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WEAR RESISTANT COATINGS FOR REACTOR  
COMPONENTS IN LIQUID SODIUM ENVIRONMENTS

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ABSTRACT

Rubbing surfaces of critical components for the coming generation of the nation's liquid-metal-cooled-fast-breeder reactors must withstand severe environments of high temperature, liquid-metal corrosion, and nuclear irradiation. For some component requirements, the use of the better known bearing materials and hardfacings has been shown to be inadequate or impractical. For several applications, bulk (> 25 micron thick) coatings have provided the only successful solution to friction problems in high temperature sodium. Coating processes that have been or are being evaluated include plasma spray, detonation gun, spark-discharge, sputtering, and diffusion coating processes. Testing included friction and wear tests in up to 650°C sodium, sodium corrosion tests for up to one year, thermal cycling, bond strength tests, and irradiation tests in a fast reactor. For one

particularly severe application, a specially modified commercial coating of chromium carbide in a 15 volume percent nichrome binder, applied by a commercial detonation gun process, has so far been found to be most acceptable in meeting the friction, corrosion, and irradiation damage criteria. Much of the test data reported is on this coating and its antecedent modifications.

# Wear Resistant Coatings For Reactor Components In Liquid Sodium Environments

By R. N. Johnson, S. L. Schrock & G. A. Whitlow

## INTRODUCTION

Rubbing surfaces of critical components for the coming generation of the nation's liquid-metal-cooled-fast-breeder reactors must withstand severe environments of high temperature, liquid metal corrosion, and nuclear irradiation. During the design of the Fast Flux Test Facility (the USAEC's sodium-cooled fast test reactor now being built at Hanford) it became apparent that some rubbing surfaces in the core of the reactor required materials capable of providing low coefficient of friction in sodium at temperatures from 230°C to 650°C. Our objective was to identify a material combination which would exhibit adequate service life in the reactor core environment and provide a friction coefficient of 0.4 or less at 230°C. This was found to be a stringent requirement since sodium is an extremely poor lubricant and is also exceptionally effective in stripping oxide layers from most material surfaces. The net result is that many materials in contact with each other in sodium have the same high friction and self-welding tendencies found in ultra-high vacuum environments. In some ways, vacuum environments are considerably less severe, because sodium, in addition to enhancing materials self-welding, can be a highly

corrosive media in which mass transfer takes place and which precludes the use of nearly all known liquid or solid lubricants.

In order to identify materials capable of meeting the friction criteria, friction screening tests were performed on over 65 materials combinations, including metals, ceramics, and cermets both in solid forms and as coatings applied by a variety of processes. During the early materials screening period, literature searches<sup>(1)</sup> and review of earlier program results<sup>(2)</sup> indicated that one of the most promising classes of materials that should be examined was the bonded carbides. Hoffman, et al<sup>(2)</sup> stated that after extensive screening of a wide variety of materials in wear tests in sodium, the bonded carbides appeared to be the only materials as a class which consistently exhibited good wear and friction behavior at high (above 500°C) temperatures in sodium.

Subsequent friction screening tests confirmed that the bonded carbides provided the lowest frictions and in particular the chromium carbide base materials were selected for primary development efforts and titanium carbide base materials were selected for back-up development. A number of methods of attaching wear materials to the component surfaces were investigated and included mechanical attachments, welding, explosive bonding, and a variety of coating processes. Some method of coating appeared to offer the most desirable method of attachment

provided a reliable process could be found which met the qualification criteria. The qualification criteria were as follows:

- The material shall have a coefficient of friction of 0.4 or less in sodium at 230°C and no more than 0.9 at 625°C.
- The coating shall not corrode more than 1/2 the coating thickness over its service life.
- The material shall sustain the equivalent of 60 reactor scram cycles (cool from 625°C to 425°C in 1 minute in sodium) without cracking, spalling or flaking.
- The material shall be capable of withstanding fast neutron exposures of  $8 \times 10^{22}$  n/cm<sup>2</sup> without spalling or flaking or failing to perform its function as a low friction surface.
- The material shall not transmute to undesirable radioactive products (e.g. <sup>60</sup>Co) which can contaminate downstream components and piping.
- The material shall be capable of being attached to core components in such a way that dimensional tolerances are maintained and cold-work levels of substrate materials are unchanged. (20% cold-work is required in the 316 stainless steel fuel ducts for irradiation swelling resistance).

