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ANALYSIS OF A REFRACTORY COATING SYSTEM FOR THE THERMAL PROTECTION OF TITANIUM

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SEPTEMBER 1963

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ANALYSIS OF A REFRACTORY COATING SYSTEM FOR THE THERMAL PROTECTION OF TITANIUM

Technical Report AMRA TR 63-13

by

Raymond L. Farrow and Milton Levy

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U.S. ARMY MATERIALS RESEARCH AGENCY

ANALYSIS OF A REFRACTORY COATING SYSTEM FOR THE THERMAL PROTECTION OF TITANIUM

ABSTRACT

Metallic and ceramic refractory coatings are being considered to extend the useful life of titanium under conditions of high temperatures and erosive atmospheres. The effects of the refractory composite system of flame-sprayed nickel-chrome, aluminum oxide, and copper, on the thermal characteristics of a titanium tube were investigated.

The refractory composite system was examined metallographically for adhesion of coating to coating, and coating to substrate, porosity of coatings, and effect of deposition on the structure of the titanium substrate.

A comparison of the weights of the composite titanium tube system and a similar size steel tube was made. A weight reduction of 19 percent is effected by the use of the coated titanium system. The advantages and disadvantages of each coating are discussed, and suggestions for future work are presented.

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INTRODUCTION

The demand for a highly mobile armed force requires that weapons be developed with lightweight, high-strength structural materials. Several alpha-beta type titanium alloys have been developed which meet these requirements. However, the use of titanium in ordnance weapon systems is limited to operating temperatures below 1000 F. In addition, titanium is subject to erosion under conditions of high chamber pressures (above 5000 psi) and high velocities of propellant exhaust gases. Metallic and ceramic flame-sprayed coatings are being considered to extend the useful life of titanium under these conditions.

In general, the effects of these coatings are not necessarily defined and most evaluations have been attempted on flat plates. Since many weapon systems (guns, mortars, etc.) prescribe a cylindrical shape, a tube has been employed in the study covered by this report to simulate actual conditions more closely. In addition, one end has been closed to produce hot-zone conditions which are found in many weapon systems. Also, internal heating was used to simulate the radial heat flow which occurs during the firing of a weapon.

Aluminum oxide, nickel-chrome, and copper coatings were applied to a titanium tube by means of an oxygen-acetylene flame-spraying technique. These coatings were selected on the basis of prior applications¹ and laboratory investigations² using coated flat plates. The coatings were applied internally and externally, with the internal coatings serving as a protective shield against erosive hot gases and the external coatings as heat-sink materials.

Since the major objective was to study the effects of the coatings on the thermal characteristics of a titanium tube, experiments were restricted to one titanium tube of 1/4-inch wall thickness. This thickness more accurately approximates ordnance requirements and is a convenient size for measurements.

In many cases combinations of different coatings have been studied as a single composite system. In this study the effect of each coating was investigated after it was applied, by measuring the temperature at selected points under steady-state conditions. Since many coatings now used are relatively recent developments, the necessary thermal and physical properties data are often unavailable for determining their effects prior to laboratory experimentation. Thus, experimental results under fixed conditions are required.

MATERIALS USED

As previously mentioned, a cylindrical shape was chosen because of possible gun or launcher-tube application. For this reason, and considering the availability of material, a titanium cylinder 17 inches long was chosen. This cylinder had an inside diameter of 4.25 inches and a wall thickness of 0.250 inch with a maximum variation of 0.001 inch. Chemical analysis indicated the following major elements were alloyed with the titanium:

Alloy Element	Al	V	Sn	Fe	Cu
Weight Percent	5.47	5.27	2.07	0.56	0.26

The surfaces of the titanium tube were mechanically abraded prior to application of coatings.¹

Using conventional oxygen-acetylene flame-spraying techniques, the titanium tube was coated both internally and externally. The inside of the tube was sprayed with a 0.005-inch-thick nickel-chrome coating which served as an intermediate coating for a 0.012-inch-thick coating of aluminum oxide. Copper was flame-sprayed on the exterior of the tube to provide a heat-sink coating. To determine the effect of copper coating thickness, a 0.026-inch-thick and a 0.052-inch-thick heat sink were also investigated. Figure 1 shows a cross-sectional view of the tube and the coatings.



