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CHARACTERIZATION OF THERMALLY SPRAYED COATINGS FOR HIGH-TEMPERATURE WEAR-PROTECTION APPLICATIONS

by
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MASTER

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GENERAL ATOMIC COMPANY

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ABSTRACT

Under normal high-temperature gas-cooled reactor (HTGR) operating conditions, faying surfaces of metallic components under high contact pressure are prone to friction, wear, and self-welding damage. Component design calls for coatings for the protection of the mating surfaces. Anticipated operating temperatures up to 850° to 950°C (1562° to 1742°F) and a 40-yr design life require coatings with excellent thermal stability and adequate wear and spallation resistance, and they must be compatible with the HTGR coolant helium environment. Plasma and detonation-gun (D-gun) deposited chromium carbide-base and stabilized zirconia coatings are under consideration for wear protection of reactor components such as the thermal barrier, heat exchangers, control rods, and turbomachinery. Programs are under way to address the structural integrity, helium compatibility, and tribological behavior of relevant sprayed coatings. In this paper, the need for protection of critical metallic components and the criteria for selection of coatings are discussed. The technical background to coating development and the experience with the steam cycle HTGR (HTGR-SC) are commented upon. Coating characterization techniques employed at General Atomic Company (GA) are presented, and the progress of the experimental programs is briefly reviewed. In characterizing the coatings for HTGR applications, it is concluded that a systems approach to establish correlation between coating process parameters and coating microstructural and tribological properties for design consideration is required.

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INTRODUCTION

The environment in which structural components of high-temperature gas-cooled reactors (HTGRs) must operate poses many challenges to the design engineer. Metallic structural materials chosen for their high-temperature strength, corrosion resistance, and long-term thermal stability may suffer friction, wear, and self-welding damage when used as mating surfaces for reactor components. Self-welding occurs when metallic components are in contact under high stress at elevated temperatures, while friction and wear may take place when the mating surfaces move relative to each other. The relative movements result primarily either from thermal expansion and contraction of the components or from coolant helium flow induced vibration. The degree of self-welding and wear damage to be expected increases with increase in contact pressure, operating temperature, and service time and is different for different material couples.

In the past, experiments have been carried out to characterize the friction and wear behavior of some critical materials and surface coatings for wear protection applications in the steam cycle HTGR (HTGR-SC) (Refs. 1 to 4). This system was characterized by a primary coolant core outlet temperature of 700° to 750°C (1292° to 1382°F). As a result of increasing national energy concerns, advanced HTGR systems, such as the gas turbine (GT) and process heat (PH) HTGRs, are receiving increased attention. In these two instances, the excellent high-temperature capabilities which permit high thermal efficiencies for electrical power generation or chemical processes are the major attraction. However, the anticipated higher operating temperatures [850° to 950°C (1562° to 1742°F)] necessitate the utilization of advanced wrought and cast nickel-base superalloys. Furthermore, new components such as turbomachines and intermediate heat exchangers (IHXs) are unique to the HTGR-GT and HTGR-PH systems, respectively. As a result of these changes, a significant amount of data is needed for advanced HTGR component development.

Surface coatings which provide low friction coefficients and excellent wear and spallation resistance are generally considered to be one of the most feasible ways to combat high-temperature wear. Commercially available plasma sprayed and detonation-gun (D-gun) deposited chromium carbide-base and zirconium oxide-base coatings are currently under consideration for friction and wear protection of the advanced HTGR systems. The purpose of this paper is to briefly summarize the needs for wear protection of various HTGR components and to discuss the criteria of coating selection. The technical background of the coating development and experience with the HTGR-SC are also commented upon. The testing techniques required for coating characterization are presented, and the progress of the experimental programs currently being performed at GA is reviewed.

2. HTGR WEAR PROTECTION NEEDS

The technical considerations pertaining to the friction, wear, and self-welding protection needs for the major components of HTGRs are summarized in Table 1. Components discussed are the thermal barrier, control rod drive mechanisms, reactor internals, heat exchangers, and turbomachinery. Background and experience with the HTGR-SC pertinent to each particular component are also included.

TABLE 1
HTGR WEAR PROTECTION NEEDS

Key Component	Technical Considerations	Activities and Comments
Thermal barrier	The major concerns are sliding wear and self-welding of coverplates and attachment fixtures. There is also possible fatigue loading in the attachment fixtures due to chattering (stick-slip sliding at low sliding velocity) (Refs. 2, 4).	Previous work on full-scale components (Ref. 4) and experimental specimens (Ref. 2) under HTGR-SC conditions with testing temperatures up to 816°C (1500°F) has shown that chromium carbide-nichrome coatings provide good wear protection. Work under HTGR-GT and HTGR-PH conditions is in progress.
Control rod drive mechanisms	Wear coatings are needed in high-stress flexible joints, etc. In addition, neutron irradiation damage of coatings must be considered.	Preliminary results of irradiation testing reported by the Hanford Engineering Development Laboratory (Ref. 5) have shown that D-gun applied chromium carbide-nichrome coatings are capable of withstanding 8×10^{22} n/cm^2 fast-neutron irradiation.
Reactor internals	The core lateral restraint and peripheral seal are subject to motions that have the potential to cause wear damage. Another concern is that there are locations where contact occurs between metals and the graphite reflectors, and this requires evaluation of adhesion between graphite and metal.	Previous studies on graphite-metal compatibility indicated that metals are subject to carburization (Ref. 6). Additional work on friction and wear between coatings, metals, and graphite is required.

TABLE 1 (Continued)

Key Component	Technical Considerations	Activities and Comments
Heat exchangers	Tube damage caused by interactions between the tubes and tube-support plate is the major concern in recuperator, precooler, core auxiliary heat exchanger, and intermediate heat exchanger design. Wear protection devices such as wear shields and ring assemblies are used in some heat exchanger designs. Coating residual stresses which could cause distortion of protection devices with thin cross sections may pose some limitation for coating application. Other solutions under development include applying insert material to the support plate as cushioning or applying a wear coating directly to the tube.	Preliminary studies (Ref. 7) of the tribological properties of high-temperature self-lubricating materials under simulated HTGR-SC conditions have shown them to be feasible as insert material. In the application of coatings on tubes, there is concern about the creep and creep-fatigue properties of the tube being degraded (Ref. 3). Qualification of applying a coating to the tube will require information on the effects of coatings on the properties of substrate alloys.
Turbomachinery	An in-reactor turbomachine will exhibit some unique features. Preliminary study indicates that fretting wear at the turbine blade root and self-welding and sliding wear at the turbine inlet volute, rotor, casing, and duct will be important and that coatings are called for to provide protection of critical components.	Evaluation of chromium carbide-base and stabilized zirconium oxide-base coatings and alternate commercial coatings is under way.

3. COATING SELECTION CRITERIA

In general, the coatings selected for HTGR applications are required to provide a low friction coefficient, adequate wear and spallation resistance, and compatibility with the HTGR helium environment over the 40-yr reactor design life. In some cases resistance to irradiation damage is also important. The key considerations for coating selection are discussed in this section.

3.1. ELEVATED-TEMPERATURE STRUCTURE STABILITY

At elevated-temperature service conditions, carbide- and oxide-base coating materials are often subject to transformation from one phase to another. It is the nature of the thermal spraying process that the chemical compositions and crystallographic structures of the coating materials change during deposition. Carbides and oxides may decompose at extremely high temperatures, causing chemical changes, or one component of a compound may be oxidized preferentially during deposition, causing a shift in chemistry.

When the deposited coatings are employed in high-temperature service, further phase transformation takes place. Phase transformation of carbides or oxides in a coating involves a structural change which is usually accompanied by a volume change. This may result in large strains in the coating which are an important source of high stress concentrations and promote coating spallation (Refs. 1, 8). In addition, the physical and mechanical properties of the coating may also change, resulting in different friction and wear characteristics.

3.2. COMPATIBILITY WITH SUBSTRATE ALLOYS

One of the major factors that contribute to coating spallation is the thermal expansion coefficient mismatch between coatings and substrate materials. The thermal expansion mismatch is greatly reduced by employing metallic binders in carbide or oxide coatings. The binder materials selected are usually similar in chemical composition to the substrate materials. Increasing the content of metallic binders in a coating generally increases the coating spallation resistance; however, the wear resistant properties are inherently degraded (Ref. 2). Characterizing the binder content in a coating to achieve optimum wear and spallation resistance is a major consideration.

Another concern is the interdiffusion between coatings and substrate materials. Primarily, interdiffusion may take place between metallic binders and the substrate alloys. In addition, the transformation of unstable carbides or oxides to a more stable phase at high temperature may cause carbon or oxygen transport between coating and substrate. The effect of this interdiffusion on the coating and substrate service behavior is a critical criterion in coating selection.

3.3. COMPATIBILITY WITH HTGR HELIUM

The HTGR coolant helium contains residual amounts of H_2, CO, CH_4, H_2O, etc. The environment is normally characterized by a very low oxygen potential. The gaseous species can permeate through a coating and react either with the coating or with the substrate. In service at elevated temperatures, oxidation may occur on the substrate alloys at the coating-substrate interface (Ref. 1). Subsequently, the interfacial oxidation weakens the coating-substrate bonding and promotes early coating spallation. The HTGR helium environment is also known to be carburizing to several high-temperature wrought and cast alloys (Ref. 9). Recent experimental results showed that substrate alloys of chromium carbide-nichrome coated specimens are also subject to carburization. As will be discussed in a later section, the mechanism of carburization in this latter case is not clear at this time.

Thermally sprayed coatings inherently contain some porosity in the as-deposited condition. It is believed that interconnected pores can provide fast transport of oxidizing and/or carburizing molecules through the coatings and are responsible for the substrate interfacial oxidation and/or carburization. The relative amount of porosity, the average pore size, and the distribution of pores vary widely in the coatings produced by various processes. Improving the coating processing techniques to obtain high-density, fine-pore coatings is very beneficial with respect to retarding substrate corrosion.