This paper describes the coating processes investigated

and the results of wear and friction tests, sodium corrosion tests, thermal cycling, mechanical integrity tests, and neutron irradiation tests performed in order to qualify candidate materials and attachment process.



DESCRIPTION OF COATING PROCESSES AND  
COATING COMPOSITIONS

Spark Transfer Coating

Spark transfer coating has its widest industrial usage in the application of tungsten carbide films to complex geometry surfaces. Essentially the process consists of discharging stored energy from high voltage capacitors through an electrode of the material to be deposited. In the resulting spark, a small amount of material is removed from the electrode and welded to the substrate material. The process was found to be capable of depositing coatings of a wide variety of materials in thicknesses of 2.5 microns (.0001") to 62 microns (.0025"). Little surface heating occurred (small parts could be hand held during coating) so thermally induced distortion of parts or modification of bulk metallurgical structures was not a problem. Bond strengths of carbide coatings applied by spark transfer appeared to be excellent in that qualitative tests such as severe bending and "hammer and chisel" tests were usually unsuccessful in dislodging any material. Capital equipment costs were low (state-of-the-art equipment was purchased for under \$5000). Deposition rate for full coating thickness was usually in the range of 1 to 2 in<sup>2</sup>/minute. As-deposited surface roughness ranged from about 60 μ-in AA for well-optimized tungsten carbide coatings to > 250 μ-in AA for some of the

less-developed experimental chromium, titanium, and niobium carbide compositions and other cermets which were deposited by the spark transfer process. Even with decidedly non-optimum coating parameters and surface finishes, the chromium carbide coatings showed friction coefficients in sodium which averaged less than half those of the other carbides. These initial results encouraged further development of chromium carbide base coatings by other deposition processes.

Development of the spark transfer process for reactor applications has not progressed beyond the initial screening studies due to the early success of concurrent developments (the D-gun coating described below) and time and manpower which would be necessary to develop the process to the same degree of optimization for chromium carbide coatings as had been done for tungsten carbide. The process is still being considered as a "back-up" process for further development as needs and resources allow.

#### Sputtering

Coatings of chromium carbide + 15% nichrome were applied by sputtering to Type 316 stainless steel substrates. Coatings were 4 to 5 mils (100 to 125 $\mu$ ) thick and were deposited at 125°C and at 600°C at deposition rates of 23 $\mu$ /hr. The coatings appeared to be very hard and tightly adherent in the as-deposited condition, but after heating to 625°C to simulate in-reactor

temperatures, both the low temperature and high temperature deposition coatings showed cracking with the low temperature coating showing both cracking and spalling. It is possible that further development effort, perhaps using graded coatings, could overcome the cracking problems; however, no further work is anticipated at this time.

#### Plasma Spray

A number of chromium carbide and titanium carbide base coatings on 316 stainless steel and Inconel 718 substrates were prepared by a non-transferred, D. C.-constricted plasma-arc with fully shielded effluent, using argon gas. The coatings exhibited good wear behavior, but, as shown below, were eliminated for in-reactor applications by the cracking and spalling tendencies found under both irradiation and thermal cycling tests.

#### Detonation Gun

The detonation-gun coating of chromium carbide plus 15 vol. % nichrome has been selected as the reference process and material for the coating of reactor core components for the FFTF. In the detonation gun process, the powdered coating material is introduced into the chamber of the gun along with a metered quantity of oxygen and acetylene. The mixture is detonated by a spark plug and in the resulting explosion, the powdered materials are heated to a plastic or molten state and accelerated down the gun barrel to impinge on the substrate at approximately three

times sonic velocity. The combination of hot particles and the high kinetic energy of impact creates a coating which is typically more dense and which has a higher bond strength than similar coatings applied by plasma spraying. Much of the test data presented in this paper will be on coatings applied by the detonation gun technique.