Figure 1. CROSS-SECTION OF COATED TITANIUM TUBE

The nickel-chrome wire used had a composition of 60% Ni, 25% Fe, and 15% Cr.³ However, since thermal data on this material was not available, the data used was that given for Nichrome wire having a composition of 60% Ni, 24% Fe, and 16% Cr. Since the compositions are approximately the same, it was felt that this data would be quite similar for both compositions.

The thermal data for both the titanium and the coatings are contained in Table I.

TABLE	I
-------	---

Material	Density (lb/cu.ft)*	Thermal Conductivity (BTU/hr-ft F)**	Total Normal Emissivity
Titanium	280 ⁴	7.9 ⁶	•31 ⁶
Nickel-Chrome	387 ^a	7.97†	.64
Aluminum Oxide	180 ⁵	4.6⁵‡	. 68⁵
Copper	470 ³	206.0 ⁸	.012(cleaned) ⁴ .25(calorized) ⁵ .83(oxidized) ⁵

PHYSICAL PROPERTIES OF MATERIALS

NOTE: Superscript numerals indicate References.

*Density data assumes a coating porosity based on past experience. **Thermal conductivity data given for average temperatures of 700-1250 F. †Data presented is for Nichrome wire at 75 F. ‡Data presented is for a porosity of 23.4%.

TEST PROCEDURE

In the experimental setup, shown in Figure 2, the titanium cylinder was mounted in a horizontal position, providing a more severe test than if the heat were allowed to rise vertically out of the tube. One end of the tube was supported on a narrow wedge of refractory brick so that thermal conduction would not cause a large heat loss. The opposite end was similarly supported on a brick and in addition a 1-3/4-inch layer of refractory brick surrounded the entire end (the length of tube covered was also 1-3/4 inch) to prohibit air flow at this end and to produce a "closed end" effect. The lower edge of the tube was held a minimum of 4 inches above the table and the top and sides kept free from obstructions to allow natural convection effects to take place on the exterior surface. In actual usage the more effective heat-transfer method of at least some forced convection might be expected.

Heating was accomplished by means of a 25-inch-long silicon-carbide (Globar) heating element 7/8 inch in diameter and with a hot zone 14 inches in length. This Globar was mounted horizontally along the internal axis



19-066-1923/ORD-62 Figure 2. APPARATUS FOR DETERMINATION OF THERMAL CHARACTERISTICS OF COATINGS.

of the tube. It was supported at the closed end by inserting it in a small hole drilled through the center of the blocking refractory brick. In order to keep the open end of the tube free from obstructions and allow a natural air flow, the Globar was supported externally by means of a 1/4-inch-thick Transite plate placed 3-1/2 inches from the end of the tube. This plate also served to provide a means of positioning internal thermocouples.

Power to the Globar heating element was supplied by a motor-driven four-gang autotransformer with an output capacity of 31 kva.

Internal and external temperatures were measured and temperature distribution noted by the continuous recording of 24 selectively placed thermocouples. Temperatures were recorded on two chart recorders; one, a 20-point recorder with a 2000 F temperature limit, was used to monitor 19 thermocouples placed on both internal and external walls; the other, a 6-point millivolt recorder, was used to measure 5 internal air temperatures. Figure 3 illustrates the thermocouple positions around the tube. One thermocouple position of each recorder was used as a reference point so that compensation for any increase in the recorder case temperature or for drifting could be made. All data presented has been corrected for room temperature (75 F).



