

FLAME-SPRAYED METALLIC AND CERAMIC COATINGS FOR ARMY APPLICATIONS

by

MILTON LEVY

and

ALBERT P. LEVITT



MATERIALS ENGINEERING DIVISION

U. S. ARMY MATERIALS RESEARCH AGENCY
WATERTOWN, MASSACHUSETTS 02172

MAY 1964

CONTENTS

Pag	,e
INTRODUCTION	i
MATERIALS	
Physical and Chemical Properties	r
Flame-Spray Coatings 4	-
FLAME-SPRAY PROCESS	•
SELECTION OF COATINGS)
SURFACE PREPARATION OF BASIC MATERIAL FOR FLAME-SPRAY COATINGS 10)
APPLICATION OF FLAME-SPRAYED CERAMIC AND METAL COATINGS 10)
Launcher-Type Weapon System	-
Coating of Nozzles - Launcher-Type System	}
Coating of Other Titanium and Aluminum Components - Launcher-Type Weapon System	ŀ
Rocket Motor Bodies - Experimental Weapon System 14	ŀ
Test Nozzles - Experimental Weapon System 16	>
Application of Flame-Sprayed Ceramic and Metal Coatings to Metals Processing	5
DISCUSSION AND RECOMMENDATIONS FOR FUTURE STUDIES	7

INTRODUCTION

The drive toward ever higher operating temperatures in Army weapon systems continues unabated since the thermal efficiency and effectiveness of such systems are proportional to their operating temperatures. In the case of missiles and rockets, advances in propellant technology and in system design have outstripped materials development, so that at the present time and in the foreseeable future, lack of suitable materials to resist the extremely high temperatures encountered in such systems is the primary barrier to their continued development. Two major problem areas are involved - internally in the propulsion system and externally on the nose cone and leading edges of aerodynamic control surfaces. Specific components include combustion chamber liners, nozzles, nose cones, vanes, etc.

Since the components encounter temperatures well above the melting point of steel, over 5000 F, it is obvious that they must either be cooled or constructed of materials which are more refractory than steel. Cooling or use of a heat sink involves penalties in weight and/or reliability which may severely limit the performance of some systems. Currently available refractory materials include metals such as tungsten, tantalum, molybdenum, etc., ceramics such as alumina, zirconium, etc., and cermets which are combinations of metals and ceramics.

In general, the refractory metals have the limitations of very high density and poor oxidation resistance, while the ceramic and cermet bodies suffer from low tensile strength and brittleness. In spite of their limitations, all of these materials will continue to be used under conditions where their advantages are optimized and their limitations countervailed by other materials in the structure.

In particular, flame-sprayed ceramic coatings have already been successfully used to protect the metal parts of missiles and other weapon systems against high temperature, high velocity, erosive and corrosive gases for short times. Their high melting points and low thermal conductivities permit higher operating temperatures and reduce the underlying metal temperature. A 10-mil oxide coating on a rocket nozzle may temporarily sustain a temperature gradient of almost 1800 F. Furthermore, relatively thin ceramic coatings protect the metals without adding appreciable weight.

In order to broaden the use and range of application of these coatings, with their special advantages, to components of Army weapon systems, the Army Materials Research Agency (AMRA) has initiated a ceramic coating research and development program.

The objectives of this report are to:

l. Present in detail the applications of flame-sprayed ceramic coatings to Army weapons components and to metal processing that have been developed to date under this program.

2. Outline future research and development studies which are essential to continued progress in this important field.

MATERIALS

Physical and Chemical Properties

Primary refractory substances (Table I) have been combined with each other and metals to produce bonded ceramics and cermets. The application of ceramic coatings to metal parts protects the structural material from the erosive action and chemical attack of combustion gases, the fuel and high temperatures. The porous nature of flame-sprayed ceramic coatings gives them a mechanical flexibility that is several orders of magnitude greater than solid-body structures of the same materials.¹

Table II lists the properties of three ceramic coatings and also stainless steel. Thermal expansions, thermal conductivities, and densities are lower for the oxides than for steel, while melting points and hardnesses are higher.

