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SODIUM COMPATIBILITY STUDIES
OF LOW FRICTION CARBIDE COATINGS
FOR REACTOR APPLICATION

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ABSTRACT

Design requirements for low friction materials in the Fast Flux Test Facility (FFTF) have led to an experimental sodium compatibility program, the objective of which is to select and qualify a low friction coating for the fuel assembly duct load pad. This paper describes the results for chromium carbide and titanium carbide based coatings on stainless steel exposed to 1160°F sodium for several thousand hours. A chromium carbide coating (with a nichrome binder) having an average corrosion rate of approximately 0.25 mpy exhibits optimum sodium compatibility behavior of the materials examined. Both plasma sprayed chromium carbide and titanium carbide based coatings were found to be unstable when exposed to sodium.

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1. INTRODUCTION

In sodium cooled, nuclear reactors there are numerous interface areas, where contact between components can lead to wear, friction and self welding problems. Due to the heavy stresses imposed on components such as load pads, bearings and guide tubes, the use of low friction, wear resistant materials becomes necessary. Thus, in the design of the Fast Flux Test Facility (FFTF), an optimum friction coefficient between the load pads on adjacent fuel assembly ducts is an important safety and reliability requirement.

Accordingly, under USAEC sponsorship, current experimental programs at the authors' and other contractors establishments^(1,2,3) have as their objective the selection of a suitable materials combination for application in duct load pads. The preferred candidate must provide the required low coefficient of friction at refueling temperatures and maintain its integrity and properties during the service life of the assembly. At Westinghouse,⁽⁴⁾ work is underway in two areas: firstly, measurement of friction coefficients and wear rates and secondly, stability and compatibility under sodium conditions prototypic of those which will be encountered during FFTF operation.

The purpose of this paper is to review the compatibility of chromium carbide and titanium carbide based coatings exposed to 1160°F sodium, and, their stability when thermally cycled in sodium between 800 and 1160°F. Final selection of the optimum materials combination will be based on an overall view of results of friction and wear studies, irradiation behavior and the current series of sodium compatibility tests reported herein.

2. MATERIALS

Based on a literature survey a number of materials combinations utilizing carbide coatings were identified as meriting additional study for this application. A test program was designed to use samples measuring 0.75 x 0.75 x 0.180 inch with a finished coating thickness on both flat faces of four to six mils, in which the substrate is 20 percent cold worked Type 316 stainless steel. Various types of coatings listed in Table 2 are applied by the manufacturer, Union Carbide Corporation. Prior to coating the specimens, the surfaces of all samples are subjected to an aluminum oxide

grit blast treatment. The coating is applied to the substrate by either of two processes.

The first process applies the coating via a detonation or "D-gun" which resembles a large-caliber machine gun. Measured quantities of oxygen, acetylene, and particles of the desired coating and binder are metered into the firing chamber and a timed spark detonates the mixture. This creates a hot, high speed gas stream, which instantly heats the particles to a plastic state, and hurls them at supersonic velocity (2500 fps) from the gun barrel. The near molten particles impinge on the surface of the sample, where a microscopic welding action produces a tenacious bond. Rapid fire detonations, during automatically controlled passes across the work piece, build up the coating to a specified thickness. Although temperatures above 6000°F are reached inside the gun, the specimen surface remains below 300°F. After coating, all specimens were nondimensionally finished using a silicon carbide impregnated brush to a 125 RMS or better finish.

The second type of coating process used by Union Carbide Corporation is conventional plasma spray. The torch produces and controls a high velocity inert gas stream at approximately 30,000°F. Coating materials are introduced into the arc in a powder form, where the particles are melted and accelerated toward the work piece. As the particles strike, a high density, integrally bonded coating is formed. After coating, a non-dimensional finishing treatment is performed similar to the "D-gun" process.

In the initial series of duct load pad specimens, i.e. those designated original LCIC (see Table I), the coating extended all the way to the edge on two sides of the sample and some overspray onto the thickness dimension occurred. All other specimens were coated with four feathered edges on each flat face, i.e. the coating thickness gradually decreased from approximately 4 mils to 0 over a distance of 1/16 inch. This latter condition more closely simulated the actual duct load pad configuration.