3.4. FRICTION AND WEAR BEHAVIOR

The friction and wear behavior of a coating is determined by the coating physical and mechanical properties and the testing conditions. Coating hardness, density, microstructure, surface finishing, and carbide or oxide phase stability are the most important properties affecting coating service performance. Since the operating conditions in an HTGR vary from component to component, and the mode of relative movements between the mating surfaces also varies with different components, as mentioned in Section 2, the friction and wear resistance requirements in an HTGR component depend on the specific application. It is generally true, however, that by improving the coating properties and compatibility with the substrate and HTGR environment, the friction and wear resistance is also enhanced.

4. CHARACTERIZATION OF COATINGS

This section discusses some of the techniques for metallurgical characterization that are required to qualify thermally sprayed coatings for HTGR wear protection application. Plasma sprayed and D-gun deposited coatings are fairly well established processes and are in commercial production (Refs. 10, 11). However, it must be noted that the deposited structure and its properties are very dependent on the type of application device and on the operating parameters. In reality, it is very difficult to predict or to describe the exact composition, phases, and structure of a coating after deposition. Characterization of coatings to better understand their properties is essential. Furthermore, the corrosion characteristics and the friction and wear behavior of coatings under simulated HTGR operating conditions are required to evaluate the coating service performance for design considerations.

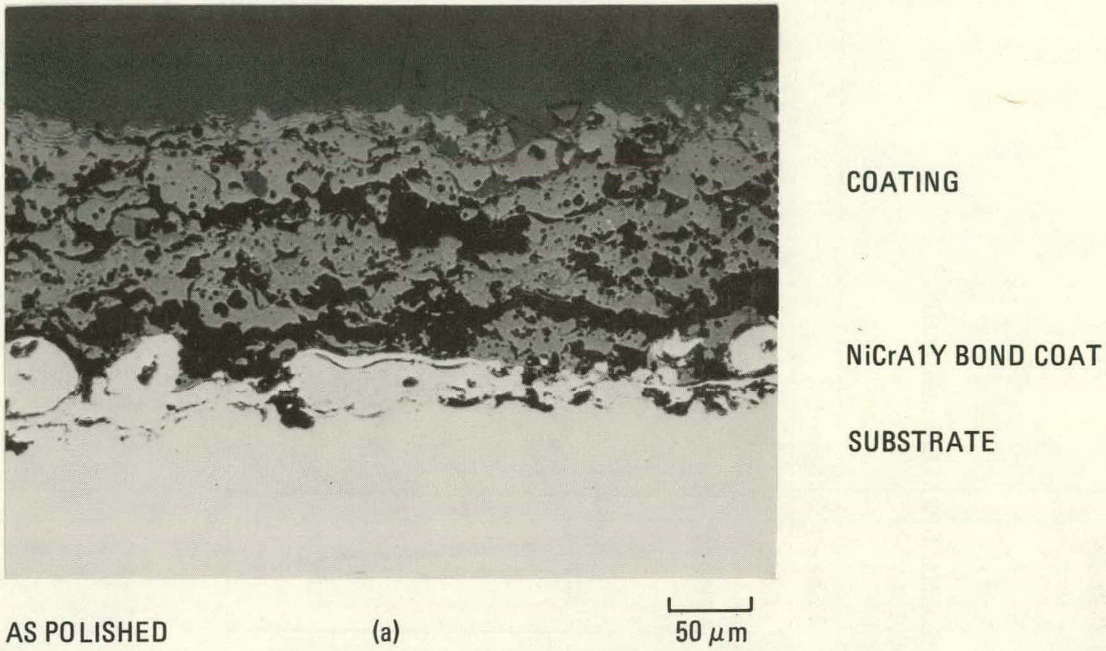
The coatings discussed here are primarily the chromium carbide-base coatings, since coatings of this type have been evaluated fairly extensively under HTGR-SC conditions. Some discussion will also be devoted to stabilized zirconia-base coatings. Stabilized zirconia-base coatings have received attention in the gas turbine industry and are currently being considered for possible HTGR applications.

4.1. MICROSTRUCTURAL ANALYSIS

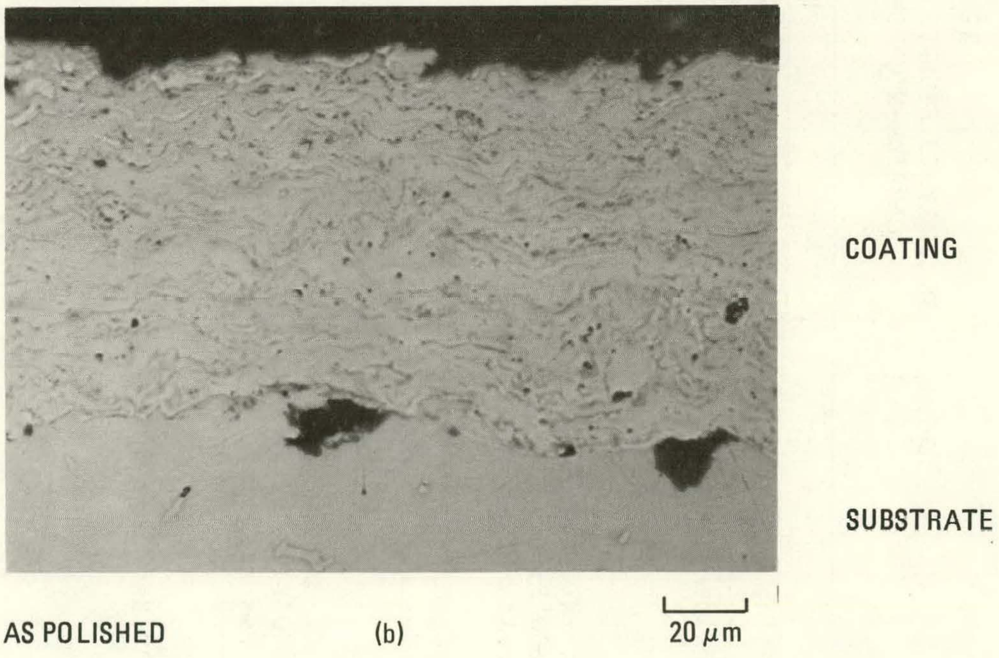
In general, optical metallography provides most of the information needed to characterize coating microstructure. Thermally sprayed coatings usually exhibit a lamellar structure consisting of thin lenticular particles or splates. Under normal resolution of an optical microscope, coating structure such as lamellar layers, oxides, metallic binder, pore size and distribution, and coating-substrate interfacial contamination can be easily observed. As illustrated in Fig. 1(a), a plasma sprayed yttria (20 wt %) stabilized ZrO_2 coating on Hastelloy Alloy X (Hastelloy X) with a thin layer of NiCrAlY as a bond coat shows a large amount of pores and oxide formation in the NiCrAlY layer and the NiCrAlY-substrate interface. This is an example of a poorly processed coating. The coating spalled when it was exposed at 982°C (1800°F) to a helium environment for one day. Figure 1(b) shows a D-gun deposited $Cr_{23}C_6$-NiCr (80-20 vol%) coating on an IN 100 substrate. The lamellar structure can be seen clearly, and the coating contains very little porosity and oxide formation. The coating-substrate interface shows only minor contamination. This coating usually exhibits high hardness and density, excellent adhesion, and good wear resistance properties.

X-ray diffraction is the most powerful and the least expensive technique for identifying coating crystallographic structures. In the as-deposited condition, because of the high quenching rate of the coating materials from the molten state, the coating exhibits high thermal and residual stresses. This is characterized by a broadened and diffused diffraction pattern. Also, the as-deposited coating is usually comprised of mixed amorphous phases, and it is difficult to identify them. A common practice is to briefly apply a heat treatment to relieve the residual stresses. Table 2 presents some x-ray diffraction results on plasma sprayed chromium carbide-nichrome coatings. The stress-relief treatment employed was 1 hr at 871°C (1600°F).

A scanning electron microscope (SEM) is of particular interest in providing micrographs with a tremendous depth of field. This is valuable for surface analysis. Figure 2 shows SEM micrographs of plasma sprayed and D-gun deposited coating surfaces. The D-gun deposited coating shows a finer particle size and is more uniformly distributed than the plasma sprayed coating. Consequently, the properties of a D-gun deposited coating are generally superior to those of a plasma deposited coating. Another



AS POLISHED (a)



AS POLISHED (b)

Fig. 1. Optical micrographs of (a) plasma sprayed ZrO_2-20 wt % Y_2O_3 coating with NiCrAlY bond coat on Hastelloy X and (b) D-gun deposited $Cr_{23}C_6$-NiCr (80-20 vol %) coating on IN 100. Both coatings are in the as-deposited condition.

TABLE 2
X-RAY PHASE ANALYSIS RESULTS FOR PLASMA SPRAYED CHROMIUM CARBIDE-NICHROME COATINGS[a]

Coating Type/Condition	Phases Present					
	$Cr_{.62}C_{.35}N_{.03}$	Cr_3C_2	Cr_7C_3	$Cr_{23}C_6$	NiCr	Cr_2O_3
Cr_3C_2-NiCr/as-deposited	Major (diffused pattern)	Minor	Minor	--	Major	--
Cr_3C_2-NiCr/871°C (1600°F) 1 h, stress relieved	--	Major	Minor	--	Major	--
$Cr_{23}C_6$-NiCr/as-deposited	--	--	--	Major (diffused pattern)	Major (diffused pattern)	--
$Cr_{23}C_6$-NiCr/871°C (1600°F) 1 h, stress relieved	--	--	Minor	Major	Major	Minor

[a] Ref. 1.