▲ SURFACE THERMOCOUPLES

O AIR THERMOCOUPLES

INTERNAL THERMOCOUPLES (TOP VIEW)



BOTTOM THERMOCOUPLES

▲ TOP AND SIDE THERMOCOUPLES

O IMBEDDED THERMOCOUPLES

EXTERNAL THERMOCOUPLES (TOP VIEW)

Figure 3. THERMOCOUPLE POSITIONS

On the interior surface the thermocouples were held in place by the slight spring tension of the thermocouple wire itself. This method offered a convenient and consistent technique for all test conditions, since the thermocouples could not be spot-welded to aluminum oxide. However, on the exterior surface, the thermocouples were spot-welded since the surface was metallic for all test conditions. In addition, three of the thermo-couples were spot-welded into small holes (1/16-inch diameter) which had been drilled into the external surface of the titanium tube to a depth of 1/3 to 2/3 of the wall thickness.

The thermocouples used were chromel-alumel type of 22-gage wire. The junction ends were provided with ceramic insulators which, particularly in the case of internal positioning, provided the necessary rigidity for proper

alignment. The thermocouples were not calibrated; however, since only comparative results were desired, the estimated accuracy of ± 10 F was considered sufficient.

The test procedure was the same for each test, the variables being the Globar temperature and the various coating combinations used. The length of time of each test was not an important factor, since steadystate conditions were used and cooling rates were determined for the higher temperature tests. In all, ll tests were made using selected temperatures and progressive combinations of coatings. Table II lists these general conditions for each test.

Test No.	Globar Temperature F	Internal Coatings	External Coatings
1	1200	None	None
2	1900	None	None
3	2500	None	None
4	1450	NiCr(0.005 in.)	None
5	2500	NiCr	None
6	1450	$NiCr+Al_2O_3(0.012 in.)$	None
7	2500	NiCr+Al ₂ 03	None
8	1450	NiCr+Al ₂ O ₃ Copper(0.026	
9	2500	NiCr+Al ₂ O ₃	Copper
9 - A	2500	NiCr+Alg03	Copper and Copper Oxide
10	1450	NiCr+AlgO ₃ Copper(0.0	
11	2500	NiCr+AlgO3	Copper
ll-A	2500	NiCr+Al ₂ 03	Copper and Copper Oxide

TEST OPERATING CONDITIONS

In actual operation, the Globar was heated from room temperature to the test temperature at a rapid rate. The temperature was maintained until steady-state conditions were achieved at the thermocouple points (about 11 minutes after the Globar temperature had been reached). Steady-state conditions were maintained for a minimum of 30 minutes, after which time the Globar power was shut off and the entire system was allowed to cool to room temperature. After each run at maximum temperature the tube was removed and the next required coating was applied. Upon reassembly of the test setup and the repositioning of the thermocouples, the next test series was run.

When thermal experimentation was completed, the tube was sectioned for visual and metallographic examinations.

RESULTS AND DISCUSSION

A preliminary examination of the results revealed that temperature distribution patterns were similar in both low- and high-temperature tests. Thus, the results discussed will be those obtained at Globar temperatures of 2500 F where more severe thermal conditions prevail.

The first test at 2500 F (test 3) involved heating the uncoated titanium tube. This test provided a reference base for the study of coating effects. An analysis of the temperatures recorded showed that the internal temperature readings were very high compared to the readings obtained from the thermocouples imbedded in the titanium itself. Since the internal thermocouples were all located within the radiating hot zone of the Globar and have a high emissivity value⁹ (thus a high absorptivity value) it is felt that they were partially heated by direct radiant energy. The external surface thermocouples did, to some extent, disagree with the imbedded thermocouple readings. The theoretical temperature difference from the point of the imbedded thermocouples to the surface is 5 F, while temperature differences up to 20 F were noted. This difference is thought to be due to varying convection currents cooling the exposed surface thermocouple junctions. Nevertheless, the thermocouples did provide the necessary data for indication of temperature distribution.

By averaging temperatures internally and externally according to zones along the tube, the temperature variation from the hot zone (enclosed end of tube) to the cooler zone was found to be 270 F internally and 165 F externally. The titanium reached an average temperature of 870 F. Figures 4 and 5 show the temperature distribution by zones for the internal and external surfaces. Temperature data obtained under each test condition is contained in Table III. Temperature variation is defined as the temperature difference between the hottest and coolest zones of the tube. This data is presented for both the internal and external surfaces.

