AD-600 043

IIT RESEARCH INSTITUTE
Technology Center
Chicago 16, Illinois

Contract NOw 64-0140-C

HIGH-TEMPERATURE OXIDATION PROTECTIVE COATINGS FOR VANADIUM-BASE ALLOYS

IITRI-B6019-3

(Bimonthly Report)

February 1, 1964 - March 31, 1964

Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.

May 1, 1964

HIGH-TEMPERATURE OXIDATION PROTECTIVE
COATINGS FOR VANADIUM-BASE ALLOYS

ABSTRACT

The objective of this program is the development of oxidation protective coatings for vanadium-base alloys for use at 1800° to 2500°F. The effect of the pack siliconizing process on the mechanical properties of .020" thick sheet of V-60 w/o Cb - 1 w/o Ti is being studied. Samples are being evaluated before and after various high temperature exposures.

Development of an oxidation resistant slurry or liquid cementation type coating for V-60 w/o Cb - 1 w/o Ti is progressing. Five slurry compositions containing tin, silicon, silver, copper, aluminum, and columbium have been investigated, and several of these show good coverage, even at corners and edges.

HIGH-TEMPERATURE OXIDATION PROTECTIVE COATINGS FOR VANADIUM-BASE ALLOYS

I. INTRODUCTION

This is the third bimonthly progress report on IITRI Project B6019, "High-Temperature Oxidation Protective Coatings for Vanadium-Base Alloys," covering the period February 1 to March 31, 1964. This program is a continuation of work previously conducted under Contract NOw 61-0806-c and N600 (19)-59182.

In previous work, pack-siliconizing coating processes were developed to protect vanadium-base alloys from oxidation at temperatures between 1200° and 2800°F. Pack parameters were estab lished for coating various sizes of specimens of V-60 Cb and V-20 Cb base alloys.* In addition, the applicability of the coating process to other high-strength alloys currently under development** was also investigated. Coating performance was evaluated in static air in an oxygen-hydrogen flame, at reduced pressures, and under stress. Also, coated samples have been supplied to various laboratories and aerospace organizations participating in a data exchange program+ for further evaluation. The results to date are quite encouraging and indicate considerable potential for the coated vanadium alloys in a variety of aerospace applications.

Th. current program has several objectives, the major ones are as follows:

1. Determination of the influence of the coating and process on the mechanical properties of alloys.
2. Influence of stress on coating performance.
3. Development of a slurry coating process.
4. Further evaluation of the influence of selected environments (i.e., low pressure, high air mass flow) on coating performance.

---

* Compositions are reported in weight per cent.

** Contract No. NOw 64-0239-c

\+ Contract No. NOw 62-0101-c

II. EXPERIMENTAL RESULTS

A. Influence of the Coating and Cooling Process on the Mechanical Properties of Vanadium-Columbium Alloys

This portion of the program is concerned mainly with the influence of the coating and coating process on the mechanical properties of vanadium-columbium alloys during high-temperature exposure in a wide variety of environments, such as static and dynamic oxidizing environments and reduced pressures. The influence of stress on the coating under these conditions is also being studied.

Mechanical evaluation of the uncoated alloys at temperatures between -320°F and 2700°F have been reported under Contract No. NOw-62-0101-c, "Pilot Evaluation of Vanadium Alloys," Final Report IITRI-B231-10, January, 1964.

Mechanical evaluation of coating influence on pack-siliconized V-60Cb-1Ti, both before and after exposure is currently in progress. The standard IITRI process is being used for coating all specimens, and the test conditions under study are shown in Table I. Results from this portion of the program are scattered and incomplete at the present time; consequently, presentation of the data is being postponed until a more complete evaluation can be made.

The evaluation program that has been designed represents a selection of tests which are very meaningful in determining the potential of coated refractory metals for use in skin applications on reentry vehicles. The temperature-dependent strength characteristics which are being determined are, of course, applicable to the use of this material in other environments.

B. Slurry and Liquid Cementation Type Coatings

Studies have been initiated in this area to develop a suitable oxidation-resistant coating for V-60Cb-1Ti which can be applied by painting, spraying, or dipping.