The oxides, because of their low thermal conductivities, reduce the temperature of the metal backing by insulating it. They also resist chemical attack because of their high chemical stability, but the porosity of these coatings limits this protection to short times.

Densities of the coatings are less than those of steel, and thus the coatings do not greatly increase weights. Since melting points, as well as hardnesses, are far higher than those of steel, these coatings are not rapidly worn away or melted by high-velocity, high-temperature gases.

These properties indicate that ceramic coatings are an improvement over bare steel for resisting the erosion and corrosion of combustion gases, at least for short times.

Flame Spray Coatings

The ceramic and metal materials available commercially in rod, powder and wire forms are tabulated in Table III. Almost any material which melts rather than sublimes (materials which dissociate may or may not produce a coating) and forms droplets rather than threads (glass forms fibers rather than a coating) can be applied as a coating. The following ceramic materials have been flame-sprayed successfully: alumina (Al₂O₃), zirconia (ZrO₂), mullite (3Al₂O₃, 2SiO₂), magnesia (Mg₂SiO₄), zircon (ZrSiO₄), spinel (MgO Al₂O₃), chromia (Cr₂O₃), ceria (CeO₂), titania (TiO₂), molybdenum disilicide (Mo Si₂), chromium carbide, chromium-nickel boride (Cr₂NiB₄), tungstencarbon and tungsten-boron compounds, nickel aluminide (NiAl), molybdenum aluminide (MoAl₂), nickel magnesia. The advent of higher heating sources,

¹NORTON COMPANY. Technical Bulletin R. E. 1.9.

TABLE I Properties of Primary Refractory Substances and Metals

	Melting		Thermal	_	Tensile	Modulus of	Thermal Shock	bility to
Material		Density g/cu cm	Conduc- tivity*	Thermal Expansion**	Strength† (psi)	Elasticity† (psi x 10 ⁶)	Resist- ance	Oxidation in Air
	Ceramic Flame-Spray Materials							
Alumina Al ₂ 0 ₃	3720	4.00	30.0 2400	4.72 77-1470	35,800 77	52.4	Good	Not affected
Beryllia BeO	4600	3.00	104.0 2190	5.10 77-2300	13,800 77	42.8	Very good	Not affected
Graphite C	6400	2.25	220.0 2000	4.30 77-104	2,400 77	2.2	Very good	Oxidizes at 1180 F
Magnesia MgO	4800	3.62	40.8 2012	7.40 66-3270		2.4	Fair	Not affected
Silica SiO ₂	3100	2.32	13.3 2370	0.30 66-1832			Very good	Not affected
Thoria ThO ₂	5500	9.60	21.0 2000	5.28 77-1472	14,000 77	7.9	Poor	Not affected
Zirconia ZrO ₂	4900	5.80	14.3 2400	2.78 35-2552	17,900 77	4.8	Fair	Not affected
Zirconium Silicate ZrO ₂ SiO ₂	4600	4.56	14.2 2000	2.83 66-2282	12,700 77	4.0	Very good	Not affected
Refractory	Hard Me	tals						
Boron Car- bide B ₄ C	4260	2.52			22,500 1800	42.0	Poor	Oxidizes at elev. temp.
Chromium Carbide Cr ₃ C ₂	3440	6.68						Not affected
Hafnium Carbide HfC	7030	12.20						
Molybdenum Carbide Mo ₂ C	4190	8.90		:		32.7		Oxidizes at elev. temp.
Silicon Carbide SiC	4900	3.20	70.7-121.8 2012	2.61 32-3092		·	Good	Oxidizes at 1475 F
Tantalum Carbide TaC	7020	14.50	154.0 77	4.55	4000 70	41.5		Oxidizes
Titanium Carbide TiC	5880	4.90	119.0	4.12 70-1100	8000 2200	45.0	Very good	Oxidizes at 2150 F
Tungsten Carbide WC	4710	15.80		4.06 77+	50,000 77	102.0		
Vanadium Carbide VC	5130	5.80				39.0		
Zirconium Boride ZrB ₂	5500	6.10	160.0 390	3.03 77-1830			Good	Not affected
Zirconium Carbide ZrC	5750	6.90	142.0 77	3.74 70-1100	15,850 2200			Oxidizes