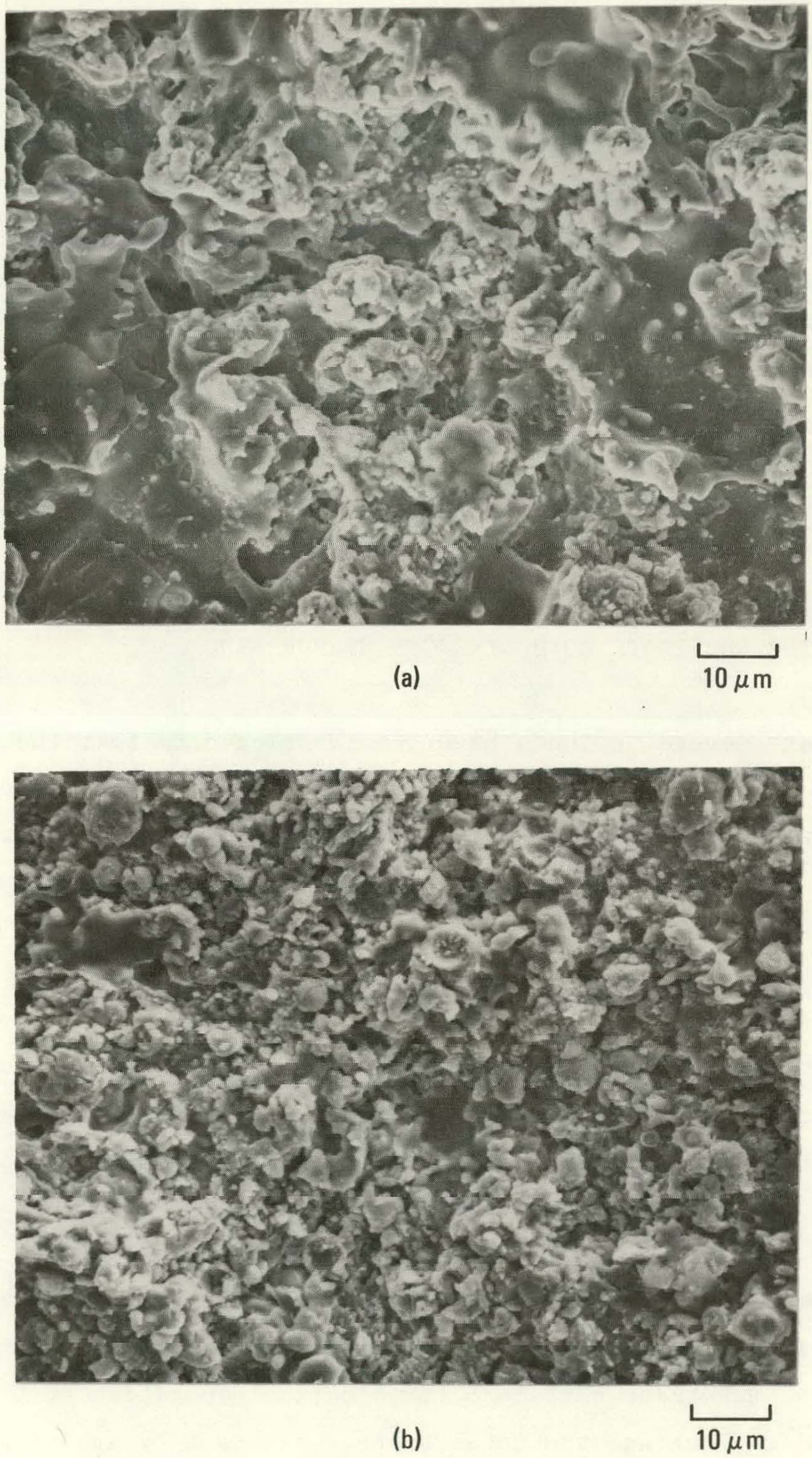


Fig. 2. Scanning electron micrographs showing surfaces of (a) plasma sprayed $Cr_{23}C_6$-NiCr (75-25 vol %) and (b) D-gun deposited Cr_3C_2-NiCr (80-20 vol %) coatings in the as-deposited condition

interesting feature of the SEM is that when it is used in conjunction with an energy dispersive x-ray analysis (EDX) device, the relative contents of chemical composition and distribution of elements in a coating can be easily obtained. Figure 3 shows micrographs of x-ray mapping obtained from SEM-EDX. The specimen shown is plasma sprayed Cr_3C_2-NiCr (75-25 vol %) on Hastelloy X after exposure to a simulated HTGR helium environment containing 200/20/10/1 μatm of $H_2/CH_4/CO/H_2O$, respectively, at 871°C (1600°F) for 3000 h. The coating spalled off the substrate after exposure, and the results demonstrated that interdiffusion of chromium and iron occurred between the coating and substrate alloy.

Other techniques, such as transmission electron microscopy (TEM), are useful in identifying crystallographic and microstructural features such as grain size, phases, and deformation structures.

4.2. COATING-SUBSTRATE BOND STRENGTH MEASUREMENT

Although several methods have been developed to test the adhesion of coating to substrate alloys, there is no technique which can provide the true coating bond strength (Ref. 12). Qualitative testing methods such as mechanical bending and twisting, impact, scribing, and indentation techniques are useful to simulate the service behavior of the components rather than to provide comparative information about different processes or different systems. Quantitative testing methods such as tensile and shear, peel, and ultrasonic techniques are usually employed to obtain bond strength data on coated specimens. Of these, tensile and shear tests are the most often employed because they are relatively easy and inexpensive to conduct.

The mechanism by which a thermally sprayed coating is bonded to a substrate is primarily mechanical interlocking. This is achieved by grit-blasting the substrate surface before coating deposition to obtain a clean surface and to increase the total surface area and by applying a supersonic

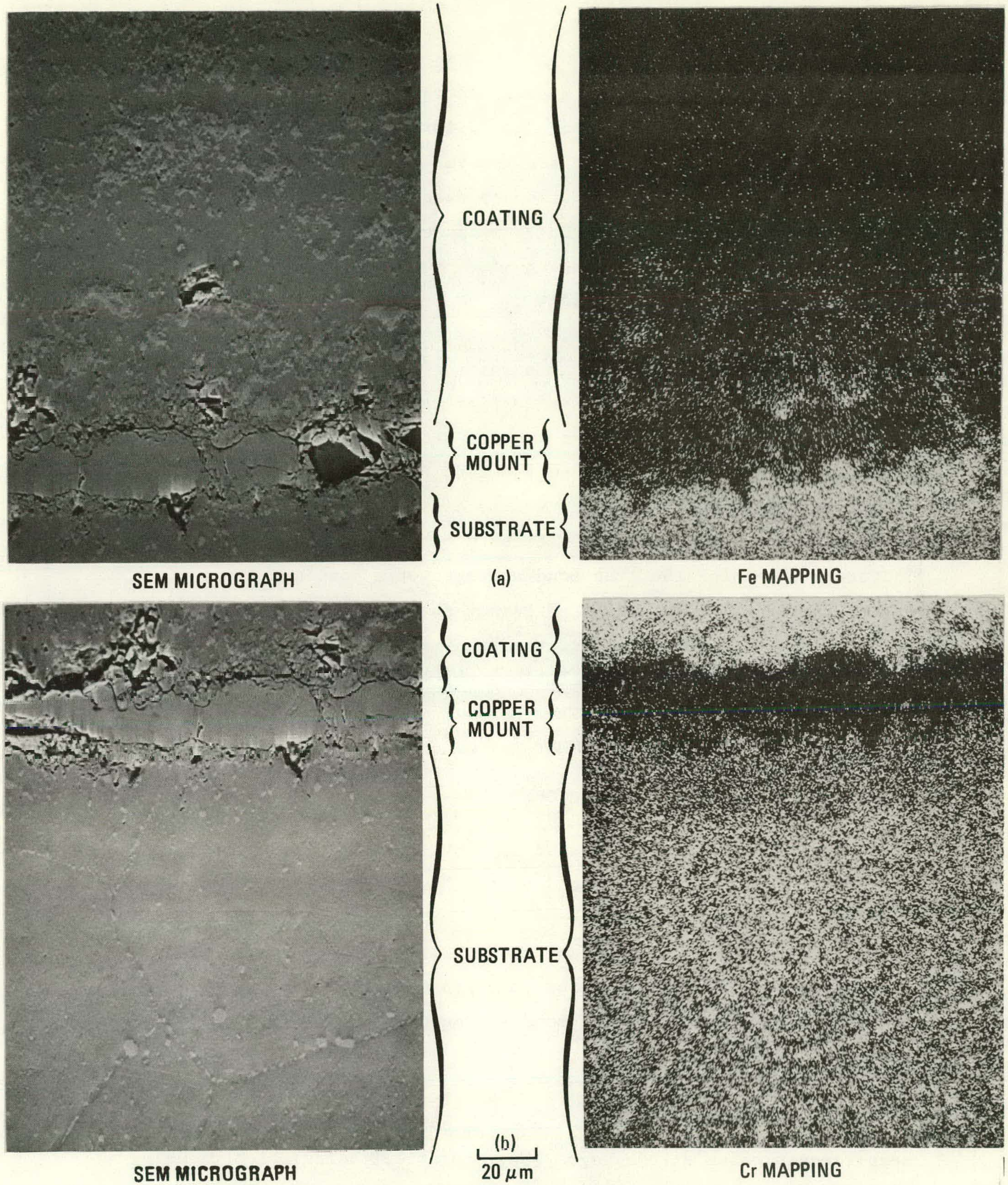


Fig. 3. Scanning electron micrographs and their corresponding x-ray mappings showing (a) iron and (b) chromium distribution. The specimen is a plasma sprayed Cr_3C_2-NiCr coating on Hastelloy X exposed for 3000 h to HTGR impure helium at 871°C (1600°F). The coating spalled after exposure.

gas velocity to create a high kinetic energy of impact of the coating material to the substrate during deposition. The result of these processes is that high residual stresses are generated in both the coating and substrate which consequently introduce deceptive stress concentration factors and make true bond strength measurement impossible. This is particularly true of shear testing since the residual stress is in general greater in the lateral direction.

