 11-15 Feb. 2001, (Minerals, Metals and Materials Society/AIME, 2001) 181-196.
2. "Standard Test Methods for Tension Testing of Metallic Materials," *Annual Book of ASTM Standards*, vol. 03.01 (West Conshohocken, PA: ASTM, 1999), Designation E8-99.
3. Wallace, T.A.; Clark, R.K.; Sankaran, S.N.; and Wiedemann, K.E., "Oxidation Characteristics of Ti-33Al-6Nb-1.4Ta," *Environmental Effects on Advanced Materials*, ed. R.H. Jones and R.E. Ricker (Warrendale, PA; The Minerals, Metals, and Materials Society, 1991) 79-89.
4. Haanappel, V.A.C.; Glatz, W.; Clemens, H.; and Stroosnijder, M.F., "The isothermal and cyclic oxidation behaviour of Ti-48Al-2Cr at 700C," *Materials at High Temperatures*, **14**(1), 19-25 (1997).
5. Leholm, R.; Clemens, H.; and Kestler, H., "Powder Metallurgy (PM) Gamma-Based Titanium Aluminide Structures For Use in Various High Temperature Aerospace Applications," *Gamma Titanium Aluminides 1999*, ed. Y-W. Kim, D. M. Dimiduk, and M. H. Loretto (Warrendale, PA; The Minerals, Metals, and Materials Society, 1999) 25-33.