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A REVIEW OF SOME CURRENT NASA-LEWIS SPONSORED COATING RESEARCH

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TECHNICAL PAPER proposed for presentation at 16th Refractory Composites Working Group Cosponsored by the National Aeronautics and Space Administration and the U.S. Air Force
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INTRODUCTION

There is a continued need to protect high-temperature aerospace materials from oxidation and atmospheric contamination. To meet this need, the Lewis Research Center of NASA is currently supporting a number of programs to protect nickel and cobalt based superalloys, dispersion strengthened materials, chromium alloys, and columbium and tantalum alloys. Applications range from aircraft gas turbine engine blades and vanes requiring more than 3000 hours protection at temperatures approaching 2000° F, to lift engine parts, advanced engine components, and space shuttle thermal protection systems which operate near 2200° F and above but for much shorter times. Some of the contractual and in-house research efforts directed toward these problems are presented in the following sections.

COATINGS FOR SUPERALLOYS

Aircraft gas turbine vanes, even though air cooled, often experience hot spot temperatures of 2000° F or more. In order to form a rational basis to improve coatings for vane materials, an effort was made to evaluate the protection ability of vendor-applied aluminide coatings when exposed to an environment of simulated engine combustion products (Ref. 1). The objectives of the program were to obtain data on the chemistry, structure, and life of selected commercial coatings on the nickel-base alloys IN-100 and B-1900, and on the cobalt-base alloys WI-52 and X-40 as a function of temperature. In order to do this, simulated air foil specimens (Misco-type thermal fatigue paddle specimens) were exposed to Mach 0.7, JP-5 combustion products using 1 hour exposures at maximum measured temperatures of between 1845° and 2050° F. Exposures were followed by air blast quenching. Careful temperature calibration showed the maximum temperature to exist on only a very small area of the specimen trailing edge - the leading edge was generally approximately 300° F cooler. While the specimens were tested to a given weight loss, failure was determined from a metallographic chordwise cross section through the hot zone. The location of the first point where the aluminide coating layer began to break up into islands was used with the temperature calibration to establish the temperature at which first failure occurred. Thus, a time-failure temperature data point was established.

This program showed that some commercial coatings do offer better protection than others in the tests employed. Based on the above failure criteria, the best coating on a nickel-base alloy had a 3000-hour life at about 1870° F; the best coating on a cobalt alloy had a projected 3000-hour life at about 1800° F. Both increased aluminum content and minor silicon additions appeared to improve performance in coatings on nickel-base alloys while high aluminum content and carbide layer formation beneath the coating were factors in improving coatings for cobalt alloys.

Simulated engine environment tests are also being carried on at NASA's Lewis Research Center. Only one of the systems tested in reference 1 has been similarly tested in the NASA natural gas fueled Mach I burner rigs, however. Standard wedge-shaped NASA erosion bars of vendor aluminide coated WI-52 were tested at surface temperatures of 1900, 2000, and 2100° F. Here, time to first visual failure, rather than a metallographic aluminide break-up criteria, was used to establish coating life. Testing was generally continued somewhat past this visual failure. Thus, metallographic examination of such specimens, all having a large hot zone, showed considerable aluminide layer breakup. While the log life against temperature relation determined by NASA (Ref. 2) was followed by the reference 1 metallographic data, the failure criteria were significantly different. The NASA data are presented in figure 1 and reported reference 1 data also based on time to first visual failure are added for comparison. Note that on this basis the reference 1 data show much longer lives at all temperatures. Since both tests used one-hour exposures followed by air blast quenching, other factors appear to have produced these as yet unresolved differences. Possible factors that could be involved, aside from differences in gas velocities and combustion products, are hot zone size (30 cm^2 at NASA, 2 cm^2 in Ref. 1) and specimen geometry.

While the test results above differed significantly in time to failure, results from these programs have shown that certain problems arise when aluminide coatings are used at high operating temperatures. One such factor is the development of large aluminide grains whose boundaries are perpendicular to the specimen surface. These boundaries become depleted in aluminum and serve as short circuit paths for oxidation attack. To eliminate this problem, a contractual program is exploring the effects of incorporating fine aluminum oxide particles or fine chromium metal particles into an aluminide pack coating (Ref. 3). The intent of these additions was to refine the grain structure of the aluminide coatings and to eliminate the detrimental perpendicular grain boundaries. Preliminary metallographic evidence shows that some structural modification has been achieved. Flame tunnel and burner rig tests at 2000° F show that coatings modified with either or both of these additions perform significantly better than unmodified coatings. For example, in Mach 0.5 burner rig tests at 2000° F, unmodified coatings exhibited a life of 260 hours while those with the very fine alumina or chromium additions survived for more than 550 hours. Evaluation and testing of improved versions of these systems are continuing.