As the residual stresses in a coating increase with coating thickness, the maximum thickness of a given coating that can be applied is often limited. This is of particular concern since in tensile testing an adhesive of known strength is employed to pull the coating off the substrate. Adhesives can penetrate porous coatings and thereby give misleading results. Also, the strength of the adhesive is another limiting factor in obtaining the true bond strength of a coating, since it cannot exceed the adhesive strength. Figure 4 shows a tensile testing specimen arrangement and a photograph of the specimen after testing. Some of the test results are presented in Table 3.

4.3. RESIDUAL STRESS MEASUREMENT

As mentioned previously, residual stresses are created in a coating when coating materials are cooled rapidly from the molten state during the deposition process. The effects of the high residual stresses on the coatings are threefold: (1) they may cause cracking of the coating, as shown in Fig. 5(a); (2) they may cause distortion of the parts being coated, especially for thin-cross-section specimens, as shown in Fig. 5(b); and (3) they may decrease the bond strength and cause coating spallation (Ref. 11).

The residual stresses in a coating can be measured by dynamic measurements using strain gages, by theoretical calculation based on an elastic model of the substrate deformation, or by other methods as reviewed

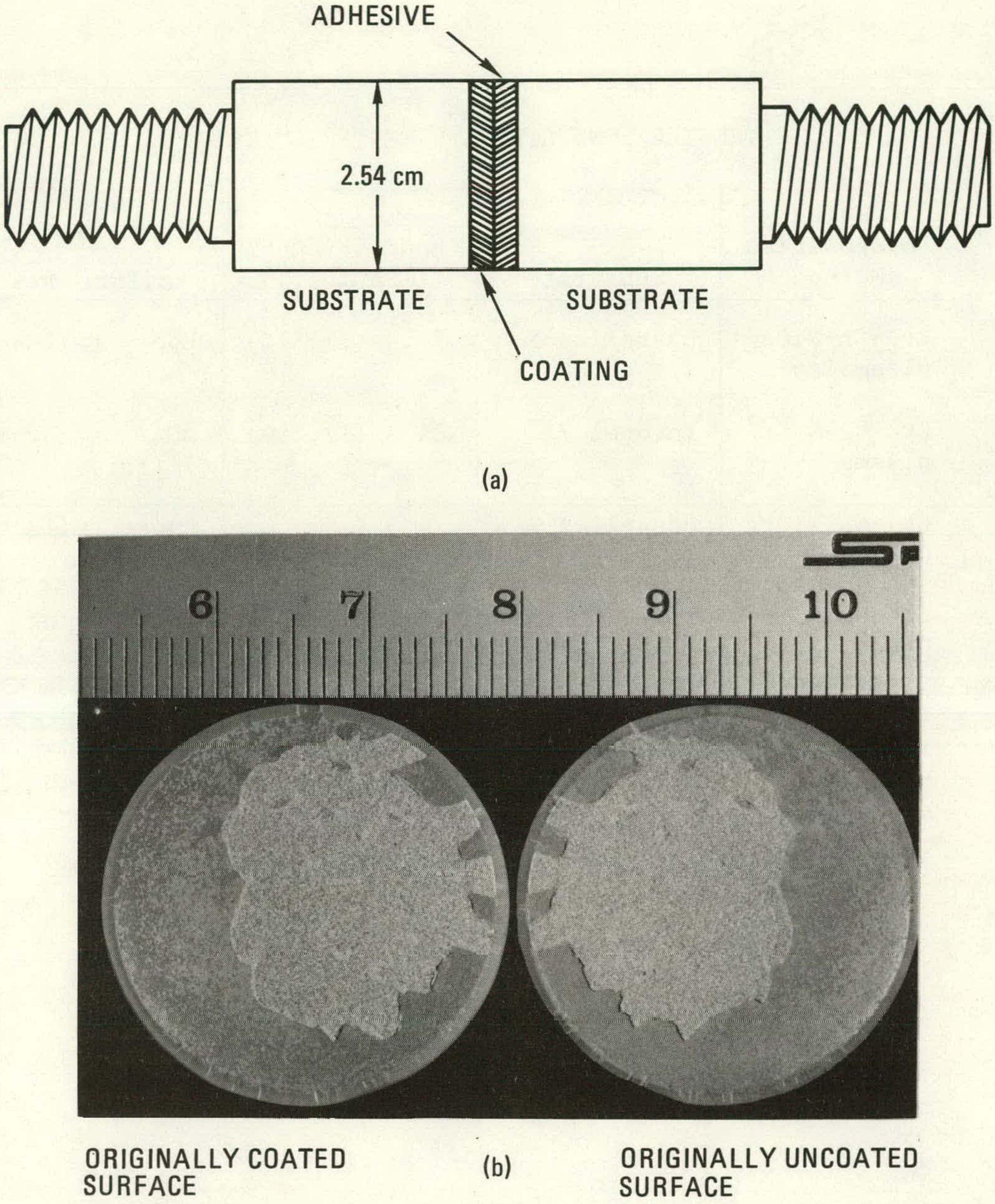


Fig. 4. (a) Tensile specimen for coating bond strength test, and (b) photograph of specimen after testing. The coating was partially separated from the originally coated surface. The coating is a plasma sprayed $Cr_{23}C_6$-NiCr coating on Inconel 718, and the adhesive employed is Scotchweld EC2186 made by the 3M Company with a bond strength of 89.6 MPa (13,000 psi).

TABLE 3
TENSILE BOND STRENGTH TEST RESULTS[(a)]

Coating/ Disposition Method	Substrate	Bond Strength [MPa (psi)]	Failure Mode
$Cr_{23}C_6$-NiCr/ plasma spray	Hastelloy X	79.4 (11,510)	Epoxy failure
$Cr_{23}C_6$-NiCr/ plasma spray	Inconel 718	84.5 (12,250)	80% coating failure
$Cr_{23}C_6$-NiCr/ D-gun	Hastelloy X	74.5 (10,800)	Epoxy failure
$Cr_{23}C_6$-NiCr/ D-gun	2-1/4 Cr-1 Mo steel	82.1 (11,905)	50% coating failure

(a) The adhesive employed was Scotchweld EC2186 manufactured by the 3M Company. The tensile bond strength of this adhesive has been determined to be 89.6 MPa (13,000 psi).

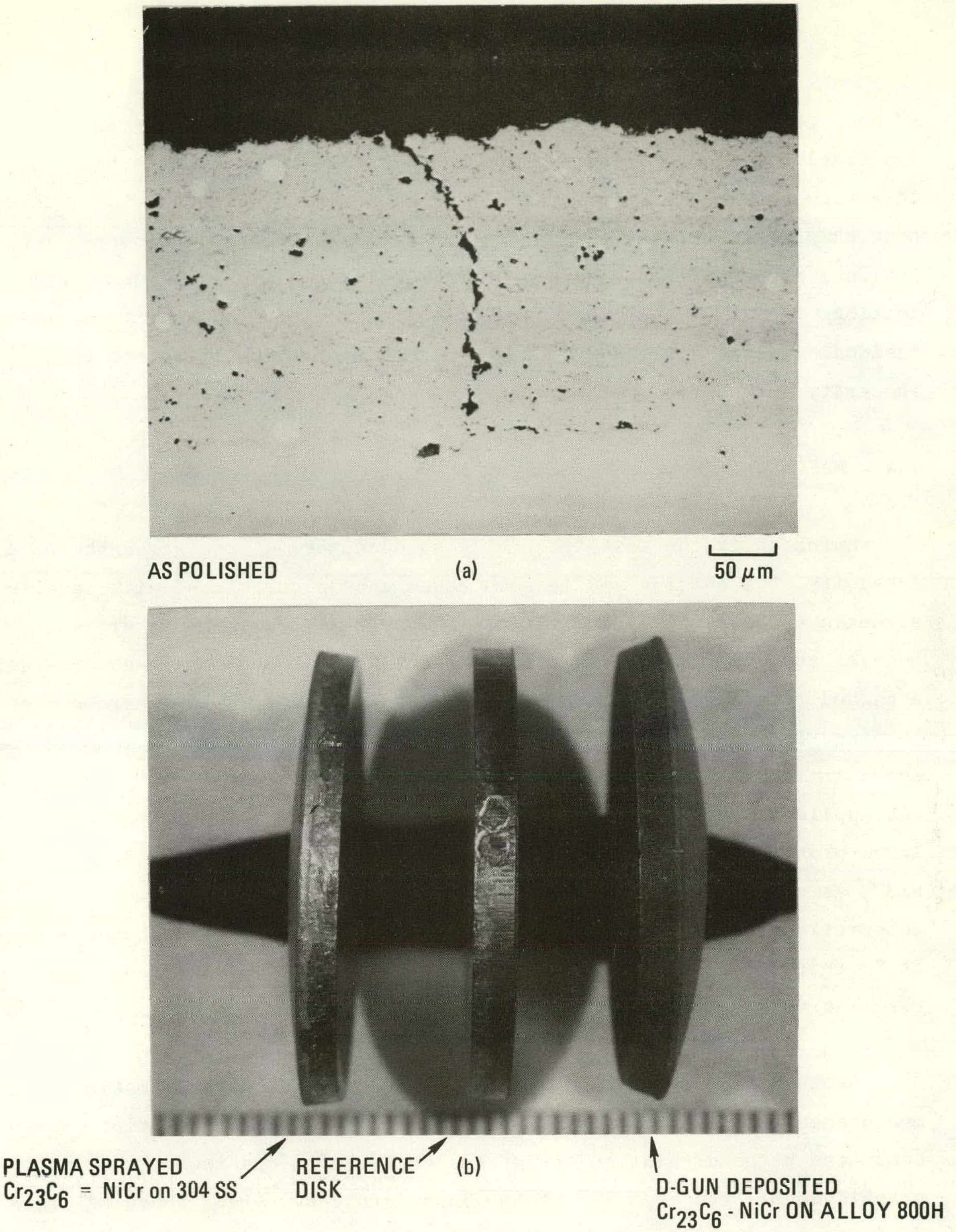


Fig. 5. (a) Optical micrograph showing a residual stress induced crack in a D-gun deposited Cr_3C_2-NiCr coating on Alloy 800H, and (b) photograph showing residual stress induced distortion of coated specimens after elevated-temperature exposure in HTGR helium at 982°C (1800°F). The plasma sprayed coating has been exposed for 3500 h and the D-gun deposited coating for 16,500 h. The reference disk is a 2.54 cm diameter by 0.32 cm thick as-machined Alloy 800H specimen.

in Ref. 11. Since the residual stresses may set a limitation on thickness applicable to a particular coating and may significantly affect the coating integrity, control of the stress level in a coating is essential. This can be accomplished by controlling the deposition parameters to obtain low residual stresses in a coating. Fortunately, because relatively thin coatings (about 0.01 cm thick) are required for HTGR applications, the residual stresses in these coatings do not significantly affect the coating integrity and service performance.