#### Materials Selected for Evaluation

After friction screening tests had been completed, materials remaining for final testing and evaluation included chromium carbide and titanium carbide coatings, each containing 15 vol.% of a binder. Typically, coatings were 75 to 125  $\mu$  (3 to 5 mils) thick and were applied to grit-blasted 316 SS or Inconel 718 substrates. The materials and compositions are listed in Table 1. Although chromium carbide coatings showed the lowest friction, titanium carbide was also included in case sodium corrosion tests showed excessive attack on the chromium carbide materials. As will be shown later, an unexpected result was that the titanium carbide compositions showed the more severe sodium exposure effects.

Table 1Carbide Coating Compositions Evaluated

<u>Coating Designation</u>	<u>Starting Composition</u>	<u>Application Method</u>	<u>Remarks</u>
LC-1H	Cr <sub>3</sub> C <sub>2</sub> -15 Vol.% Nichrome	D-Gun	Reference Coating
LC-1C	Cr <sub>3</sub> C <sub>2</sub> -12 Vol.% Nichrome	D-Gun	Back-up Coating
CN-1P	Cr <sub>3</sub> C <sub>2</sub> -15 Vol.% Nichrome	Plasma	Failed Irradiation Test
CI	Cr <sub>3</sub> C <sub>2</sub> -15 Vol.% In. 718*	Plasma	Failed Irradiation Test
CI-D	Cr <sub>3</sub> C <sub>2</sub> -15 Vol.% In. 718*	D-Gun	Back-up Coating
CM	Cr <sub>3</sub> C <sub>2</sub> -15 Vol. % Mo	Plasma	Failed Irradiation & Thermal Cycling
TM	TiC - 15 Vol.% Mo	Plasma	Failed Corrosion Test
TN	TiC - 15 Vol.% Nichrome	D-Gun	Failed Corrosion Test

\* Inconel 718 - TM - International Nickel Co.

## TESTING PROCEDURES AND RESULTS

### Friction and Wear Tests

Wear tests were conducted by Atomics International, Liquid Metal Engineering Center and Westinghouse Advanced Reactors Division (3, 4, 5) in a cooperative program with the Hanford Engineering Development Laboratory. In all cases, tests were conducted over temperature ranges from 200°C to 625°C in high purity sodium (oxygen content less than 5 ppm measured by total amalgamation or less than 1 ppm measured by vanadium wire analysis). Test specimen geometry varied somewhat at each of the three test sites, but all used a general pin-on-plate, oscillatory rubbing with flat-on-flat interface configurations. Loads ranged from 300 psi to 1000 psi for most tests.

Figure 1 shows some of the early data developed in screening tests which led to the further testing and development of chromium carbide coatings. The chromium carbide coatings were the only coatings or materials found which consistently met the friction criteria over all temperature ranges.

Surface finish was found to have an effect on the friction behavior of the chromium carbide coatings. The best friction results were obtained on coatings which were brush finished with a fine silicon carbide impregnated nylon brush to a finish

of 80 to 125  $\mu$ -in AA. The resulting surface texture is best described as a smooth, "pebbly" finish. When the coating was applied by the spark transfer technique, a surface finish of 80 to 250  $\mu$ -in AA or rougher was obtained which resulted in inconsistent friction coefficients averaging higher than the brush-finished D-Gun coating or a lapped-finished D-Gun coating. A lapped finish of 5 to 16  $\mu$ -in AA also resulted in inconsistent friction behavior intermediate between the brush-finished and the spark-transfer coatings.

Qualification tests of over 1000 inches of rubbing in sodium at 625°C and loads up to 1000 psi have shown no significant wear on the chromium carbide coatings.

#### Sodium Compatibility Tests

Sodium compatibility testing is necessary to assure (1) that the chromium carbides are chemically stable and do not dissociate over a period of time in sodium, and (2) that the leaching of binder materials, such as nickel and chromium from nichrome, does not result in a physical breakdown of the coating during the service life of the component.