^{*}Btu/hr/sq ft per in. of thickness at temperature (F)
**n x 10-6 in/in/deg F in given temperature range
†At temperature (F)
†At 70 F

TABLE II

Properties of Sprayed Oxide Coatings Versus Stainless Steel

	Alumina	Zirconium Silicate	Zirconia	Stainless Steel
Thermal Expansion (X10 ⁻⁶ in/in/deg F)	4.72 77-1470	2.83 66-2282	2.78 32-2552	11.2 32-1800
Thermal Conductivity (Btu/hr/sq ft.in/deg F)	30.00 (2400)	14.20 (2000)	14.30 (2400)	185.0
Density g/cu cm	4.00	4.56	5.80	7.8
Melting Point deg F	3720	4600	4900	2600
Hardness (Knoop)	2000	1000	1000	400

 $\label{thm:table_III} \textbf{Commercially Available Flame-Spray Materials}$

Rod	Powder	Wire
Aluminum Oxide	Nickel Chromium Boron Alloys	Aluminum
Zirconium Oxide	Stainless Steel, Type 316	Copper
Chromic Oxide	High Chromium Stainless	Lead
Zirconium Silicate	Nickel-Chromium	Monel
Spinel	Aluminum-Iron Bronze	Nickel
Alundum	Aluminum	Nickel-Chrome
	Copper	Stainless Steel 18-8 Grades
	Aluminum Oxide	Stainless Steel Type 420
	Zirconium Oxide	Stainless Steel Type 316
	Tungsten Carbide	Tin
	Nickel-Magnesia	Zinc
	Brass	Molybond
	Bronze	
	Nickel	
	Tin	
	Zinc	
	Stainless Steel, Type 420	
	Stainless Steel. Type 18-8 Grades	

such as the plasma jet, will enable materials of greater refractoriness to be applied as coatings; this will extend the application of flame-sprayed coatings beyond the 4000 to 6000 F range.

FLAME-SPRAY PROCESS

Ceramic coatings have been conveniently applied by spraying or dipping the article to be coated, using a water suspension of the coating material. The coating is then bonded by heat. Flame-spray application combines both operations in one. The flame-spray process involves the utilization of a mixture of oxygen and acetylene to melt a powder or rod and direct the particles toward the surface being coated where they plastically deform, adhere and solidify. The cross-section of a typical flame-sprayed coating on a metallic substrate is shown in Figure 1.



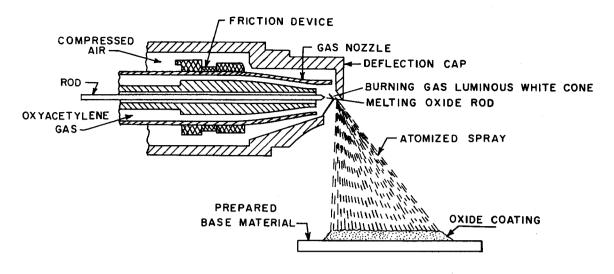
19-066-279/ORD-62

Figure 1. TYPICAL BOND BETWEEN FLAME-SPRAYED COATING AND METALLIC SUBSTRATE

The powder technicque utilizes a system in which powders (ceramic or metal) are fed by gravity through a metering valve and drawn at reduced pressure into an aspirator chamber, where they are propelled into the flame by a jet of fuel gas (Figure 2). Compressed air is not used to propel the powder.

The rod (ceramic) technique utilizes oxyacetylene gas premixed in the chamber and fed to the nozzle, where it burns at a temperature in excess of 5000 F. The rod melts in the luminous white cone of the burning

AULT, N. N. Characteristics of Refractory Oxide Coatings Produced by Flame-Spraying. Journal of the American Ceramic Society, v. 40, no. 3, March 1957, p. 69-74.