At NASA Lewis, supporting efforts on in-house deposited aluminide coatings are exploring the effects of pack additions, activators, time, and temperature on coating microstructure, chemistry, and oxidation protection. The effect of cyclic furnace testing on in-house and commercial aluminide coating life is being compared to Mach 1 burner rig test results. At this early stage in the program, it appears that for some systems at least, the less expensive cyclic furnace oxidation tests can provide considerable insight into burner rig behavior (Ref. 2).

Research on the effect of thermal cycling on spallation of aluminum oxide scale is being conducted on bulk nickel aluminide specimens. Early results show that several elements improve scale adherence during cyclic furnace oxidation testing. Finally, improved analytical techniques are being sought so that aluminide coatings can be characterized on a quantitative basis and so that compositional changes can be better followed during oxidation testing. Results to date, have indicated that the use of an ion beam mass spectrometer probe can be very useful in the qualitative depthwise detection of expected and unexpected elements without sectioning the specimen. This device is also capable of detecting light elements such as fluorine that are present at concentrations beyond the lower limits of microprobe detection. In the same study, as would be anticipated, the electron microprobe offered useful microstructural analysis but it is clear that better methods and procedures are still needed to convert the raw instrument data into quantitative analytical information.

Aside from aluminide coatings, other approaches are being supported to provide oxidation protection for superalloys. Metalliding is being explored as a means of coating the high strength nickel superalloy NASA-TRW VIA with duplex layers of Mn, Cr, Y, Ta, and/or Zr (Ref. 4). Alloy coatings of Co-Cr-Al-Y are being applied by physical vapor deposition (Ref. 5). Currently, neither program has progressed sufficiently to establish system potential. At NASA-Lewis, however, cladding studies have been underway for some time to unite weak but highly oxidation resistant Ni-Cr, Ni-Cr-Al, and Fe-Cr-Al-Y alloys with stronger but less oxidation resistant superalloys such as IN-100 and WI-52 (Ref. 6). Cyclic furnace oxidation tests have shown several very promising combinations. A five mil Fe-25Cr-4Al-0.6Y cladding protected WI-52 for considerably longer than a commercial aluminide coating as shown in figure 2 (Ref. 2). Under 1 hour cyclic exposure conditions, the cladding lasted nearly 400 hours while the coating took only around 30 hours to exhibit a net loss in weight.

To explore alternate methods of depositing both alloy claddings and highly modified aluminide coatings, slurry/sinter and slurry/sinter/aluminide processes are under development at Lewis for both nickel and cobalt based materials. Several promising systems in the Ni-Cr-Al systems have been deposited and testing efforts continue in this area.

COATINGS FOR DISPERSION STRENGTHENED NICKEL AND NiCr ALLOY

Presently, one or two contractual programs are being considered to develop diffusion-resistant protective coatings for thoria dispersion strengthened nickel and nickel-chromium materials. These materials are of interest for advanced aircraft gas turbine applications at temperatures to about 2200° F. In-house efforts have been primarily directed towards studying the oxidation behavior of the unprotected materials under a variety of environmental conditions (Ref. 7). For example, contrary to the very small weight gains or losses detected on TD-NiCr in cyclic furnace tests, weight losses of over 40 mg/cm^2 occur in 100 hours of Mach 1 burner rig testing (1 hr cycles) at 2000° F (Ref. 8). Clads of some of the more promising oxidation resistant alloys (Ref. 9) have been applied to NASA burner rig specimens of TD-NiCr and are awaiting their scheduled testing. Figure 3 shows a comparison of the weight change behavior of uncoated TD-NiCr and of TD-NiCr protected by reference 10 Ni-Cr-Al-Si slurry coatings at 2100° F. The coating reduced weight loss by a factor of ten or more during this time period but metallographic examination after 100 hours of testing showed that coating failure was imminent.

Aside from turbine engine usage, dispersion strengthened materials offer interesting properties for thermal radiative panels to protect the space shuttle during atmospheric reentry. One hundred mission reuse capability is desired for such protection systems with only minimum refurbishment. For this reason, low pressure oxidation studies on TD-Ni and TD-NiCr are also in progress at Lewis Research Center to determine the extent of chromium vaporization and/or oxidation at temperatures near 2200° F and pressures near 10 mm.