3. EXPERIMENTAL TECHNIQUES

The experimental studies reported in this paper are divided into the two areas of sodium compatibility and thermal cycling stability.

a) Sodium Compatibility

During reactor service the duct load pad will experience long term exposure to 1150°F sodium. The sodium compatibility program is designed to simulate this exposure. A schematic diagram of a materials test loop, in which the compatibility studies are being conducted is shown in Figure 1. Flow, in this austenitic stainless steel loop begins at the pump and continues through the tube side of an economizer, an air cooler, a cold leg test section, a flowmeter, and back to the electromagnetic pump. By-pass lines for sodium impurity monitoring and control are also included in the loop. The operating conditions of these loops include a hot leg test section temperature of 1150°F, with a velocity of 1 fps, a loop temperature difference (ΔT) at

460°F, and a sodium oxide level of 0.5 to 1 ppm as determined by the vanadium wire equilibration device.

At regular intervals during the test, samples are removed from the hot leg and placed in a portable argon glove box that is positioned above and temporarily attached to the hot leg expansion tank in the loop system. Residual sodium is removed by immersing the cooled samples in successive baths of butanol, methanol, and demineralized water. The specimens are then dried in a vacuum furnace for one hour at 100°C. After cooling, the specimens are weighed to five decimal places and sodium effects evaluated by chemical, metallurgical, and quality assurance (dimensioning surface roughness, etc.) analyses. Average corrosion rates in mils of thickness lost per year, i.e. mpy calculated using the density values shown in Table I are quoted in the text for use by reactor design engineers.

b) Thermal Cycling Stability

During the duct lifetime, the pad will undergo temperature fluctuations due to refueling and to other operational transients. The variation of scrams with operating time is unlikely to be linear, and it is impossible to estimate the exact number of transients which will take place or the temperature variations during each transient. Thermal cycling stability tests are therefore based on the estimated number of cycles plus an arbitrary number of additional cycles.

The experimental facility used in this work is similar to that described in the previous section, with the exception that the hot expansion tank (see Figure 1) was replaced by a fixed argon containing glove box. By mechanical manipulation, test specimens can be transferred between the 1160°F hot leg and an adjacent 800°F sodium quench tank, without coming into contact with air. This thermal cycling facility is designed for automatic linear temperature ramping from 800 to 1160°F at a rate of 50°F/hr, and the test cycle shown in Table 2 is based on anticipated conditions to be encountered during service.

Specimens that are exposed to this in-sodium cycling are removed after 15, 30 and 60 cycles directly into the argon atmosphere glove box, whereupon residual sodium is removed as previously described. The effects of this temperature cycling are then determined by macro and microstructural examinations.

4. RESULTS

In the compatibility part of this program, chromium carbide coated samples have been sodium exposed for times up to 6500 hours and titanium carbide coatings for up to 3500 hours. The results of these exposures are presented together with thermal cycling observations in the next two subsections.

a) Chromium Carbide Base Coatings

In the first sodium compatibility series, specimens of the original chromium carbide/nichrome binder coating deteriorated markedly. After approxi-

mately 2000 hours at 1160°F, severe chipping and/or cracking near the coating/substrate interface was observed. This spalling was subsequently shown to be due to reaction between coating contaminants and sodium in poorly adherent areas of the coating and not per se to sodium exposure effects. Two samples from this original LCIC coated stainless steel material did not exhibit severe spalling, and, hence, were allowed to accumulate further exposure time. As can be seen from Figure 2, the slope of the weight change versus time curve, approached a constant value after a very short exposure time, and after approximately 4000 hours, the average corrosion rate of 0.5 mpy remained essentially constant.

Sodium compatibility studies covering the later chromium carbide combinations detailed in Table I, did not visually reveal any deterioration in the coating. Exposure to sodium resulted in weight losses which were dependent on time, as shown in Figure 3. The average corrosion rates for these coatings are generally ≤ 0.25 at the maximum measured exposure time.