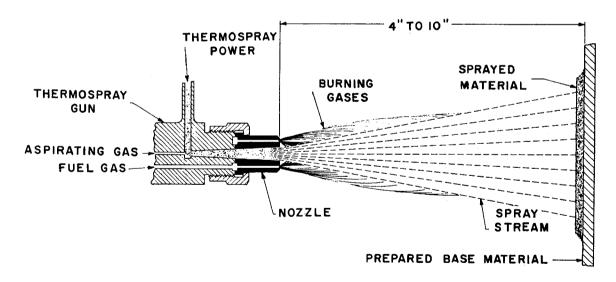
19-066-282/ORD-62

SPRAYING DISTANCE 1½" MINIMUM, 8" MAXIMUM COATING THICKNESS 0.002" TO 0.100"

Figure 2. MOGUL GUN FOR FLAME SPRAYING ROD

gas and small particles are projected off at high velocity by compressed air to strike the surface to be coated while still in plastic condition (Figure 3).

Similarly, metallizing, whereby pure or alloyed metal (in the form of wire) is melted in an oxyacetylene flame and atomized by a blast of compressed air into a fine spray, has also been utilized.



19-066-281/ORD-62

Figure 3. METCO THERMOSPRAY GUN

SELECTION OF COATINGS

Selection of the proper coating is important in the successful use of the flame-spray process. Properties of the deposited materials must be considered when evaluating their suitability for specific components in relation to the service requirements of the components. For example, alumina is applied where its lower density is an advantage and where its lower temperature melting point is not detrimental. Its low emissivity is an advantage in combustion chambers and in other areas where high reflectivity is desired. Zirconia is favored where higher melting temperatures and thermal shock resistance are needed in rocket nozzle applications.

In addition, the thermal expansivities of both coating and base material should be compatible, so that the coating will not lose its adherence to the base material under conditions of thermal stress. The mechanical bonding of flame-sprayed ceramic coatings provides more flexibility than bonding of coatings that are dependent upon chemical or other bonding mechanisms. Thus mechanical bonding permits the coating to maintain better adherence where the base material and coating have different chemical expansivities.

Flame-sprayed ceramic coatings are presently being used in the following applications:

- 1. Ramjet engine combustion chambers
- 2. Ramjet engine and after-burner combustion components.
- 3. Rocket thrust chambers and exit nozzles
- 4. Jetevators (a thrust vectoring device for rocket engines)
- 5. Turbine wheels
- 6. Burner tubes
- 7. Thermocouple tubes
- 8. Inside surface of nose cones
- 9. Fuel injectors
- 10. Graphite booster and sustainer components

Flame-sprayed metal is metallurgical material having entirely different physical and chemical properties from those of the original wire. In general, sprayed metal contains some oxide, is harder, more brittle and more porous than metal in the cast or drawn condition. These characteristics make it ideal for a bearing surface, because of oil retention in the pores. Conversely, sprayed metals, such as stainless steel, nickel or bronze, are not good for cathodic protection. Corrosion protection is obtained by using anodic materials. These protect sacrificially by electrolytic action and porosity is of no importance.

Metallizing has been utilized for the following applications:

- 1. Building up worn or mismachined parts
- 2. Providing seals which will wear when contacted
- 3. Minimizing or eliminating galling or rubbing surfaces
- 4. Preplacing of bronze filler materials
- 5. Providing base-metal protection from erosion and corrosion
- 6. Enhancing the bond between ceramic and base materials as a metallic intermediate coating.

Table I contains properties of various commercially available coating materials which may be used to aid in selecting a coating for a specific application.

SURFACE PREPARATION OF BASIC MATERIAL FOR FLAME-SPRAY COATINGS

Perfect mechanical cleanliness is necessary. Oil, grease or other foreign matter should be removed not only from the surface to be coated, but also from adjacent surfaces. Otherwise the heat generated by the coating operation may cause grease or oil to run onto the area to be coated. It is, therefore, good practice to solvent-degrease initially. Solvents used in chemical cleaning have been found to leave an invisible but objectionable film. This film must be removed for optimum adherence and abrasive blasting is the most satisfactory and versatile method.