COATINGS FOR FHROMIUM ALLOYS

Several small efforts are currently under way to protect high strength chromium alloys from oxidation and nitrogen contamination (for example, Refs. 11, 12 and 13). These efforts are in the very early stages of development. However, plasma sprayed chromium/yttria mixtures are showing promise for providing good oxidation and nitrogen embrittlement protection for at least 100 hours at 2100° F in air (Ref. 11).

COATINGS FOR COLUMBIUM AND TANTALUM ALLOYS

Portions of the thermal protection system for the space shuttle will experience temperatures above the useful upper limits of dispersion strengthened nickel or superalloys. For this reason coated columbium or tantalum heat shield systems are also under consideration. One area of interest deals with optimization and scale-up of an existing fused slurry silicide coating for promising columbium alloys. Such an effort will assure the availability of full scale thermal protection system panels with uniform, reproducible protective coatings for service to 2400° F. A second area deals with compositional modification studies that appear necessary to extend the temperature and life limits of fused slurry coatings for tantalum alloys.

Similar supporting studies are underway at NASA Lewis. Research on compositional improvement will explore the possibility of extending coating life or increasing coating reliability beyond the current state-of-the-art. A major effort will involve independent evaluation and testing of coated refractory metal systems with potential for shuttle service. Slow cycle, ambient pressure tests; slow cycle, low pressure tests; mechanical property tests; and reentry simulation tests involving simultaneous variation of stress, temperature, and pressure will be conducted. Test time will also be allocated to evaluate vendor-developed coating systems (for either tantalum or columbium alloys) which have demonstrated sufficient promise to warrant such testing.

Aside from the shuttle application, NASA Lewis has supported coating development for columbium and tantalum alloys for potential use in critical parts of advanced, high temperature aircraft gas turbine engines.

Uncooled or partially cooled refractory metal vanes offer one way to minimize requirements for cooling air in future high performance aircraft gas turbine engines. While sheet metal vanes of tantalum and columbium alloys can be easily fabricated and while they have enough strength to operate at temperatures near 2400° F, their oxidation resistance at these temperatures is poor. From 1965 to 1969, NASA supported two programs (Refs. 14 and 15) to develop coatings for potential tantalum and columbium alloy vane materials. One of the most promising coatings developed for tantalum alloy T-222 was designated NS-4. This coating was deposited as a 50 w/o W-20 w/o Mo-15 w/o V-15 w/o Ti slurry, it was then sintered and subsequently silicided. Extremely reliable cyclic furnace oxidation resistance for up to at least 800 hours at both 1600° and 2400° F and very promising oxidation resistance for up to 200 hours at 2400° F in jet fueled Mach 0.8 burner rigs was observed for this system.

The NS-4/T-222 system was further evaluated at NASA Lewis in Mach 1, natural gas burner rigs at 2200° F (the highest temperature deemed practical at the time of testing). Standard NASA erosion bars of T-222, 4- by 1- by 1/4 inch thick were used in these tests. Figure 4 shows the performance of this coating-substrate combination. Two failures occurred after 170 hours of testing and two occurred at 50 and 100 hours. Three additional specimens were not tested to failure. Two survived 87 hours and one 47 hours without failure. Note that while the longest lived specimens were removed from test 17 hours after the first white Ta_2O_5 was observed, the next longest lived specimens were left in test for 87 and 90 hours, respectively.

The oxidation damage that took place in those 90 hours can be seen at the left in figure 5. The specimen which first failed at 50 hours lost about one-half of its width in the failure area after a total of 140 hours of testing. However, this specimen was still able to withstand the gas loading of approximately 3000 psi as well as the severe Mach 1 air quenches after each exposure cycle. The early failure locations were usually in a zone about 1 inch from the specimen base having a measured temperature of around 1800° F. A lower temperature test at 1800° F maximum however, also showed failures in the same zone indicating that either stress or other factors, rather than temperature, were the primary cause of such failures.

The photographs of specimens that have survived 187 hours of test - the longest test times used in this limited study - are presented at the right in figure 5. Note that two of these specimens first failed at 170 hours but little visual damage was seen at 187 hours. The specimen at the far right failed in the cool base region at 100 hours and at the leading edge at 170 hours. Also note that the latter failures are closer to the hottest part of the specimen (about 1 in. from the tip).