Nickel-chrome was used as an internal, intermediate coating to enhance the bond between the aluminum oxide and the titanium. (Prior studies² have shown that a stronger bond results when aluminum oxide is sprayed onto the nickel-chrome rather than directly onto the titanium. Figure 6 is a photomicrograph of the cross-section of flame-sprayed aluminum oxide on titanium. The adhesion is relatively poor. Figure 7 shows that the intermediate nickel-chrome improves the adhesion of the aluminum oxide to the titanium.) Although the nickel-chrome improves adhesion, it creates a thermal problem. Due to its high emissivity factor (almost twice that of



TABLE III

		Temperature (deg	Titanium Temperature	
Test No.	Test Condition	Internal	External	(deg F)
3	Titanium only	270	165	870
5	Nickel-chrome 5 added internally		155	1005
7	Aluminum Oxide added internally	250	220	970
9	Copper added externally	250	105	930
9 -A	Copper partially oxidized	250	130	930
11	Copper added externally	250	105	895
11-A	Copper oxidized	250	170	870

TEMPERATURE DATA











the titanium), more heat was absorbed, raising the temperature of the titanium from 870 F to an average of 1005 F. Although thermal conductivity data for nickel-chrome was not available at all temperature ranges, it appears that at the operating temperatures of this test, the thermal conductivity of this coating was greater than that of the titanium. The internal temperatures varied 220 F (50 F less than with the uncoated titanium) from one end to the other, which is indicative of greater thermal conductivity. The external temperature variation decreased to only 155 F. This slight difference is attributed to the fact that thin, more conductive oxide film formed on the titanium surface in both tests; thus, the influence of the increased nickel-chrome heat conduction was not as pronounced on the external surface.

In the next test conducted, a final internal coating of aluminum oxide was deposited over the nickel-chrome intermediate to provide protection for the titanium against erosive exhaust gases. Although the emissivity of the aluminum oxide coating is similar to that of the nickelchrome, its lower thermal conductivity (less than 60 percent of that of the nickel-chrome in this temperature range) reduces the heat flow to the titanium. Over-all, a titanium temperature of 970 F is attained, or a reduction of 35 F is effected. The exterior surface recordings showed an average drop of somewhat more than 35 F. This is due to the fact that the titanium-oxide coating which had formed during the previous test had not been completely removed (as it had between tests 3 and 5), resulting in the formation of a thicker oxide film on the external surface during this test. The internal thermocouples all showed a sharp rise in temperature. It is felt that this occurs because of the added effect of reflection from both the surface and the internal areas of this semitransparent ceramic coating¹⁰ on the thermocouples. The low thermal conductivity of aluminum oxide caused local hot spots. Also an internal temperature variation of 250 F and an external variation of 220 F was observed from one end to the other.

The addition of an external copper coating 0.026-inch thick, acting as a heat sink, served to reduce the over-all temperature of the titanium by approximately 40 F to an average temperature of 930 F. The internal temperature variations, meanwhile, remained essentially constant, since the alumina internal coating still encouraged localized hot zones. However, due to the very high thermal conductivity of copper, the external surface showed a more uniform temperature distribution along the tube, and temperature variations of only 105 F resulted. As the test continued, a thin copper oxide film developed unevenly along the tube, causing an increase in surface temperature variations of 130 F. Because this was a thin oxide film, no further reduction of over-all temperature was noted.

The second external copper coating, which resulted in an over-all heat sink layer 0.052-inch thick, produced a further temperature drop in the titanium, to give an average temperature of 895 F. After steady-state conditions had been reached, an oxide layer again formed on the copper coating. This time, however, the temperature was maintained and a thicker oxide film was allowed to develop. After a true black layer had formed, a temperature drop of 25 F was noted in the titanium. Thus, an average . temperature of 870 F was achieved in the tube. Temperature variations along the external surface increased to 170 F; this is thought to be due to the poor conduction of the copper oxide layer¹¹ and the unevenness of this layer, causing varied emissivity factors.