In addition to removal of any objectionable film, the blasting provides the second requirement of sufficient roughening to offer maximum mechanical anchorage for the coating. Roughening should be uniform to provide as many re-entrant angles and sharp peaks as possible. This insures a maximum degree of coating adherence. The mechanism of particle attachment to the base and to each other is not yet exactly known. There is considerable mechanical interlock between particles and even a minor amount of welding at some points. There is also oxide cementation between particles.

APPLICATION OF FLAME-SPRAYED CERAMIC AND METAL COATINGS

Army Materials Research Agency is conducting research and development on flame-sprayed metal, ceramic and cermet coatings. Due to the increased interest in flame-sprayed coatings, considerable time and effort have been devoted to assisting other groups within and external to AMRA. The following section of the report presents the flame-sprayed coating applications performed to assist other organizations with problems relating to Army weapons components and metals processing.

Launcher-Type Weapon System

The prime consideration in the design and construction of the weapon system is its ability to resist successfully the severe shock loads, high stress and erosion encountered under firing conditions. These qualities must be maintained with a minimum of constructional weight. A high strength-to-weight ratio material is required in conjunction with the adequate modulus-to-weight ratio available in alpha-beta type titanium alloys. In addition to high-strength alloys of titanium, high-strength aluminum alloys were considered. During firing, unfortunately, erosion of components of either material occurred. As a result, methods of preventing erosion during firing by the application of metallic and ceramic

coatings were investigated. The urgency of the program precluded complete studies for assessing the relative advantages of various coatings in preventing erosion.

However, it was demonstrated that several coatings are available which reduce erosion. Because of the urgent short-time nature of the project, normal laboratory verification tests of the coatings to substantiate analytical results could not be made. Thus, the actual firing tests of completed full-scale pieces provided the only check on the analytical work. Uncoated titanium nozzles exhibited severe erosion



Wtn. 681-1116A Figure 4. EROSION OF TITANIUM TEST NOZZLE - ONE ROUND

at the throat area after a single firing (Figure 4). To extend the range of usefulness of titanium in this application, it was necessary to protect the metal by application of a coating which is heat- and erosion-resistant, as well as one which is capable of being thermally cycled.

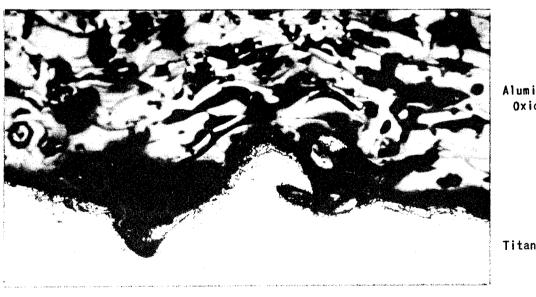
Ceramic coatings were considered because they essentially meet these requirements and flame-spraying techniques were utilized since, during processing, the temperature of the base metal does not exceed 500 F. This is particularly desirable with titanium because oxidation is minimized and no phase transformation, with resultant weakening of structure, will occur in this temperature region. A coating should be custom fitted to the particular environmental conditions it will be subjected to. Specifically, conditions of temperature, pressure, types of gases produced and their velocities should be known.

However, at the time, these data were not available and a completely systematic and thorough investigation of the problems was not possible. This is especially true when refractory coatings are used to protect rocket nozzles. Failure of the coating during a test firing may or may not be due to an inherent deficiency of the coating, since its performance depends in large measure on matching the coating thickness to the heat flux in the particular nozzle.

For example, if the coating is too thin, it may conduct too much heat to the underlying metal with the result that the metal melts and allows the coating to be washed away. If, on the other hand, the coating is too thick, it may not conduct enough heat to the base metal, with the result that the outermost surface layer of the coating overheats, melts, and flows away. There is an optimum coating thickness for a given nozzle application which is dependent on the specific conditions encountered.

The adherence of flame-sprayed ceramic coating to titanium will depend on a mechanical bonding of coating to base metal, which in turn is dependent upon the surface preparation of the base material. An investigation of the methods of surface preparation revealed that degreasing with trichloroethylene, followed by pressure blasting with Pangborn 25 angular steel grit, provided an optimum roughened surface for adherence.