Further evaluation of the NS-4/T-222 system was conducted in reference 16. This effort provided a second evaluation of the system's cyclic furnace oxidation resistance and also developed some mechanical property test data. Test specimens evaluated in this program were coated by the coating developer (Ref. 15) and were delivered for evaluation. Representative results are presented in figures 6 and 7. The cyclic furnace oxidation resistance of the NS-4 coating was found to be less consistent and somewhat poorer than observed by the coating developer. At 2400° F, early failures were observed as shown in part A of figure 6. At 1400° F, 200° F below the temperature NASA had specified for use in reference 15 as a check for silicide pest, all oxidation test specimens failed within 2 to 4 hours (Fig 6, part B). Pre-exposure at between 1600° - 2400° F, however, eliminated these early failures. For example, after 10 hours in air at 2400° F, all three specimens evaluated survived over 600 hours at 1400° F (Fig. 6; part C).

The bend ductility of the T-222, as presented in figure 7(A), was not seriously affected by either the coating process or by oxidation exposures. After 304 hours at 2400° F, for example, the substrate could be bent through an angle of 90° at a temperature of -320° F without breaking. Even after 500 hours at 1400° F (with 10 hours of preoxidation at 2400° F), a specimen could be bent 90° at -150° F.

Part B of figure 7 presents some creep data obtained at 8 ksi, 2400° F, and 500 hours. One specimen was heat treated to the coating cycle in high vacuum and then tested in high vacuum; the other was an as-coated specimen tested in air. From these data it appears that the coating partially degraded the mechanical properties of the substrate. For reasons not yet clear, specimens first oxidized at 2400° F for 304 hours and similarly creep tested developed oxidation failures within 40 hours.

In general, this study developed property data which show that when the coating remains intact, it provides relatively good protection against substrate contamination by oxygen and the attendant degradation of mechanical properties.

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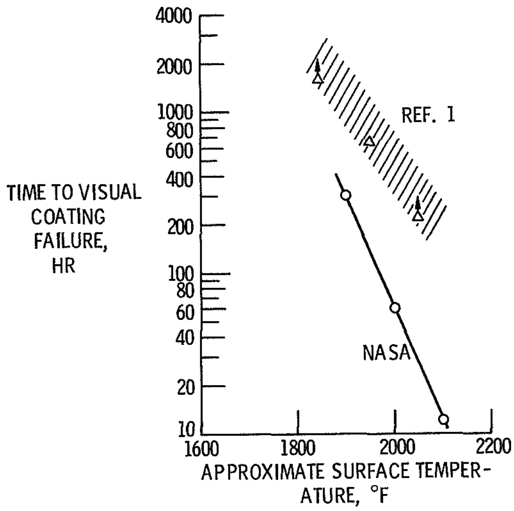

Figure 1. - Comparison of time to visual coating failure of a commercial aluminide coating on WI-52. Burner rig tests - 1 hour cycles.

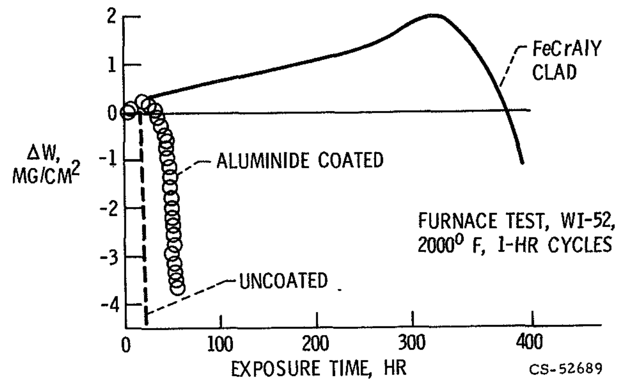

Figure 2. - Comparison of weight change behavior for aluminide coated WI-52 and FeCrAlY clad WI-52 tested using 1-hour cycles.

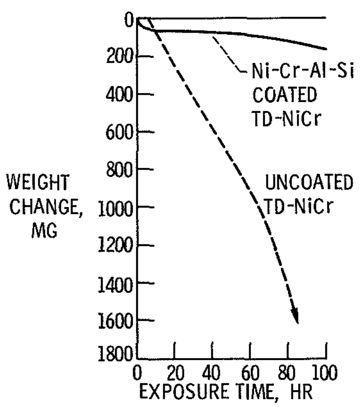

Figure 3. - Resistance of uncoated and slurry coated TD-NiCr to Mach 1 - 2100° F. Burner rig testing (1 hr cycles).