As a result of these potential problems, a portion of the present program is directed at evaluating the effects of long term (8000 hours) high temperature (625°C) sodium exposure on the various coating combinations. This program <sup>(6)</sup> is being conducted in austenitic stainless steel systems which include

provisions for impurity monitoring and control. Test conditions encompass a hot leg test temperature of 625°C, with a velocity of 1 fps, a loop temperature difference ( $\Delta T$ ) of 238°C, and a sodium oxide level of 0.5 to 1.0 ppm as determined by VWED (Vanadium Wire Equilibration Device).

Samples (0.75" x 0.75" x 0.180" with a 0.003" to 0.005" thick coating on both squared faces) are periodically withdrawn from the system hot leg into an argon atmosphere. Residual sodium is removed from the samples by successive rinses in alcohol and water. After vacuum drying and microweighing, sodium effects are determined by chemical, metallographic and electron microprobe analyses. Average corrosion rates in mils of thickness lost per year (mpy) are calculated on the basis of weight loss and coating density values.

Titanium carbide base coatings exhibited high corrosion rates due to coating instability, and were soon eliminated from the program. The as-deposited titanium carbide showed a non-stoichiometric composition of  $TiC_{0.7}$  before sodium exposure and a stoichiometric TiC composition after exposure. The coating failure was attributed to the stresses created by the volume changes occurring during carburization of the coating. (Sodium maintains an equilibrium carbon level by removal of carbon from the stainless steel loop system.)

Early chromium carbide coatings suffered from coating process control problems resulting in some specimens exhibiting cracking through a contaminated layer in the coating after



2000 hrs sodium exposure at 625°C. Nevertheless, some specimens attained 8000 hours exposure time and exhibited a corrosion rate of 0.3 mpy. After the process control problems were resolved, exposure to sodium of the later chromium carbide combinations resulted in time dependent weight losses with average corrosion rates of approximately 0.25 mpy. Figure 2 shows a comparison of the chromium carbide and titanium carbide corrosion rates.

Although extensive sodium penetration of the coatings occurs, no changes in cross sectional microstructure of the D-gun applied chromium carbide coatings were observed. The weight losses were attributed to loss of binder material to the sodium possibly coupled with loss of chromium carbide. Surface analyses showed, for example, that the reference chromium carbide/nichrome (LC-1H) coating lost nickel from the nichrome binder to the sodium, but this did not result in marked surface deterioration. Some internal cracking was observed, however, in the plasma sprayed CM and CN-1P coatings at exposure times greater than 1000 hours.

#### Thermal Cycling Tests

An inherent problem with many coatings is a tendency to physically disintegrate during thermal transients. Hence, a third part of the present program involved tests designed to simulate temperature fluctuations experienced by the reactor component during service. The experimental facility used in

this work is similar to the sodium compatibility loops, except that the loop is equipped such that by mechanical manipulation, test specimens can be transferred between the 625°C hot leg and an adjacent 427°C sodium quench tank, without coming into contact with air. A thermal cycle consists of holding a specimen at 625°C for a minimum of 8 hours and a maximum of 4 days, quench to 427°C in approximately 1 minute, raise to 625°C at a rate of 28°C/hr. Specimens exposed to this in-sodium cycling are removed after 15, 30 and 60 cycles directly into an argon atmosphere and cleaned as described in the previous section. Temperature cycling effects are then determined metallographically.

D-gun applied chromium carbide coatings have shown no deterioration as a result of thermal cycling. Plasma sprayed chromium carbide/molybdenum, CM coating, has, however, shown coating disintegration after 29 thermal cycles. The fracture occurred near the coating/substrate interface and is attributed to the mismatch in thermal expansion coefficients between the CM coating and the 316 stainless steel substrate.