Due to the length of time in which hydrogen evolution took place during cleaning, it became apparent that extensive sodium penetration of the coatings had occurred. As might be expected at these relatively low corrosion rates, no changes in sample dimensions were measured. The surface finish after exposure is still good and with one exception the integrity of the coating is retained. One sample of the molybdenum binder coating, CM, exhibited some spalling at one corner of the coated face after 1030 hours exposure. In addition, cross sectional metallographic examination of one sample of the plasma sprayed, nichrome binder coating (CN-1P) revealed internal cracking parallel to the interface after 1000 hours exposure. No further changes in cross sectional microstructure have been observed in any of the exposed samples of the new coatings and this is illustrated in Figure 4 for the nichrome and Inconel 718 binder, coatings CN-1b and CI-D. The coating microstructure has a multi-layered appearance in which areas of binder, chromium carbide and porosity can clearly be identified. Examination of the coating/stainless steel interface in both types revealed a band of $M_{23}C_6$ type precipitation in the stainless steel up to a maximum of one mil from the interface both within the grains and at grain boundaries. The deformation bands in the cold worked stainless steel near the interface are also heavily decorated with precipitate particles, the majority of which are $\leq 1\mu m$ in length. Surface compositional changes, monitored in a scanning electron microscope - energy dispersive x-ray analysis system, consist chiefly of a loss of nickel in the coatings containing nichrome and Inconel 718 from the streaked binder areas as shown in Figure 5.

Thermal cycling of the chromium carbide/nichrome coated stainless steel combinations (CN-1a and CN-1b) has demonstrated their stability to fluctuations in temperature in that no coating deterioration was observed after 30 cycles. However, examination of two samples of the chromium carbide/molybdenum, CM coating, which had been cycled between 1160 and 800°F for 29 cycles revealed massive coating disintegration. It seems likely that this is related to "spottiness" previously observed for the plasma sprayed materials CM and CN-1P after 15 such cycles. One face of one of the CM samples was found to be completely void of coating after 29 cycles. The

other faces had lost up to 40% of the coating area. Visual observations suggest that fracture occurred in the coating very near to the coating/substrate interface.

b) Titanium Carbide Base Coatings

Sodium compatibility studies of titanium carbide coatings (with nichrome or molybdenum binders) were conducted in small loop systems for times up to 3500 hours. Corrosion rates up to an order of a magnitude higher than those observed for similar chromium carbide base coatings were measured after short exposure periods. For example, after 200 hours, average corrosion rates of 11 mpy were recorded for the titanium carbide coatings compared to 0.7 mpy for the chromium carbide/nichrome coating. The weight change data for these coatings as a function of exposure time is plotted in Figure 6. However, due to the spalling, lifting and in some cases removal of the coating, caution should be exercised in any subsequent use of these data.

Metallographic examination of the effects of sodium exposure on titanium carbide/molybdenum coatings indicated that the coating, which remained on the stainless steel substrate, was essentially the same as that prior to exposure, i.e. a layered structure with areas of carbide, binder and porosity. Scanning electron microscopical examination, however, further illustrated the severe coating breakdown with some microcracking apparent in the remnants of coating adhering to the substrate.

5. DISCUSSION

Studies have shown that exposure to low oxygen, flowing sodium at 1160°F for several thousand hours results in sodium penetration of the carbide coatings and associated weight losses. In the case of the high nickel binder coatings, original LCIC, CN-1a, CN-1b, and CI-D, corrosion proceeds by loss of nickel from the binder, with probable associated loss of chromium carbide. The weight change of these coatings, with the possible exception of the original LCIC, is not related to exposure time by any of the established oxidation relationships. There is some indication that the LCIC coating weight change exhibits parabolic time dependence, although this has not been firmly defined. Corrosion by loss of nickel directly to the sodium without the formation of an oxide is not surprising since related work⁽⁵⁾ has shown that in the sodium exposure of austenitic alloys, this is also a major factor in the corrosion process. When more data points are available, the possibility of a parabolic time dependence, suggesting thermal diffusion as the rate determining process for these materials, may be further explored.