4.4. HARDNESS AND DENSITY MEASUREMENTS

Hardness is the most frequently used measure of the strength and integrity of a coating and in some cases can be correlated with tensile strength and wear resistance. Coating hardness measurements are valuable because they can be made on brittle coatings while the coatings are still attached to the substrate. While it is easy to measure the hardness of a coating, it is also easy to misinterpret and misuse it. For example, as shown in Table 4, the microhardness value of a brittle coating decreases as the applied load of indentation increases. This is primarily due to the large plastic deformation and cracking in the coating caused by indentation, as shown in Fig. 6. The larger the load applied, the more plastic deformation occurs in the coating, which results in a lower hardness value. It is therefore important to specify the load applied when reporting the hardness of a coating.

Another factor which has to be taken into account when making hardness measurements is the thickness of the coating. Since indentation is usually conducted perpendicular to the cross section of a coating on a metallographic mount, the edge effect should be avoided. Also, there may be a difference in hardness in two directions owing to the anisotropic structure.

Thermally sprayed coatings inherently contain porosity in the as-deposited condition. The relative amount of porosity and the average

TABLE 4

MICROHARDNESS MEASUREMENT RESULTS OF A PLASMA SPRAYED $Cr_{23}C_6$-NiCr COATING USING DIFFERENT LOADS

	Load Applied (g)		
	100	200	300
Microhardness range (10 readings) (DPH)	572-988	593-833	490-671
Average microhardness (DPH)	757	663	559

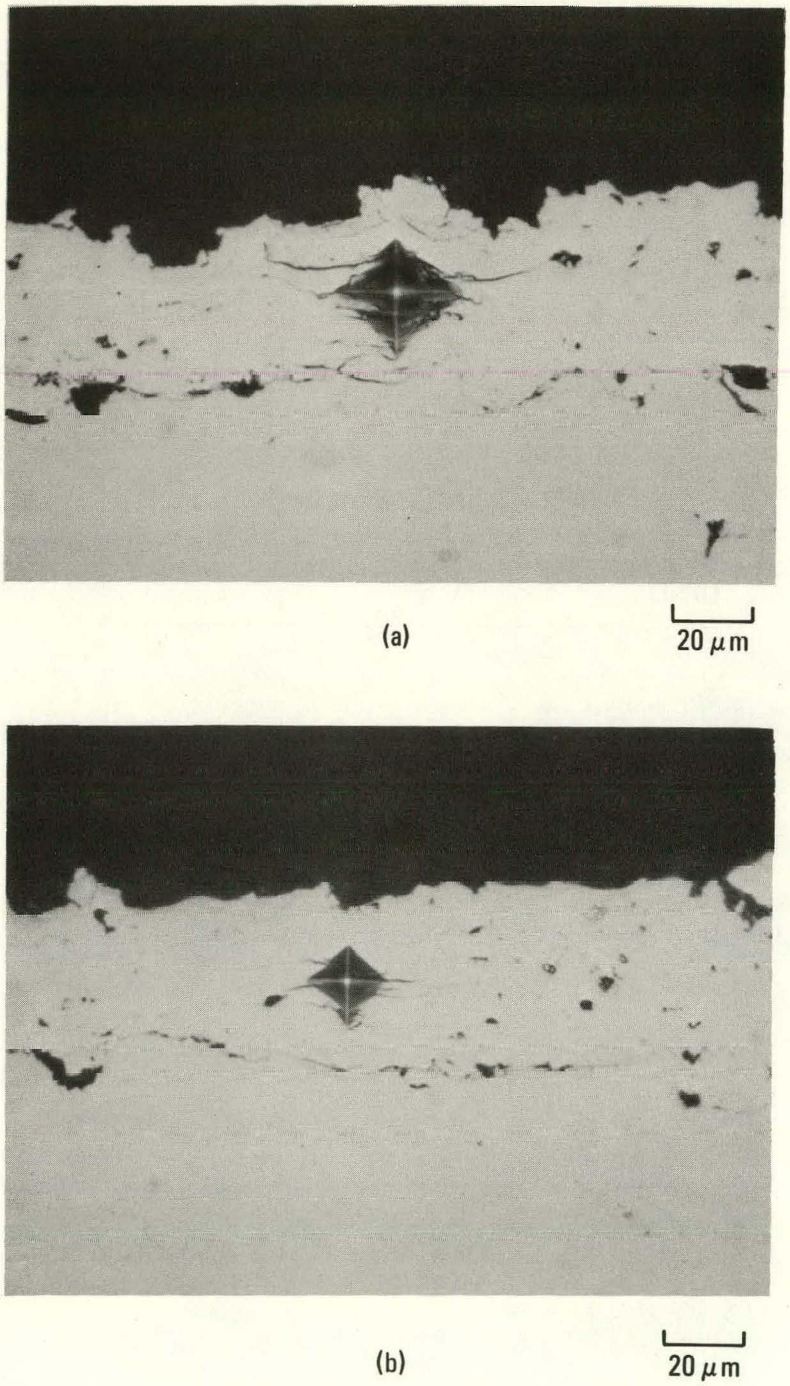


Fig. 6. Photomicrographs showing microhardness indentation on a plasma sprayed $Cr_{23}C_6$-NiCr coating. The loads applied are (a) 300 g and (b) 200 g.

pore size depend strongly on the deposition device and processing parameters. Density measurements provide a relatively good indication of coating properties such as hardness, cohesive bond strength, and corrosion and wear resistance.

It is impossible to obtain the true density of a thermally sprayed coating. However, a mercury porosimeter which permits mercury to penetrate into the interconnected pores under pressure can give a measurement close to the true density. Figure 7 shows a plot of the apparent density value versus the applied pressure. The coating tested was a plasma sprayed $Cr_{23}C_6$-NiCr coating. The apparent density value first increased with the applied pressure and then remained constant when the applied pressure reached about 1.38 MPa (200 psi), indicating that at this pressure level, the open pores in the coating were filled with mercury. One point should be noted: the mercury pressure should be kept low enough so that no damage will be done to the coating.

4.5. COMPATIBILITY STUDY OF COATING WITH SUBSTRATE ALLOY AND HTGR HELIUM ENVIRONMENT

In HTGR service, coating materials are exposed to the HTGR helium environment at elevated temperatures. The unavoidable presence of small quantities of impurities in the helium coolant requires that an understanding of the interaction of coating and substrate materials with these impurities be obtained. The impurities which are potentially important with respect to materials compatibility include H_2, H_2O, CO, CO_2, and CH_4.

Coated specimens were exposed to a simulated HTGR helium environment containing 200/20/10/1 μatm of $H_2/CH_4/CO/H_2O$, respectively, at temperatures ranging from 760° to 982°C (1400° to 1800°F). The specimens were removed from the furnace retort after spallation was observed. A detailed description of the experiment is given in Ref. 1. After exposure testing, the specimens were subjected to metallurgical evaluation using optical