In order to further analyze the coating effects, the thermal resistance coefficient was calculated, using the properties shown in Table I. This unit permits comparison of the insulating effect of the individual components of this composite system. The thermal resistance¹¹ is represented by R in the following equation:

$$R = \frac{X}{K_m A_m}$$

where

X = thickness of material, ft $K_m =$ true mean thermal conductivity, Btu/hr/ft/deg F $A_m =$ true mean area, sq ft.

For ease of calculation, the area of a one-foot length of tube was considered. Since the coatings are applied evenly along the tube, this will provide the necessary comparative data. The resistance coefficient for each material and the percentage of total resistance is shown below.

Material	Rx10 ⁻⁵	Percent Total Resistance
Titanium	212.00	89.6
Nickel-Chrome	4.47	1.9
Aluminum Oxide	18.53	7.8
Copper (both layers)	1.59	0.7
Total Values	236.59	100.0

From examination of the data, it can be seen that the nickel-chrome layer increased the absorptivity of the system but did not behave as a significant thermal barrier. On the other hand, the aluminum-oxide coating provided substantial insulation. The copper achieved the desired effect of removing some of the heat generated within the system.

Since the exterior surface appeared to play an important role in the heat transmission, a further analysis was made. The heat transfer coefficients for both normal convective and radiant heat flow were calculated. The area chosen for study was that between the closed end and the center of the tube since this area was, in general, the hottest zone.

Convective Heat Flow

For estimation of the heat-transfer coefficient from a horizontal pipe to still air (normal convection), the following dimensionless equation was used:¹¹

$$\frac{h_c D_o}{k_f} = 0.53 \left[\frac{D_o^{3\rho} f^3 g\beta f \Delta t}{\mu_f^2} \left(\frac{C_D \mu}{k} \right)_f \right]^{0.25} \qquad \dots \dots (1)$$

where

- $h_c = surface coefficient of heat transfer for natural convection,$ Btu/hr/ft²/deg F
- D_0 = outside diameter of cylinder, ft
- k_{f} = thermal conductivity of air at temperature t_{f} , $Btu/hr/ft^{2}/deg F/ft$
- ρ_{f} = density of air at t_{f} , lb/ft³
- g = acceleration due to gravity, 4.17×10^8 ft/hr²
- $\beta_{f'}$ = coefficient of volumetric expansion of air $t_f,$ reciprocal deg F
- t_f = film temperature, (surface temperature + air temperature)/2, deg F
- Δt = film temperature air temperature, deg F
- $C_{\rm D}$ = specific heat of air, Btu/lb/deg F
- μ = viscosity of air, lb/hr/ft
- $\mu_{f'} = \mu \text{ at } t_{f'}$.

Let
$$\frac{\rho^{2\beta_{g}} C_{p}}{k}$$
 be represented as Y

where

$$Y = \frac{1}{cu \ ft/deg \ F} \cdot$$

Then

$$\frac{h_c D_0}{k_f} = 0.53 (\Delta t D_0^3 Y)^{0.26}.$$

In this case values for Y are given by McAdams.¹¹

Radiant Heat Flow

In determining the coefficient of radiative heat transfer, the following equation is given:¹²

$$q_r = h_r A_s (t_s - t_a)$$
 ...(2)

where

$$q_r$$
 = rate of radiant heat flow, Btu/hr
 h_r = coefficient of radiant heat transfer, Btu/hr/ft²/deg F
 A_s = area of emitting surface, ft²
 t_s = surface temperature, deg F
 t_a = air temperature, deg F (taken as 75 F).

In addition, the Stefan-Boltzmann radiation equation is given as:

$$q_r = \epsilon \sigma A_s T_s^4$$
 ...(3)

or

$$q_r = \varepsilon \sigma A_s (T_s^4 - T_a^4)$$
 ... (3a)

for heat transfer to air assuming the area of the air is large compared to the area of the radiating surface

where

e = emissivity factor

 $\sigma = \text{Stefan-Boltzmann constant}, 0.174 \times 10^{-8} \text{Btu/hr/ft}^2/\text{deg R}^4$

 $T_s = surface temperature, deg R (Rankine)$

 $T_{\mathbf{a}} = \operatorname{air} \operatorname{temperature}, \operatorname{deg} R.$

By equating these two formulas (Equations 2 and 3a), the following equation results:

$$h_r = \varepsilon \sigma \frac{(T_s^4 - T_a^4)}{(t_s - t_a)} .$$

Due to the free passage of radiation through most gases, the radiative heat flow can be superimposed on the convective and conductive heat flows.¹² Since the conductive heat flow to the air is very small (20 Btu/ hr), the total surface heat transfer coefficient may be given as ht where ht = hr + hc.