Examination of the carbide morphology by x-ray diffraction reveals that, although the starting chromium carbide material is essentially Cr_3C_2 , after coating it consists of Cr_7C_3 and Cr_{23}C_6 . The D-gun coating process is conducted in an oxidizing atmosphere, and over half the available carbon is consumed during the process, but with the distinct possibility that there may be some free carbon present in the as-received coating. During sodium

exposure, Cr_7C_3 transforms to the more stable carbide Cr_{23}C_6 with the formation of more free carbon. Loss of carbon from the coating to the sodium may take place at the exposed surface but it seems more likely that the free carbon will combine with chromium in the coating binder.

The relatively good performance of the D-gun applied coatings CN-1a, CN-1b and CI-D in both isothermal sodium exposure and thermal cycling makes chromium carbide coatings with high nickel alloy binders appear extremely attractive for load pad application. However, in separate studies, the integrity of these coatings after exposure to sodium⁽⁶⁾ and to irradiation⁽⁷⁾ are being investigated and qualification of the above statement may subsequently be necessary.

The plasma sprayed chromium carbide coatings CN-1P, CM and CI generally exhibit a higher porosity level than the corresponding D-gun applied coatings and sodium penetration of these coatings undoubtedly occurs during exposure. Coating deterioration observed in both nichrome (CN-1P) and molybdenum (CM) containing samples took the form of separation very close to, or at the coating/substrate interface, but the cause of the observed failures is not known. In a companion program at W Hanford Company⁽⁷⁾ on irradiation behavior of coatings, similar deterioration in the plasma sprayed coatings CM and CN-1P has been recorded. Taking all these reports into consideration, it seems unlikely that the plasma sprayed coatings CM and CN-1P will be suitable for load pad application.

Titanium carbide base coatings, which were also applied by plasma spraying, showed signs of deterioration after very short sodium exposure. The sample surfaces appeared to be covered with a loosely adherent powder. In order to ascertain the cause of this degradation and powder formation, lattice parameter measurements were made. The lattice constants of the TiC in the as-received TiC/Mo coating and in a 500 hour sodium exposed TiC/Mo coating were determined to be 4.324Å and 4.327Å, respectively. Based on these data and the curve shown in Figure 7,⁽⁸⁾ it was concluded that the carbide phases in the as-received material had a stoichiometry of TiC_{0.7} while the same phase in the sodium exposed samples had exact stoichiometry; i.e. TiC. This indicated that the carbide coating had carburized to an extent that the initial carbon deficient titanium carbide was converted to stoichiometric TiC. It was also observed, that in the 500 hour sample, part of the molybdenum binder had been converted to Mo₂C, with complete conversion being observed in the 1000 hour sample. The source of the carbon may be the excess carbon in the co-exposed chromium carbide samples or the carbon in the stainless steel loop tubing.

Carburization of the non-stoichiometric titanium carbide caused changes in the lattice constant of the carbide resulting in the generation of internal stresses within the coating. Formation of the Mo₂C phase from the binder also leads to additional stresses due to volume changes resulting from the transformation. It seems, therefore, that the differences in thermal expansion coefficient and other physical and mechanical properties between TiC and Mo₂C contributed to the failure of the coating especially at the surface where severe carburization had occurred. Titanium carbide base coatings are no longer candidate materials for duct load pad application.

6. CONCLUSIONS

Based on isothermal sodium corrosion and thermal cycling studies, the D-gun applied chromium carbide coatings, with nichrome and Inconel 718 binders, are the best candidates for coating the stainless steel fuel assembly duct load pads in the FFTF. Average sodium corrosion rates of these coatings at 1160°F were ≤ 0.25 mpy. The results of sodium exposure at 1160°F or thermal cycling in sodium between 1160 and 800°F have ruled out plasma sprayed chromium carbide and titanium carbide coatings with molybdenum or nichrome binders for use in this application.