Results of adherence evaluation indicated that the bond between ceramic and titanium was not as good as that obtained between ceramic and steel or other metals. However, it was found that the flame-spray application of an intermediate coating of nickel-chromium alloy enhanced the bond between titanium and ceramic oxide (Figures 5 and 6). In addition, the nickel-chromium undercoat provided an oxidation-resistant surface which would protect the titanium from any oxidizing gases which might permeate the ceramic exterior coating. ZrO2 was selected as the exterior coat, because of its very high temperature resistance (mp 4870 F), resistance to thermal cycling and good resistance to erosion.



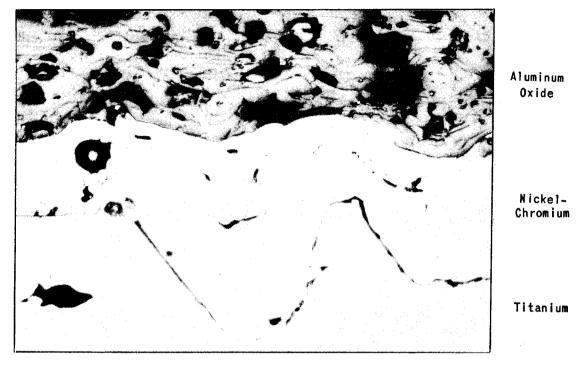
Aluminum 0xide

Titanium

19-066-280/0RD-62

X500

Figure 5. FLAME-SPRAYED ALUMINUM OXIDE ON TITANIUM



19-066-278/ORD-62

X500

Figure 6. FLAME-SPRAYED NICKEL-CHROMIUM INTERMEDIATE COATING ENHANCES
THE BOND BETWEEN CERAMIC COATING AND TITANIUM SUBSTRATE

Coating of Nozzles - Launcher-Type System

The following nozzles were coated as described below:

- The titanium nozzle was undercut 0.020 inch on the diameter to accommodate the coatings. An automatic mechanical setup was utilized which could rotate the part to be coated for concentricity of coating application and traverse the flame-spray gun to obtain the same result. Since these requirements are best met by a precision lathe with hydraulic tracer (to compensate for any change in shape or contour of nozzle), extreme care was taken to protect the lathe and accessories from any ceramic spray. This necessitated the closing up of the exhaust end of the nozzle so that no outlet for the flame was provided which resulted in temperatures beyond 500 F, but not exceeding 800 F, at the extreme end. Also, during the nickel-chromium coating process, carbon was deposited on the surface of the coating because of this containment of flame. This necessitated a light blasting technique (angular steel grit No. 25, 30 psi) to remove the carbonaceous material prior to successive passes with the nickel-chromium. It was decided that future coating applications would require the use of an extension provided with holes about its periphery to provide an escape for the flame. A nickel-chromium alloy undercoat of 0.004 inch in diameter was applied, plus an outer coat of 0.016 inch ZrO2.
- 2. A total coating thichness of 0.027 inch was applied, of which NiCr was 0.10 inch and ZrO₂ 0.017 inch. With the utilization of the extension

mentioned above, no overheating of nozzle occurred during the coating operation. The temperature did not exceed 500 F.

These rocket nozzles were tested under firing conditions. The composite coating system of nickel-chromium and zirconium oxide reduced the erosion encountered. However, after repeated firings the coatings spalled and erosion of titanium occurred. The performance of the coating system was unsatisfactory for the application.

Coating of Other Titanium and Aluminum Components - Launcher-Type Weapon System

Erosion of other titanium and aluminum components occurred similar to that encountered in the nozzle. To eliminate this erosion, these components were experimentally coated with selected flame-sprayed ceramic and/ or metallic materials.

The following coatings were successful in preventing erosion: zirconium oxide, zirconium silicate, aluminum oxide, chromic oxide, stainless steel, tungsten carbide, nickel-chromium-boron alloys. Zirconium oxide appeared to be the most satisfactory. It is to be noted that coatings for this application must withstand only one firing. Although these coatings were effective, they were not adopted for this application.