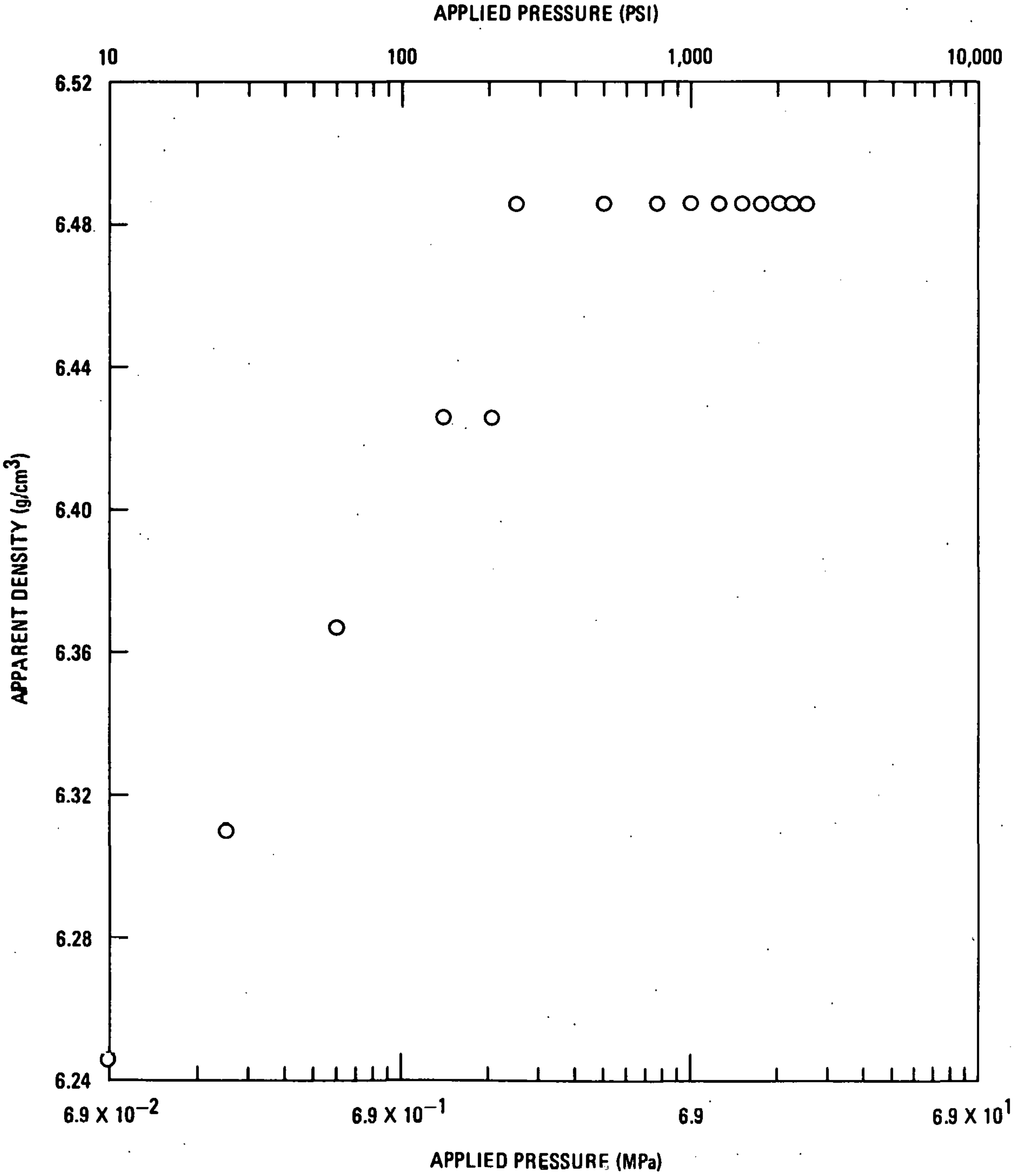


Fig. 7. Mercury porosimetric plot of the apparent density of a plasma sprayed $Cr_{23}C_6$-NiCr coating versus applied pressure

metallographic, electron microprobe, electron microscopic, and x-ray diffraction analysis techniques.

Figures 8(a) and 8(b) show the spallation charts for thermally sprayed chromium carbide-nichrome coatings. The substrate alloys are Alloy 800H and Hastelloy X. From these figures, several observations can be made:

1. Plasma sprayed coatings spalled faster than those deposited by the D-gun process.
2. $Cr_{23}C_6$-NiCr coatings are more spallation resistant than Cr_3C_2-NiCr coatings.
3. Coatings deposited on Alloy 800H spalled faster than those deposited on Hastelloy X.

Optical metallographic examination carried out on the spalled specimens revealed that oxidation took place at the coating, coating-substrate interface, and substrate, as shown in Fig. 9. The oxides which formed at the substrate near the coating-substrate interface are the major concern, since they weaken the coating-substrate bonding and eventually cause the coating to spall (Ref. 1). This is probably the reason why the coatings deposited on Hastelloy X were more spallation resistant than those deposited on Alloy 800H, since Hastelloy X is more oxidation resistant than Alloy 800H.

As mentioned earlier, the thermally sprayed coatings inherently contain fine interconnecting pores. It is these pores which allow gaseous impurities to permeate through the coating and react with the substrate. The D-gun deposited coatings, in general, exhibit less porosity than those deposited by plasma spraying processes. Thus, the spallation resistance of the D-gun coatings is significantly improved compared with that of the plasma sprayed coatings.