Figure 8 shows the values of the three coefficients (h_t, h_c, h_r) for each test condition at the above-mentioned area of the tube. By examining Figure 8, it can easily be seen that although the convective coefficient component represents between 30 and 50 percent of the total surface heat loss coefficient, this convective effect varied negligibly throughout the test series, showing that the temperature changes on the titanium surface were not enough to significantly affect convection. However, as expected, the radiation coefficient was temperature dependent in all tests, and emissivity-dependent on the varying external coatings.



Figure 8. HEAT TRANSFER COEFFICIENTS

For further analysis the heat flow from the surface of the tube may be compared with the heat flow from the Globar. Since the temperature of the silicon carbide heating element was 2500 F, and inside air temperature at the tube wall was 1200 F, the heat flow from the Globar can be determined by the use of Equation 3. The emissivity⁵ of silicon carbide was taken as 0.83 and a nominal radiating area of 19 sqare inches was used.¹³ The solution of the equation shows a heat flow of 14,600 Btu/hr from the Globar.

Figure 9 shows the percent of the total heat flow from the Globar which was emitted from the exterior surface of the tube in each test. This assumed that the heat-flow rate from the entire surface was constant and equal to the rate found at the hot zone studied. For comparative purposes, the average titanium temperature is also shown.



Figure 9. AVERAGE TITANIUM TEMPERATURE AND PERCENT OF TOTAL (GLOBAR) HEAT FLOW

When comparing Figures 8 and 9, it is noted that the variations in the percent of Globar heat flow emitted from the surface coincided with the radiational coefficient changes. In Figure 9 (tests 3, 5, 7, and 9), the heat-loss percentage followed the same trend as the titanium temperature changes. However, in tests 9-A, 11, and 11-A, the opposite was true. In test 9-A, the surface heat loss increased due to an increased emissivity, while the titanium temperature remained the same since the test was stopped before the titanium itself was affected by the surface temperature drop. In test 11, the heat loss dropped due to the removal of the copperoxide coating and the resultant lower emissivity. As was the case with the addition of the first copper layer, the titanium temperature dropped. Although the heat loss from the surface decreased, it still remained higher than that shown in test 9. This was due to the added effect of the second heat-sink layer and the increase in surface area exposed to the air. In test ll-A, the effect of a fully developed oxide coating with a high emissivity factor is exhibited in the lower titanium temperature and the higher percent of surface heat loss.

Figure 10 compares the titanium microstructure before and after the deposition process. It is evident that the deposition process has not affected the titanium structure. The adhesion of the nickel-chrome intermediate both to the titanium and the aluminum oxide is relatively good, as shown by Figure 7. The densities of the coatings are typical of flamesprayed ceramic and metallic coatings. The adhesion of the external copper on titanium is illustrated in the photomicrograph contained in Figure 11. Only a fair adhesion was observed between the copper and the titanium. Figure 12 is a cross-sectional view of the microstructure of the flamesprayed copper deposit. The deposit appears quite dense and is characterized by its lamellar structure and very fine pore size. The photomicrograph in Figure 13 shows the copper oxide film that was formed on the copper deposit during the tests. This oxide film, which is approximately 0.00025to 0.00050-inch thick, provided the highly emissive surface which was effective in reradiating the heat absorbed by the copper heat sink. Some copper oxide is dispersed throughout the copper deposit. This copper oxide was formed during the deposition process, since during deposition the substrate usually attains temperatures up to 500 F.