Rocket Motor Bodies - Experimental Weapon System

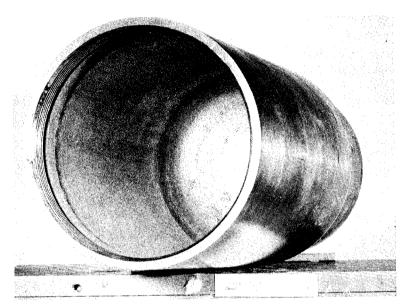
A titanium rocket motor body was fired and severe erosion was in evidence from the threaded area inward approximately four inches (Figure 7). High internal chamber pressures were encountered with temperatures probably not exceeding 2000 F. From the blue oxidation discoloration in the interior of the chamber after firing, it appears that a temperature of about 1500 F had been generated. To eliminate the erosion, flame-sprayed metal and ceramic coatings and combinations thereof were applied. The selection of coatings was based on results obtained with an experimental apparatus which could in some measure, approximate the conditions encountered in the system. The eroded area was machined as much as safety would permit to smooth out the area and the unit was flame-spray coated with stainless steel to bring the internal diameter to the specified dimension. In some areas as much as 0.100 inch Figure 7. UNCOATED TITANIUM ROCKET of coating was applied (on the diameter).



Wtn. 681-1227 MOTOR BODY AFTER FIRING

An additional rocket motor body, with no previous firing history, was flame-sprayed with an undercoat of nickel-chromium alloy, 0.010-inch diameter, and an outer coat of alumina, 0.020-inch diameter.

In subsequent firings, both rocket motor bodies exhibited no internal erosion, indicating the adequacy of the applied coatings in preventing the erosion encountered in the uncoated titanium body, Figure 8 (stainless steel coating) and Figure 9 (composite coating of Ni-Cr alloy and aluminum oxide).



wtn. 681-1282
Figure 8. TITANIUM ROCKET MOTOR BODY WITH
STAINLESS STEEL COATING

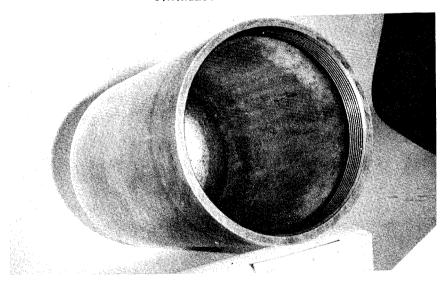


Figure 9. TITANIUM ROCKET MOTOR BODY WITH COMPOSITE COATING (NICKEL-CHROME ALLOY AND ALUMINIUM OXIDE)

Test Nozzles - Experimental Weapon System

An experimental aluminum nozzle was flame-sprayed with an intermediate coating of 0.007 inch (on the diameter) of nickel-chromium alloy and an outer coating of 0.014 inch (on the diameter) of alumina. The success of this combination of coatings in the application to rocket motor bodies warranted its use in this application. The combination of coatings proved successful in preventing erosion or "wash out".

Application of Flame-Sprayed Ceramic and Metal Coatings to Metals Processing

Uranium alloys can be readily worked to shape by the usual metal-working processes. Starting with a uranium-alloy melt, a solid cylinder 4 inches high, 13 inches in diameter with 1-inch flats machined on four sides, was melted at 2800 F (300 degrees above its melting point), in a zirconium crucible. It was then cast in a graphite mold with a mullite wash to minimize graphite contamination and subsequently rough machined to remove any contamination. The forging operation followed.

In all forging operations, two principles of operation are important. First, by working, metal physical properties are improved. The shape of the starting piece is chosen so that all parts are thoroughly deformed before final dimensions are attained. Secondly, an ingot or billet is inhomogeneous and contains voids, inclusions, recipitates and cracks. The designer must choose his blank so that the grain of the forging will run in the direction in which the greatest stresses will act in service. To prevent oxidation of uranium during the forging operation, the exterior of the cylinder was completely flame-spray coated with copper. Copper was selected on the basis of its adequate adherence, ductility and resistance to thermal shock. The coated cylinder was then forged to a 2-inch square. During the process, the copper coating spalled. Any residual copper was removed and a leading edge (chamfer) put on.