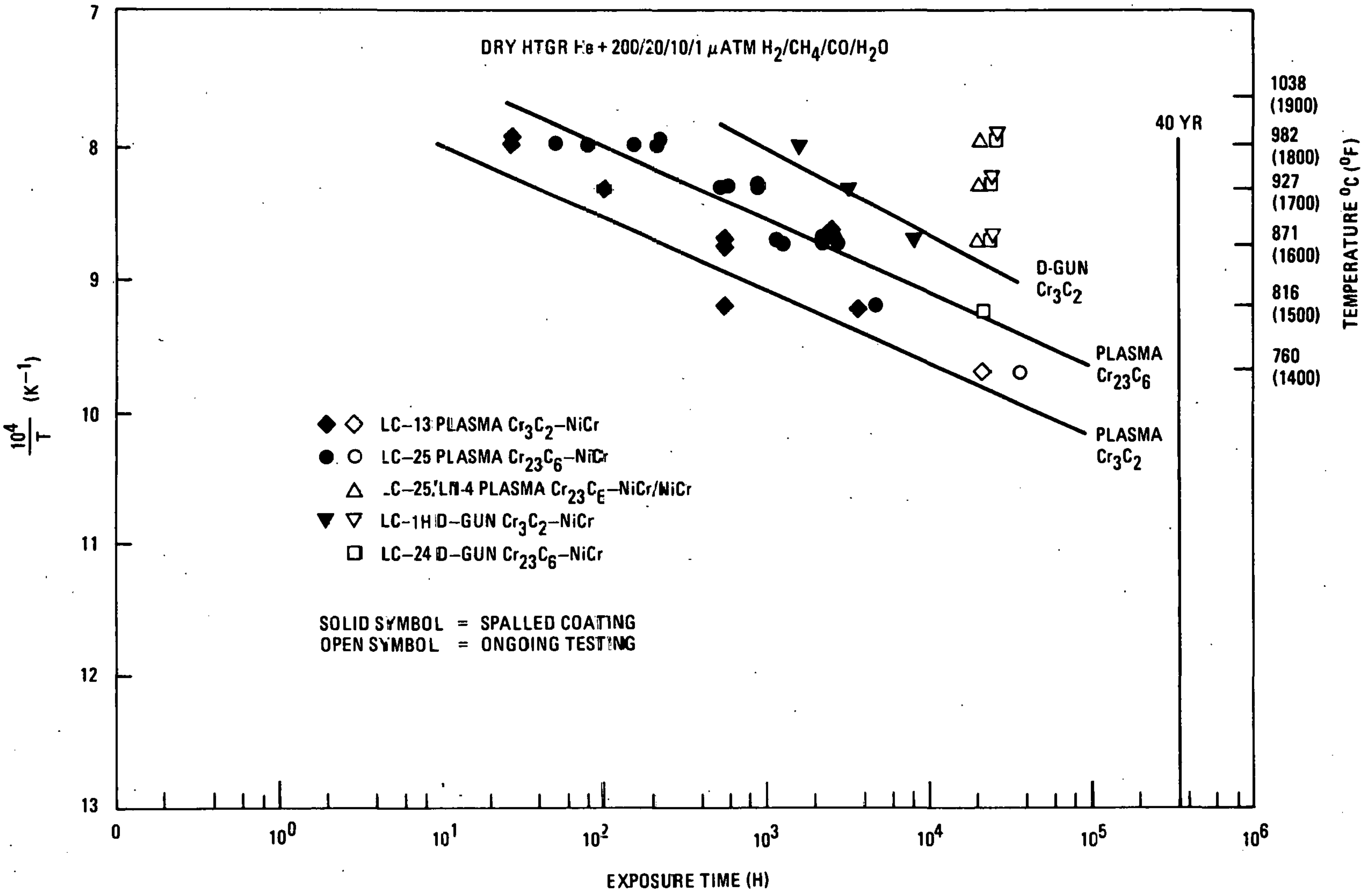


Fig. 8(a). Spallation chart of chromium carbide-nichrome coatings on Alloy 800H

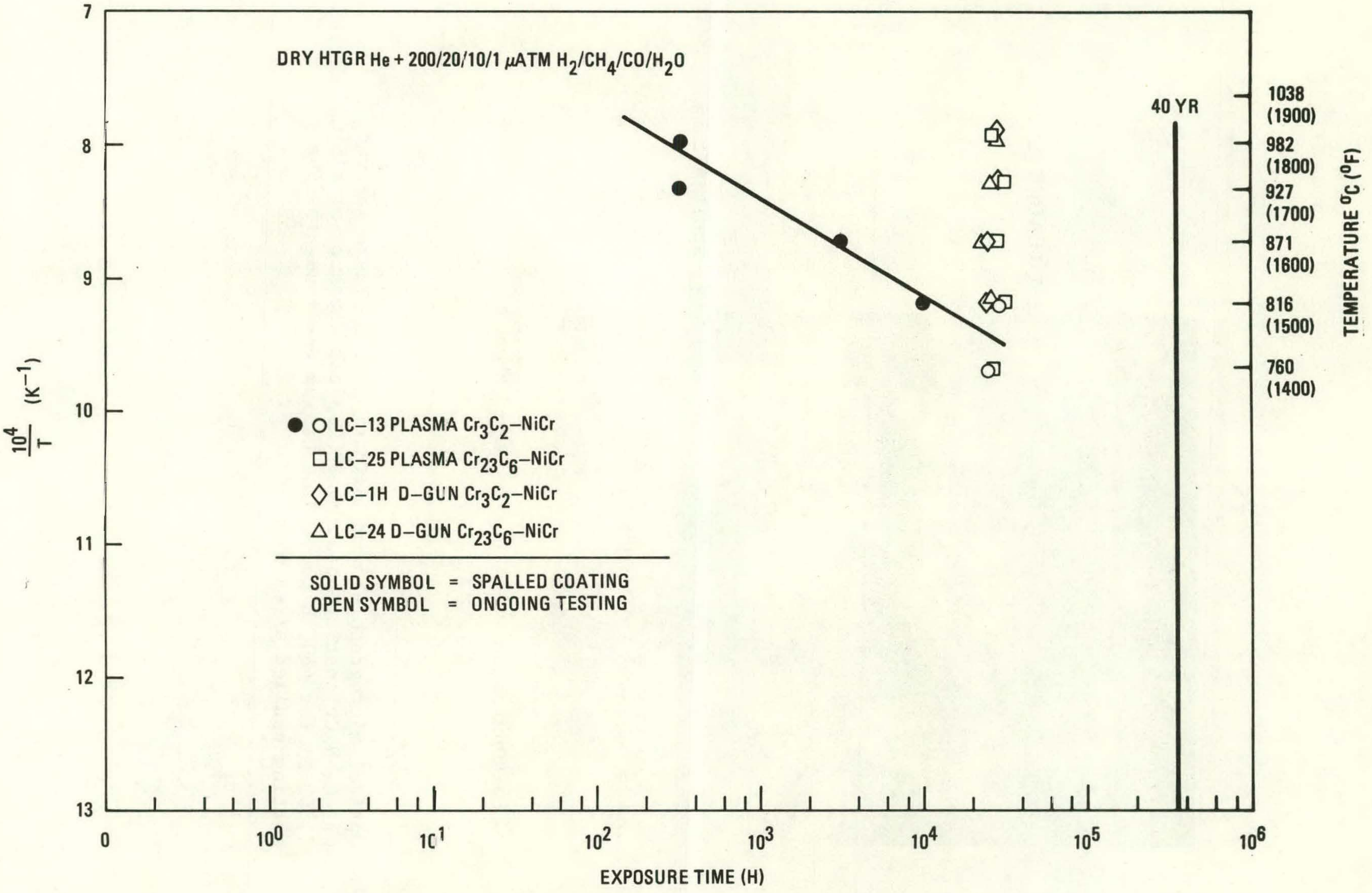


Fig. 8(b). Spallation chart of chromium carbide-nichrome coatings on Hastelloy X

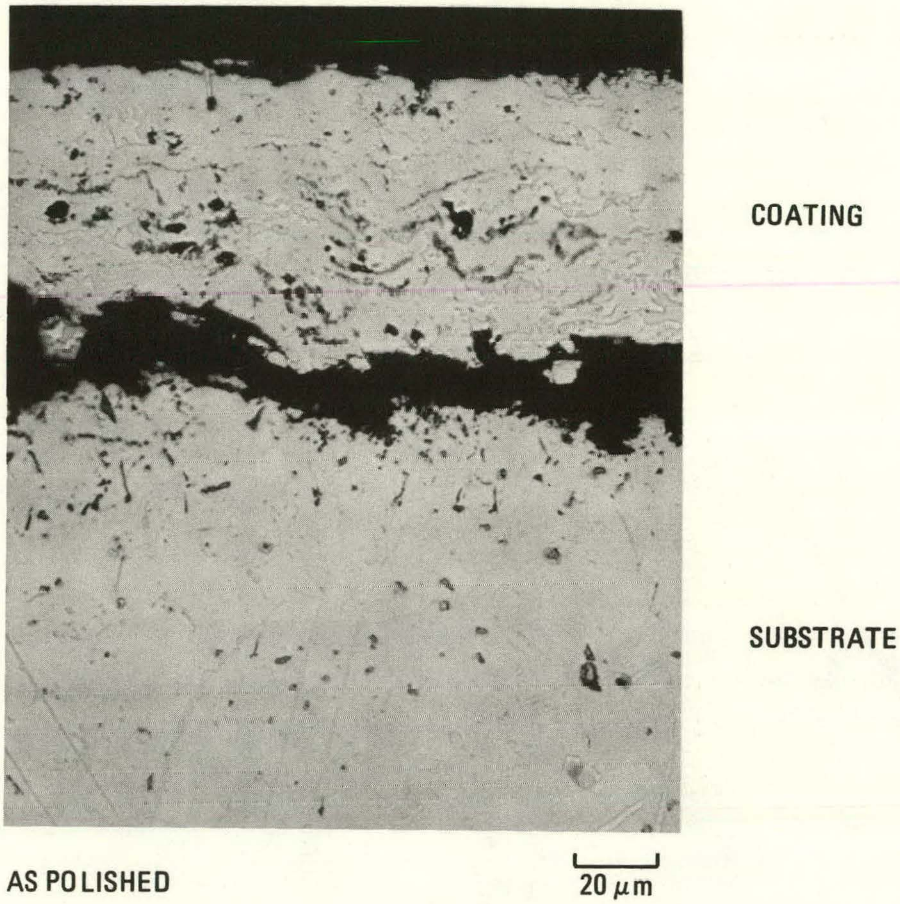


Fig. 9. Optical micrograph showing oxidation of a plasma sprayed $Cr_{23}C_6$-NiCr coating on Alloy 800H after exposure at 816°C (1500°F) for 4600 h to an HTGR helium environment. The coating spalled after exposure.

Phase analysis of the chromium carbide-nichrome coatings exposed to HTGR helium was carred out using an x-ray diffraction technique. The results showed that the three types of carbides, namely Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$, were either unstable or metastable under HTGR operating conditions. Phase transformation of these carbides took place during high-temperature helium exposure and the transformation occurred as

$$Cr_3C_2 \rightarrow Cr_7C_3 \rightarrow Cr_{23}C_6 \quad .$$

The transformation of Cr_3C_2 to Cr_7C_3 involves a structural change from a loosely packed orthorhombic structure to a closely packed hexagonal structure which is likely to be accompanied by a volume contraction. This volume contraction of the coating may produce complex stresses which promote coating spallation. This probably is part of the reason that Cr_3C_2-NiCr coatings spalled faster than $Cr_{23}C_6$-NiCr coatings.

Another important feature of this phase transformation is that as Cr_3C_2 transforms into more chromium-rich carbides, the dissociated free carbon may act as a source of substrate carburization. The effects of the sprayed chromium carbide coating on the carburization behavior of the substrate have recently been investigated. Figure 10 shows a photomicrograph of a plasma sprayed Cr_3C_2-NiCr coating on a Hastelloy X specimen after being exposed for 330 h at 982°C (1800°F) to an HTGR helium environment containing 200/20/10/~1 μatm of $H_2/CH_4/CO/H_2O$, respectively. The metallography shown in Fig. 10 was obtained by the differential interference contrast (DIC) method using an optical microscope with polarized light. The substrate surface underneath the coating was carburized substantially, whereas the uncoated side did not show significant evidence of carburization, suggesting that the chromium carbide coating promotes carburization of the substrate alloys. The HTGR environment is known to be carburizing to many high-temperature alloys (Ref. 8). It is not clear at this time whether the coating might reduce the local oxygen potential of the coating-substrate interface, thereby

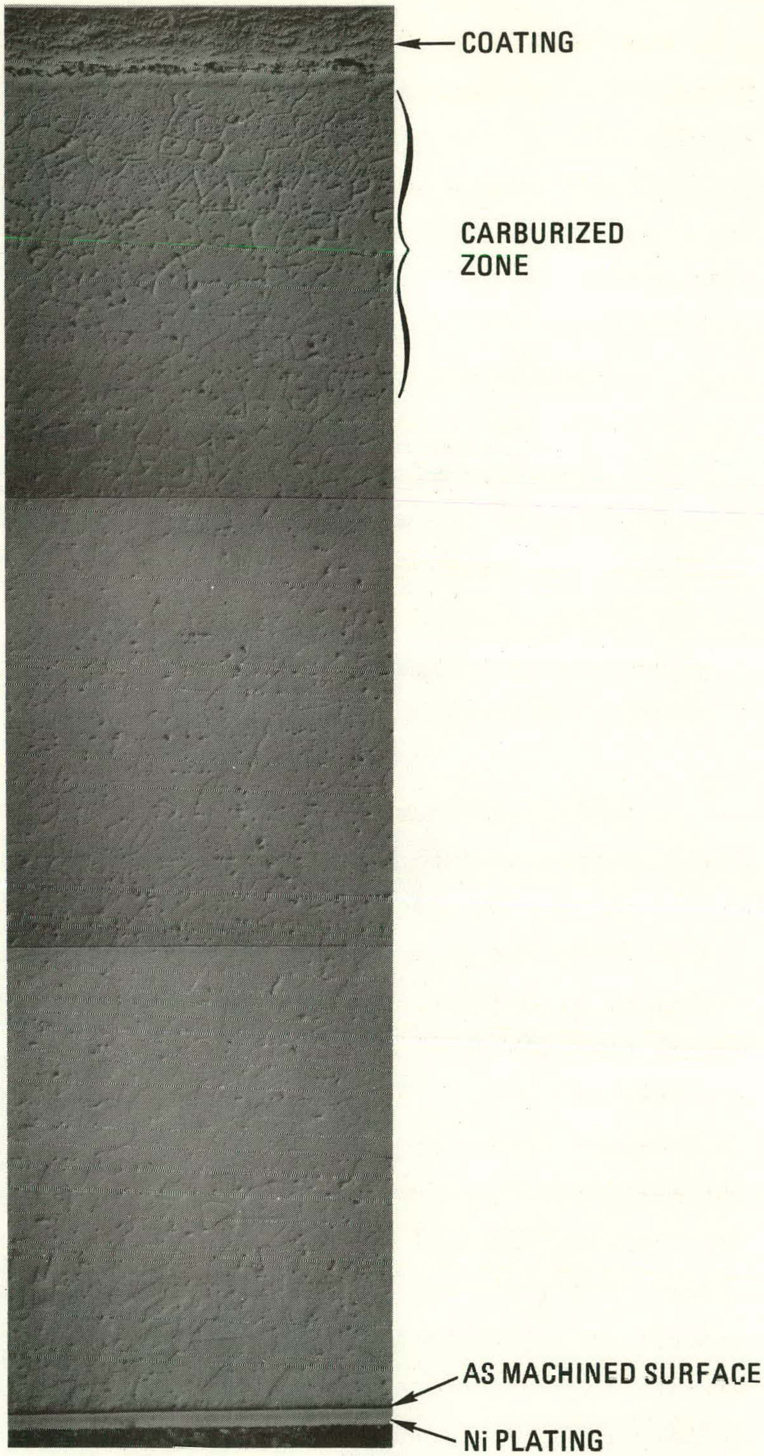


Fig. 10. Optical micrograph showing carburization of substrate (Hastelloy X) beneath a plasma sprayed Cr_3C_2-NiCr coating after exposure to HTGR helium at 982°C (1800°F) for 330 h

accelerating the carburization process. However, it is believed that the accelerated carburization of the substrate is due, in part, to the dissociation of the unstable and metastable carbides of the coatings, which provides free carbon as a carburization source.