This work has the objective of increasing the versatility of the silicide coating process by developing a procedure adaptable to large

TABLE I

SUMMARY OF MECHANICAL TESTING PROGRAM ON PACK-SILICONIZED V-60Cb-1Ti

Condition	Determinations
As-siliconized	Ultimate tensile strength and elongation as a function of temperature.
	Ultimate tensile strength and elongation as a function of temperature with the coating machined off.
After static oxidation	Ultimate tensile strength and elongation as a function of temperature after ten and twenty-five 4-hr oxidation cycles at 1800°, 2100°, and 2400°F.
	Creep properties of coated specimen and influence of stress exposure on subsequent low-temperature properties.
After oxidation testing at reduced pressures	Ultimate tensile strength and elongation after five 4-hr oxidation cycles as follows: (1) 100 μ at 1800° and 2300°F (2) 1 μ at 1800° and 2300°F (3) 0.1 μ at 1800° and 2300°F
After dynamic oxidation testing at 1 atm	Ultimate tensile strength and elongation after twenty-five 1/4-hr cycles at 1800°, 2100°, and 2400°F.

intricate structures. The slurry coatings that are being studied should also be capable of providing better self-healing capabilities and greater tolerance for plastic deformation at low temperatures.

The first phase of the program was to study coatings applied by dipping specimens of V-60Cb-1Ti (3/4 x 3/4 x 0.020 in. thick) that had been grit-blasted to produce a more suitable surface for slurry application. The slurries are composed of metal powders suspended in a nitrocellulose lacquer, and the samples are air dried after dipping.

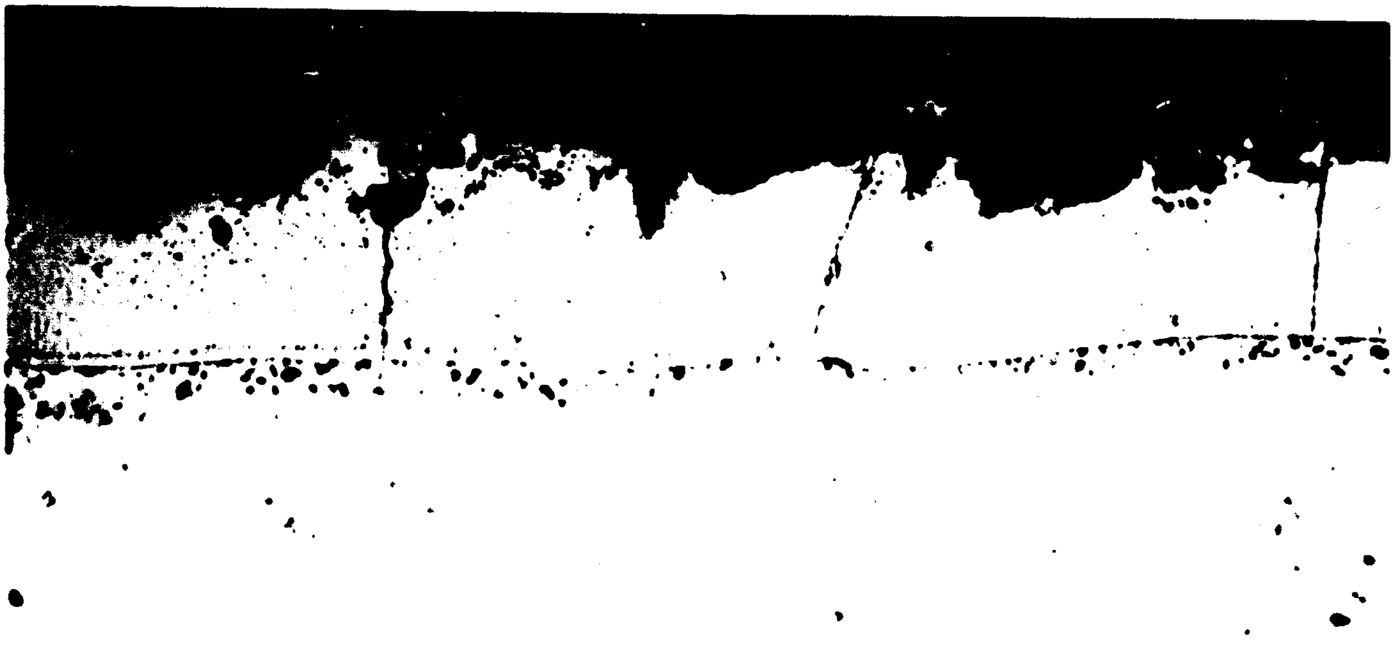
The slurries studied to date have all been vacuum-treated from 1/2 to 2 hr at temperatures from 1800° to 2200°F after application to the V-60Cb-1Ti substrate. The slurry compositions investigated to date are shown below.

75Sn-25Si
75Ag-25Si
80Cu-20Si
68.5Sn-20Al-11.5Si
85Sn-25Al-7.5Cb-2.5Si

All of these compositions produced dense, adherent, metallic coatings after heat treatment except the 75Ag-25Si. This composition produced a coating that was very powdery and non-adherent. This failure can be explained by the fact that the vapor pressure of silver is too high for vacuum treatment, all of the silver evaporates from the specimen surface in a very short time, leaving no vehicle by which the silicon can come into intimate contact with the substrate to produce a diffusion coating. Silicon, of course, is solid at the diffusion treating temperature.