## Irradiation Tests

Small discs of 316 stainless steel and Inconel 718 were coated on one side with a candidate chromium carbide material and were inserted in stainless steel capsules filled with sodium. The capsules were sealed by welding and were irradiated in the EBR-II reactor in Idaho Falls. A number of capsules are now being irradiated to fluences as high as  $3 \times 10^{22}$  n/cm<sup>2</sup>. Two capsules have been removed for examination so far, after receiving neutron fluences of approximately  $1 \times 10^{22}$  n/cm<sup>2</sup>. Irradiation temperatures were 450°C (844°F) and 585°C (1083°F) respectively. The materials in Table 1 which have been irradiated and examined so far include LC-1H, ~~CM-1P~~, CI and CM coatings. In addition, the LC-1C and CI-D coatings are being irradiated but are not yet available for examination. The titanium carbide coatings (TM and TN) were eliminated from consideration by corrosion test results and thus were not included in the irradiation tests.

Post-irradiation examination and testing<sup>(7)</sup> included visual and low-magnification examination, weight and thickness change measurements, optical metallography, scanning microprobe examination, x-ray analysis, and bond strength testing.

Visual examination revealed that the plasma sprayed coatings of all compositions showed tendencies for cracking and spalling, both within the coating and at or near the coating-

substrate interface. The observed effects ranged from barely detectable cracks or no externally observable cracks on some of the CN-1P (chromium carbide - 15% nichrome) coated specimens to essentially complete removal of the coating on the CM (Chromium carbide - 15 Vol. % Mo) coated specimens. All the plasma-sprayed coatings showed at least some cracking within the coating and at the interface under metallographic examination, however. Figure 3 is an example of the cracking found in the CN-1P specimens.

None of the 24 D-gun coated specimens showed any cracking or spalling tendencies by either visual or metallographic examination. Figure 4 shows the D-gun applied chromium carbide - 15% nichrome coating (LC-1H) after irradiation. The voids seen in the coating interface resulted from the "pull-out" of  $Al_2O_3$  particles during metallographic preparation. The  $Al_2O_3$  particles were eliminated in later coatings by improvements in the pre-coating grit blasting operation. There were no observable differences between the irradiated and un-irradiated conditions of the D-gun coatings when examined by metallography or by electron microprobe. X-ray results showed no compositional changes and only slight line sharpening of the pattern after irradiation. Bond strength tests were conducted by an epoxy lift-off tensile test. In all cases, both before and after irradiation, failures occurred in the epoxy at tensile strengths up to 13,000 psi. Perhaps one of the more significant indications of the coating integrity was found unintentionally when attempts to remove samples of coating by hammer and chisel methods for X-ray analysis proved unsuccessful.

## SUMMARY AND CONCLUSIONS

Wear tests have shown chromium carbide coatings to have the lowest friction and best wear resistance in sodium at temperatures from 200°C to 625°C of any of a wide variety of materials tested. The next best material from a wear performance viewpoint, titanium carbide-base coatings, failed the sodium corrosion tests due at least in part to carbon loss during deposition, and subsequent carburization during sodium exposure. Further friction tests, sodium corrosion tests, thermal cycling tests and irradiation tests resulted in the selection of a chromium carbide - 15 Vol.% nichrome coating applied by detonation gun as the only material and coating process which has so far passed all qualification tests for usage on stainless steel components in liquid-metal-cooled nuclear reactors. An identical composition coating applied by a plasma spray process failed to remain intact during irradiation to  $1 \times 10^{22}$  n/cm<sup>2</sup>.