Another concern, besides carburization and oxidation, is interdiffusion of the alloying elements between coating and substrate during high-temperature service. An electron microprobe study was carried out on coated Alloy 800H specimens exposed to an HTGR environment at 871°C (1600°F) for times up to 2000 h. The results showed that nickel in the NiCr phase of the coating diffused into the substrate, while iron in the substrate diffused into the coating to form an Ni-Fe-Cr alloy. Examination of the preliminary results suggests that the interdiffusion of alloying elements between the coating and substrate may be beneficial to coating and substrate compatibility.

4.6. FRICTION, WEAR, AND SELF-WELDING STUDIES

Since the primary objective of the surface coatings is to protect the high-temperature alloys from friction, wear, and self-welding damage, it is essential to understand the tribological behavior of coatings and substrate alloys under HTGR operating conditions. Friction and wear testing should be conducted such that the mode of relative movements, contact-surface geometry, contact stresses, temperature, and environment closely simulate the service situation of the components. In general, the modes of motion of mating surfaces in an HTGR can be divided into two categories: (1) sliding movements, which mainly result either from thermal expansion and contraction of components such as thermal barriers or from mechanical motion of components such as control rod drives and (2) fretting movements, which are caused either by the coolant flow induced vibration, such as in steam generators, or by mechanical vibration, such as in turbomachinery. Friction and wear testing, accordingly, is performed either in sliding or in fretting conditions.

Extensive sliding wear tests carried out at GA showed that thermally sprayed chromium carbide-nichrome coatings performed well under HTGR operating conditions (Ref. 2). Chattering (stick-slip phenomenon) occurred only at the beginning of testing. As the sliding distance increased, the rubbing surfaces reached a steady-state condition with regard to friction and wear surface oxidation, work hardening, and thermal aging, which resulted in a decreased wear rate, low friction coefficients, and disappearance of chattering. The chattering phenomenon observed in the testing did not result in significant damage to the coatings.

One of the significant findings in the sliding wear studies was that the friction coefficients of coatings increased substantially as the sliding velocity decreased, as shown in Fig. 11. This is important because the sliding velocities of HTGR components caused by thermal expansion and contraction are on the order of 7×10^{-3} mm/s or lower. The results obtained from an accelerated test using high-velocity sliding may not therefore be entirely valid for design considerations.

A preliminary study of fretting wear of a heat exchanger tube vibrating between supporting plates has been carried out (Ref. 13). The experimental results showed that the wear rate decreased with increase in the material hardness, increase in the gap between the tube and the support plate, decrease in frequency and amplitude of tube vibration, and increase in preload applied to the tube at the tube/support plate junction. In subsequent analysis of the experimental data, an empirical model was developed to describe the fretting wear damage in heat exchangers:

$$w = \alpha_1 f^{\alpha_2} \left(\frac{A_C}{D}\right)^{\alpha_3} \left(\frac{A_G}{D}\right)^{\alpha_4} \left(\frac{t}{D}\right)^{\alpha_5} e^{\alpha_6 (R_S - \bar{w} - P_L)} \quad , \qquad (1)$$

where w = weight loss in grams per cycle of vibration,

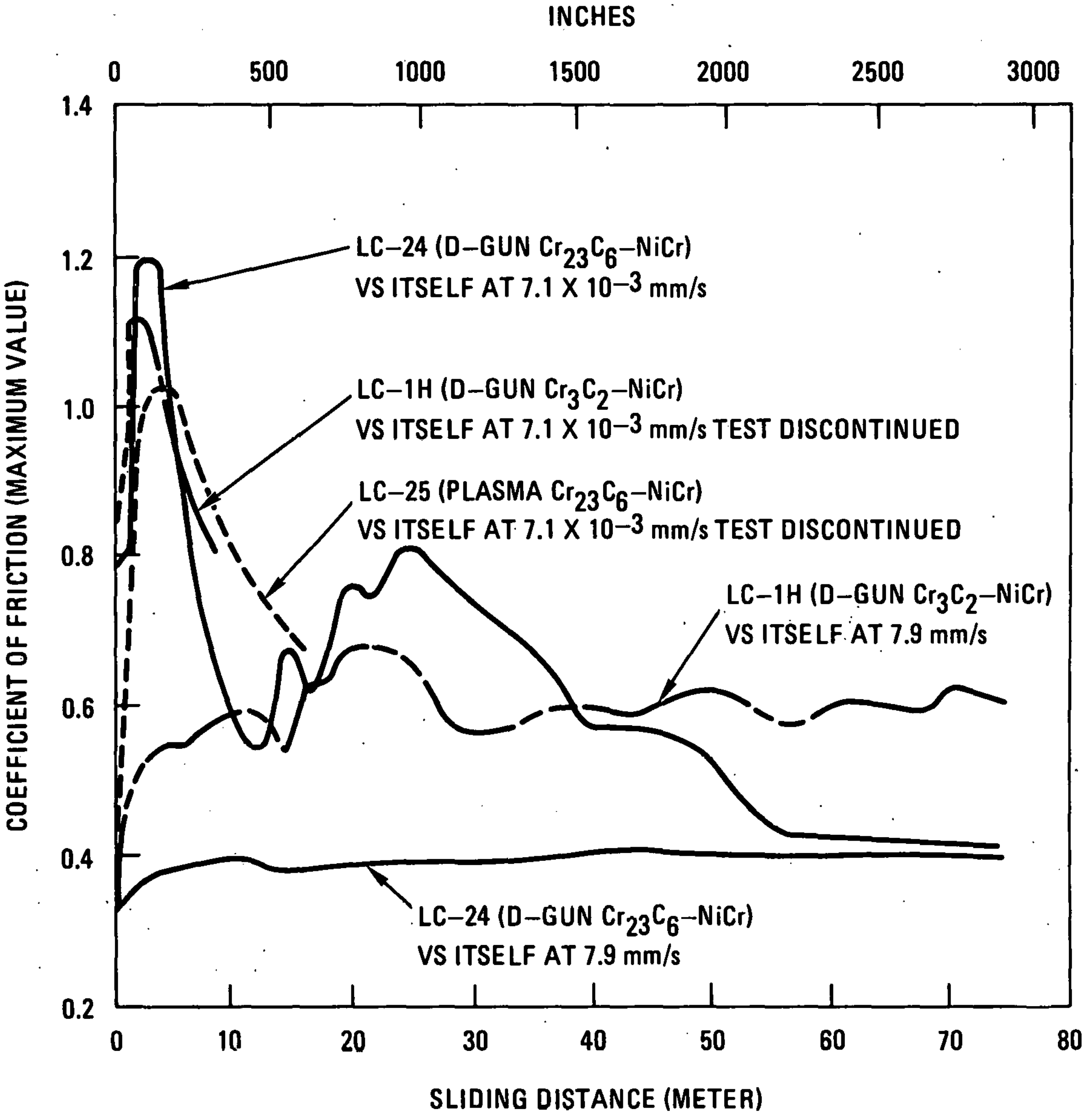


Fig. 11. Plot of friction coefficient versus sliding distance at 816°C (1500°F) showing effect of sliding velocity on coating friction coefficient (Ref. 2)

A_C = peak-to-peak transverse amplitude of the tube which would be developed at the support if the gap dimensions were very large and no load was applied to the tube at the support,

A_G = the smaller of either A_C or the diametral gap at the support plate,

D = tube diameter,

f = tube wall thickness,

R_S = amplitude of the minimum shear load required to maintain the tube stationary,

$\overline{w}$ = mean weight of tube supported at the support plate in kilograms,

P_L = preload applied to the tube at the support plate in kilograms,

α_1 through α_6 = constraints.

This empirical model does not yet take into account temperature and HTGR environmental effects. However, it is valuable in providing a basis for the quantitative analysis of the fretting wear study of heat exchangers. Similar experiments with modifications to include temperature and environmental effects on surface coatings are planned.

5. CONCLUDING REMARKS

In characterizing surface coatings for the rather complex HTGR component wear protection applications, a systems approach to establish a comprehensive engineering data base for design considerations is required. This includes development of deposition processing parameters, determination of materials properties (such as physical and mechanical properties), and understanding of coating system properties (such as compatibility with substrates and the environment and tribological behavior).

Plasma spraying and D-gun deposition are well characterized and reproducible processing techniques. Optimization of the processing parameters to achieve low residual stresses, high cohesive and adhesive bond strengths, and minimum porosity in the coatings is a major task still to be accomplished. The area where attention and effort are most needed, however, is coating system properties data development. Information on coating long-term thermal stability of phases, oxidation, carburization, spallation mechanism, and friction and wear characteristics and their impact on coating service performance is essential for coating selection considerations.

This paper describes some of the techniques used at GA for metallurgical characterization of coatings. The discussion has not been comprehensive, and a great deal of additional effort is obviously needed. However, it is hoped that through the systems approach a better understanding and sound development of thermally sprayed coatings can be achieved.

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