The 2-inch-square piece was then recoated with copper and rolled to a 5/8-inch square. The copper coating provided satisfactory oxidation protection for the uranium during the rolling operation. Most of the forging and extrusion operations are performed at one stroke on the whole of the piece of metal being worked. The size of the piece produced is, therefore, limited by the size of the machines available. In many instance a rolling mill is cheaper and faster than the press and yet does the same job, but it does the job continuously on successive portions of the metal.

The extrusion processes take advantage of the ability of a metal to be squeezed through an opening. All extrusion processes have the common feature that metal is under high hydrostatic pressure. Metals that are brittle and cannot be forged easily may be readily extruded. Indirect or backward extrusion was applied to a uranium alloy solid cylinder after heat (1800 F) had been applied for six hours. To prevent contamination or alloy reaction between uranium and the iron retort (iron forms a low melting eutectic with uranium), the cylinder was coated with flame-sprayed

copper. The coating was successful in preventing contamination and served as a lubricant during the extrusion operation, whereby the extruded product is squeezed through a die, the form being hollow to receive the extruded piece.

Flame-sprayed copper coatings have proven successful in both the rolling and extrusion processes and are currently being utilized for the development of processing procedures and evaluation of high-strength uranium.

In the casting of titanium shapes, there is the possibility of undesirable reaction between the titanium and the iron mold. It was believed that the application of a compatible, inert intermediate coating between the molten titanium and iron would prevent any such interaction. The application of a flame-sprayed ceramic coating such as alumina or zirconia (inert chemically but adherent and thermal-shock resistant) to the iron would provide such a barrier. Several iron molds were coated with alumina and zirconia. Preliminary testing indicates this procedure to be promising and further investigation is warranted.

DISCUSSION AND RECOMMENDATIONS FOR FUTURE STUDIES

The metallizing process has advanced beyond metals to include the spraying of ceramic and cermet materials, so that the process must now be referred to as flame spraying. Research and development is advancing on an entirely new flame-spraying technique which utilizes a plasma flame with temperatures up to 30,000 F, thereby extending the range of coating capabilities to refractory metals and hard metals (borides, nitrides, carbides, silicides), whose melting temperatures exceed the range of oxyacetylene flame. The very great range of operating temperatures that can be produced, the variety of materials that can be sprayed, and the basic economy of the process appear to limit possible applications only to the imagination of the designer and research-development scientist.

The foregoing report has described the various applications of flame-sprayed coatings in Army weapon systems and metals processing at AMRA. While the results obtained with some coatings have been very satisfactory, the search for new and improved high-temperature coatings must proceed at an accelerated pace in order to meet the increasing need for them in the high-temperature service of advanced weapons. Since our basic understanding of the coating process is extremely limited, it is recommended that all the factors affecting the coating process be thoroughly investigated. The specific recommendations for further research in this field follows:

- 1. Analyze and control the following variables to produce an optimum coating for each material, using oxyacetylene and plasma flame:
 - a. particle size,

- b. flame temperature,
- c. gas flow rate,
- d. temperatures and temperature gradient in base metal and flame.
- 2. Determine the effect of the following types of additives on coatings:
 - a. additives to promote heat transfer between gas and particles.
- b. additives which will react exothermally in the flame to increase the radiant heat transfer,
- c. flame catalysts, which promote reaction rate in flame and combine advantageously with the coating, e.g., lithium cobaltite flame catalyst which is isomorphic with zirconia.
- 3. Investigate the nature of the bond between coating and substrate. The data obtained from this research should provide the basis for the development of improved coatings having greater adherence and mechanical strength:
- a. determine adherence of coatings produced under various controlled conditions of flame temperature and base metal temperature,
- b. analyze the interface between coating and substrate using all suitable research techniques such as electron microscopy and X-ray diffraction.
- c. measure thermal and mechanical properties (hardness, mechanical and thermal-shock resistance, thermal conductivity, etc.).
 - 4. Develop new and improved coatings:

Systematically prepare and analyze coatings produced from the carbides, nitrides, borides and silicides of the refractory hard metals.