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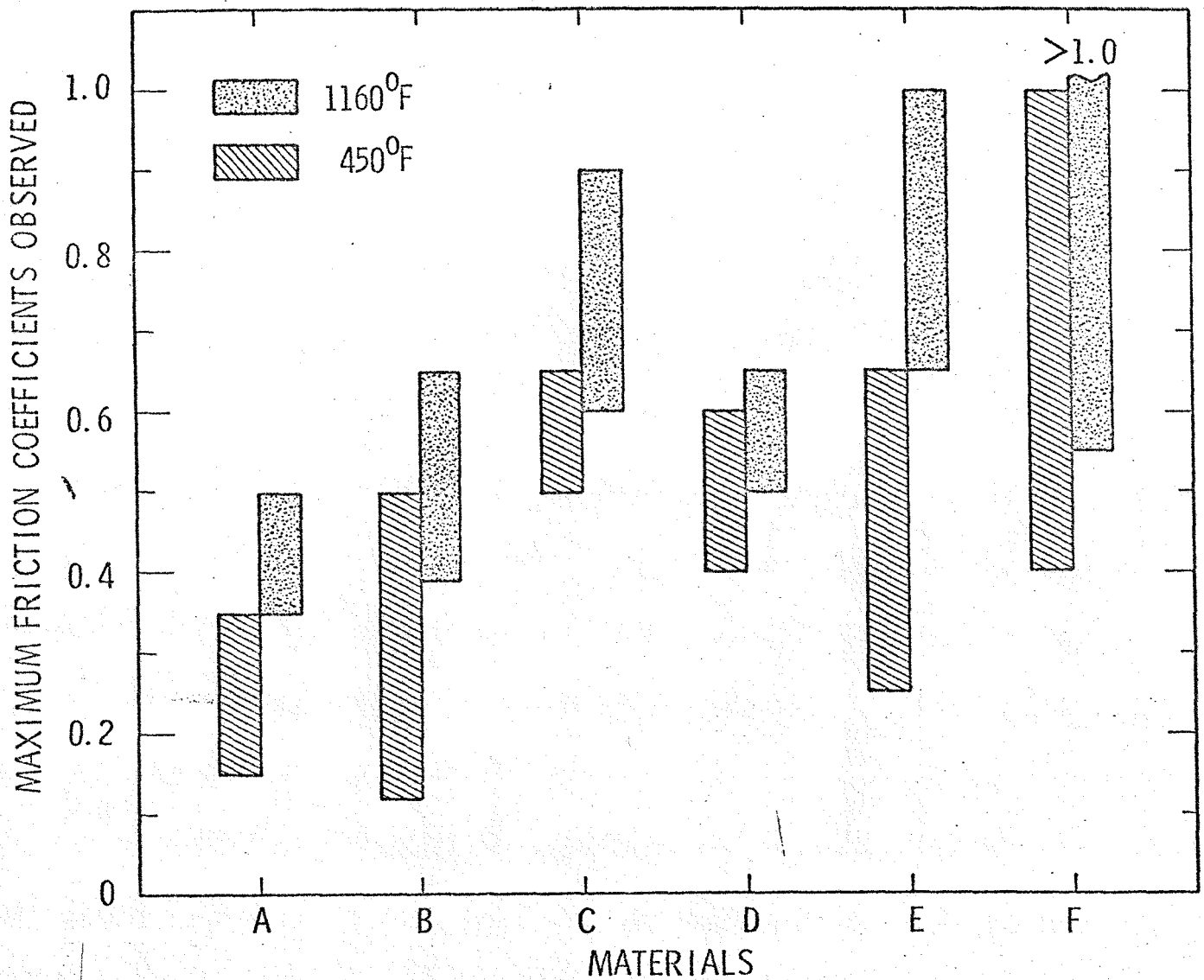
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### FIGURE CAPTIONS

- Figure 1. Friction ranges observed for various materials rubbing in sodium.
- Figure 2. Corrosion of chromium carbide and titanium carbide coatings in 625°C sodium.
- Figure 3. Cracking found in plasma-sprayed chromium carbide - 15 Vol.% nichrome coating on 316 SS after irradiation to  $1 \times 10^{22}$  n/cm<sup>2</sup>.
- Figure 4. Detonation-gun coating of chromium carbide - 15 Vol.% nichrome on 316 SS after irradiation to  $1 \times 10^{22}$  n/cm<sup>2</sup>.





- A CHROMIUM CARBIDE - 15% NICHROME D-GUN COATINGS
- B OTHER CHROMIUM CARBIDE BASE COATINGS
- C TITANIUM CARBIDE BASE COATINGS
- D CHROMIUM PLATINGS
- E CHROMIUM DIFFUSION COATINGS
- F REACTOR STRUCTURAL MATERIALS: INCONEL 718, HASTELLOY C, 316 SS, TZM.