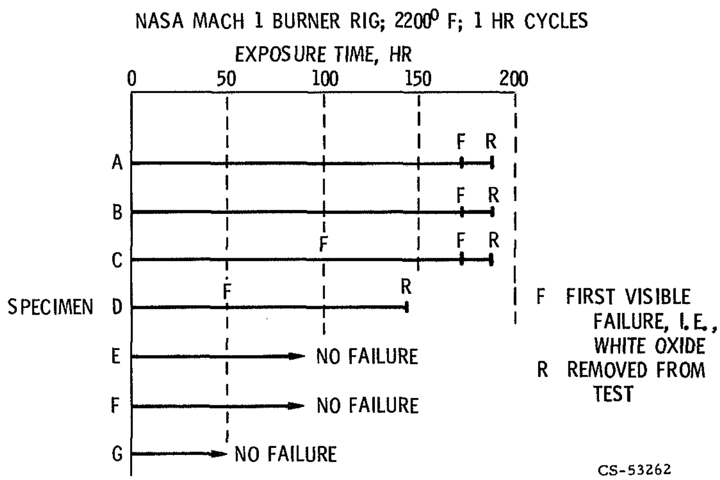

Figure 4. - Oxidation resistance of NS-4 on T-222.

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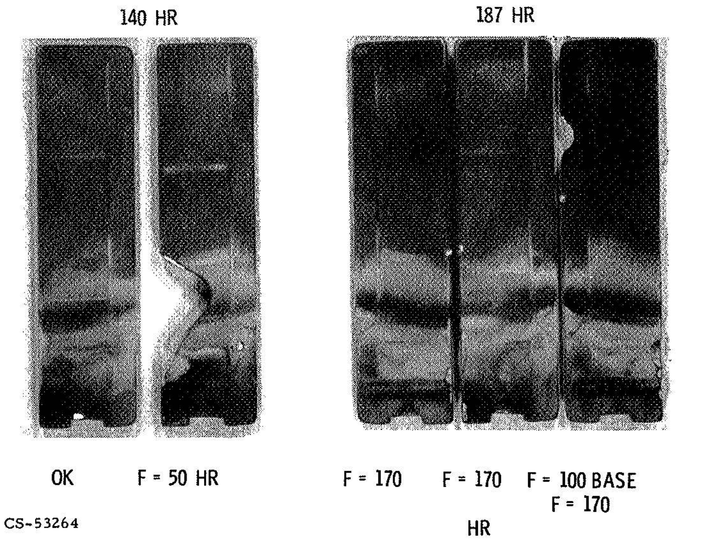

Figure 5. - Visual appearance of NS-4/T-222 after 2200° F, Mach 1 test.

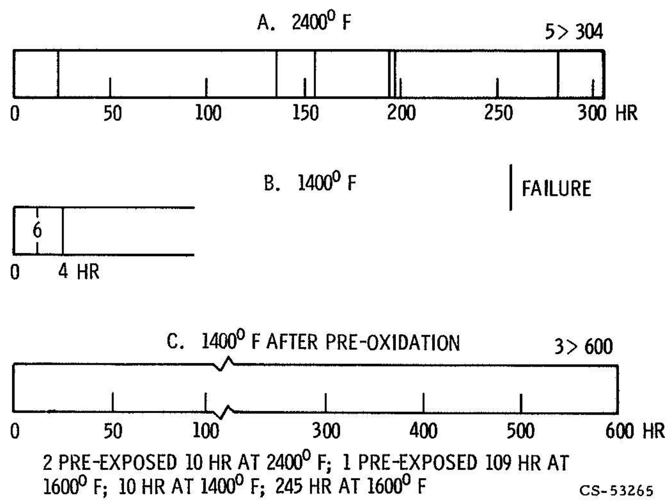

Figure 6. - Cyclic furnace oxidation resistance of NS-4/T-222.

A. BEND DUCTILITY

	T °F FOR 90° BEND
T-222, AS-RECEIVED	-320
AS-COATED	-250
304 HR, 2400° F	-320
10 HR, 2400° F; 500 HR, 1400° F	~-150

B. CREEP AT 2400° F

	STRESS, KSI	HR	ELONGATION, %
T-222 HIGH VACUUM HEAT TREATED TO DUPLICATE COATING THERMAL CYCLES; TESTED IN VACUUM	8	500	3.8
AS-COATED; TESTED IN AIR	8	500	6.8

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Figure 7. - Some mechanical properties of T-222 coated with solar NS-4.