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Note: References 1, 2, and 4 may be obtained from:

USAEC Technical Information Center
P. O. Box 62, Oak Ridge, Tenn. 37830

TABLE 1. COATINGS CONSIDERED FOR DUCT LOAD PAD APPLICATION

Coating Designation	Constituents		Coating Process	Coating Density g/cc	Remarks
	Coating	Binder			
Original	CRC	NiCr ^(a)	D-gun	6.40	LCIC process, cooler gun conditions -5 μ m Cr ₃ C ₂ - 40 μ m NiCr
CN-1a	CRC	NiCr	D-gun	6.40	LCIB process, hot gun conditions -5 μ m Cr ₃ C ₂ - 50 μ m NiCr
CN-1b	CRC	NiCr	D-gun	6.32	LCIC process, cooler gun conditions -5 μ m Cr ₃ C ₂ - 40 μ m NiCr
CN-1P	CRC	NiCr	Plasma	5.84	-5 μ m Cr ₂ C ₂ - 40 μ m NiCr
CI	CRC	Inc 718	Plasma	5.94	-5 μ m Cr ₃ C ₂ - 20 μ m Inc 718
CI-D	CRC	Inc 718	D-gun	6.34	-5 μ m Cr ₃ C ₂ - 20 μ m Inc 718
CM	CRC	Mo	Plasma	6.09	-5 μ m Cr ₃ C ₂ -5 μ m Avg. Mo
TM	TiC	Mo	Plasma	5.65	-5 μ m TiC, 5 μ m Avg. Mo
TN	TiC	NiCr	Plasma	5.5	-5 μ m TiC coated with NiCr

(a) 12 v/o NiCr; all other binders 15 v/o.

CRC: Chromium carbide (Cr₇C₃ + Cr₂₃C₆ + Cr₃C₂)

TiC: Titanium carbide

Mo: Molybdenum

NiCr: Nichrome (nominally 80Ni-20Cr)

TABLE 2. THERMAL CYCLING STABILITY TEST CONDITIONS

1. Hold at 1160°F for a minimum 8 hours and maximum of 4 days
2. Quench to 800°F in approximately 1 minute
3. Raise to 1160°F at a rate of approximately 50°F/hour
4. Repeat

Figure 1. Schematic Drawing of a Sodium Compatibility Loop System

Figure 2. Effects of Sodium Exposure Time @ 1160°F on the Weight Change of the Original LCIC, Chromium Carbide Coated, Type 316 Stainless Steel

Figure 3. Effects of Sodium Exposure Time @ 1160°F on the Weight Change of Various Chromium Carbide Base Coatings on Type 316 Stainless Steel

AS RECEIVED

EXPOSED 3148 HOURS

a) CHROMIUM CARBIDE/NICHROME, CN-1b

AS RECEIVED

EXPOSED 1488 HOURS

b) CHROMIUM CARBIDE/INCONEL 718, CI-D

25 μ m
0.001 IN.

Figure 4. Effects of Exposure to 1160°F, 0.5-1.0 ppm O₂, Flowing Sodium on the Microstructure of Chromium Carbide Coated Type 316 Stainless Steel

AS RECEIVED

EXPOSED 3148 HOURS

a) CHROMIUM CARBIDE-NICHROME, CN-16

AS RECEIVED

EXPOSED 1488 HOURS

b) CHROMIUM CARBIDE/INCONEL 718, CI-D

25 μ m
0.001 IN.

Figure 5. Effects of Exposure to 1160°F, 0.5-1.0 ppm O₂, Flowing Sodium on the Surface Appearance of Chromium Carbide Coated, Type 316 Stainless Steel

Figure 6. Effect of Sodium Exposure Time @ 1160°F on the Weight Change of Titanium Carbide Coated, Type 316 Stainless Steel

Figure 7. Relationship Between Lattice Parameter and the C/Ti Ratio in Titanium Carbide