Figure 10. TITANIUM STRUCTURE





CONCLUSIONS AND RECOMMENDATIONS

The composite coating system prevented the titanium from exceeding the critical temperature of 1000 F. Although the selection of the internal coating system of nickel-chrome and aluminum oxide was based on prior applications where adhesion and erosion resistance were of prime importance, the thermal effects produced by the use of nickel-chrome had not been considered. The present study has demonstrated that the high absorptivity of the nickel-chrome intermediate coating accounts for the temperature of the external surface of the titanium exceeding 1000 F. To prevent this temperature increase it required the combined effects of the aluminum oxide and the external heat-sink layer of copper with its highly emissive oxide film.

If the weight of this composite tube is compared with that of a similarly sized steel tube, a substantial difference is noted. A 17-inch steel tube with the same inside and outside diameters would weigh approximately 17.95 pounds, while the titanium tube, complete with the composite

coatings, weighs only 14.57 pounds. This represents a 19 percent weight saving over the steel tube. Table IV shows the weight effect of each component of the system.

TABLE IV

WEIGHT	DATA	FOR	COATED	SISTEM	COMPONENTS	

Component	Coating Porosity (%)	Calculated Weight (lb)	Percent of Total Weight
Titanium		10.27	70.5
Nickel-Chrome	24.0 ²	0.27	1.8
Aluminum Oxide	23.4 ³	0.17	1.2
Copper (first layer)	15.6 ³	1.90	13.0
Copper (second layer)	15.6	1.96	13.5
Total Composite Tube		14.57*	100.0

* *Same size steel tube weighed 17.95 pounds.

In order to achieve a further weight reduction, future tests should include investigations using aluminum as a flame-sprayed external coating.

Also, the feasibility of using molybdenum as the intermediate layer for improving the bond of the internal coating should be investigated. Molybdenum should exhibit decreased absorptivity and therefore contribute to lower external temperatures.

REFERENCES

- 1. LEVY, M., and LEVITT, A. P. Flame-Sprayed Metallic and Ceramic Coatings for Ordnance Applications. Presented at the Third International Metal Spraying Conference, Madrid, Spain, May 1962.
- LEVY, M. Flame-Sprayed Ceramic Coatings Evaluation and Applications. Presented at the 64th Annual Meeting of the American Ceramic Society, New York, 30 April - 8 May 1962.
- 3. INGHAM, H. S., and SHEPARD, A. P. *Metallizing Handbook*. 7th ed. Metallizing Engineering Co., Inc., Westbury, L. I., New York, v. I and II, 1959.
- 4. HANDBOOK OF CHEMISTRY AND PHYSICS. Charles D. Hodgman, ed., 37.ed. Chemical Rubber Publishing Co., Cleveland, Ohio.
- GOLDSMITH, A., and WATERMAN, T. E. Thermophysical Properties of Solid Materials. Armour Research Foundation, Contract AF 33(616)-5212, WADC TR 58-476, November 1960.
- MICHELS, W. C., and WILFORD, S. The Physical Properties of Titanium, I. Emissivity and Resistivity of the Commercial Metal. Journal of Applied Physics, v. 20, 1949, p. 1223-1226.
- 7. AMERICAN SOCIETY FOR METALS. Metals Handbook. Taylor Lyman, ed., Cleveland, Ohio, 1948.
- TEBO, L. J. Selected Values of the Physical Properties of Various Materials. Argonne National Laboratory, Lemont, Illinois, Contract W-31-109-eng-38, ANL-5914, September 1958.
- 9. AMERICAN INSTITUTE OF PHYSICS HANDBOOK. Dwight E. Gray, ed., McGraw-Hill Book Co., Inc., New York, 1957.
- KLEIN, J. D. Hadiation Heat Transfer to and from Ceramic Coatings on Metals. Bulletin of the American Ceramic Society, June 1961, p. 366-370.
- 11. McADAMS, W. H. Heat Transmission. McGraw-Hill Book Co., Inc., New York, 1954.
- 12. JACOB, M., and HAWKINS, G. A. Elements of Heat Transfer. John Wiley and Sons, New York, 1952.
- 13. TECHNICAL BULLETIN H. Globar Division, The Carborundum Co., Niagara Falls, New York, 1957.

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