Results with the other compositions have been more successful; they were studied metallographically to determine coating thickness uniformity and degree of corner protection. Specimens were coated with as-sheared edges; no attempt was made to finish or round the corners.

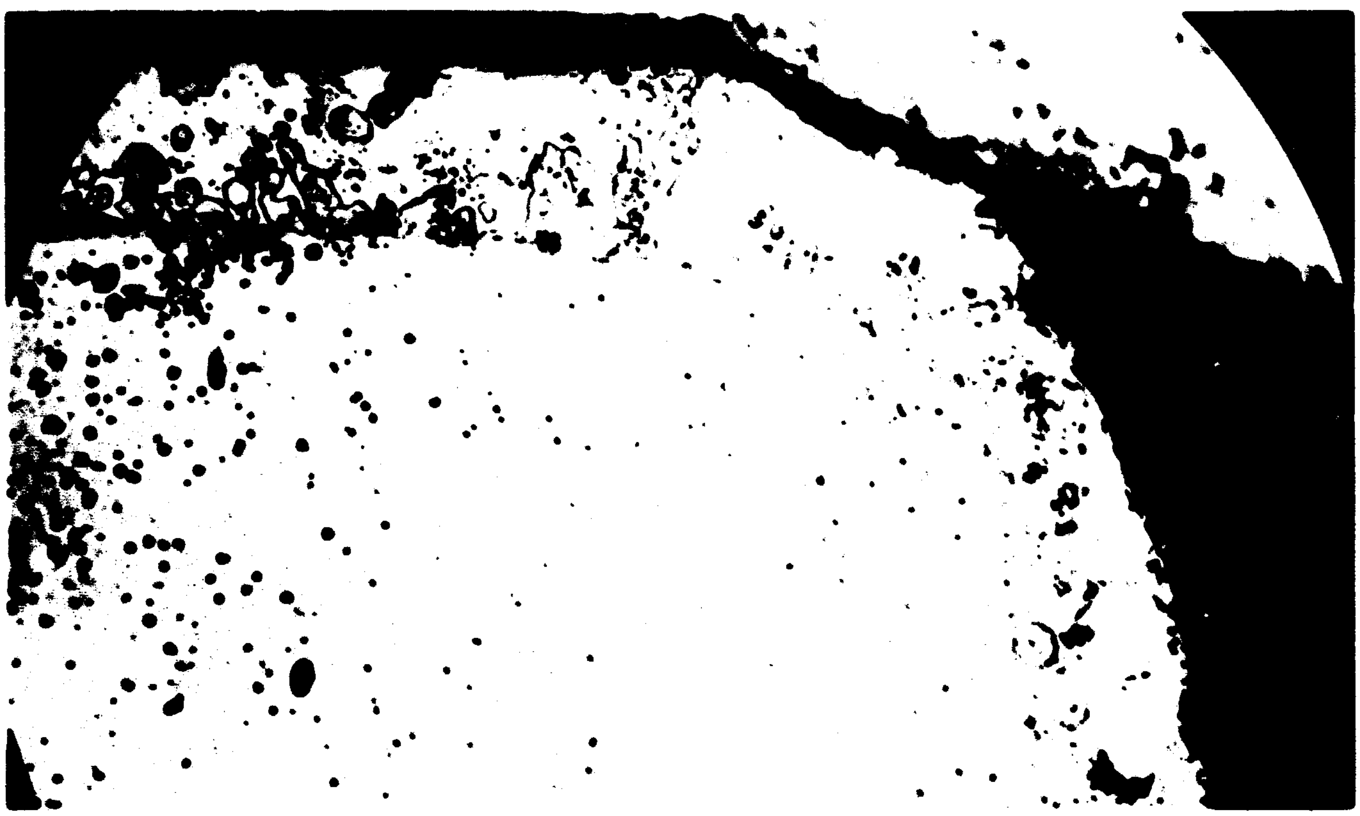
Figure 1 shows the microstructure of a 75Sn-25Si slurry coating vacuum diffused for 2 hr at 2200°F. This coating has a thickness of 2.5 mils, which was determined in previous work to be optimum. The silicide layers can be seen, but the remaining tin that should be on the surface is not visible. Work is continuing with the composition to determine



Neg. No. 26451 X400

Fig. 1

75Sn-25Si Slurry on V-60Cb-1Ti. Vacuum diffused for 2-hr at 2200°F.



Neg. No. 26449 X400

Fig. 2

80Cu-20Si Slurry on V-60Cb-1Ti. Vacuum diffused for 1 hr at 2100°F.

optimum coating conditions. Also, samples will be prepared for oxidation testing.

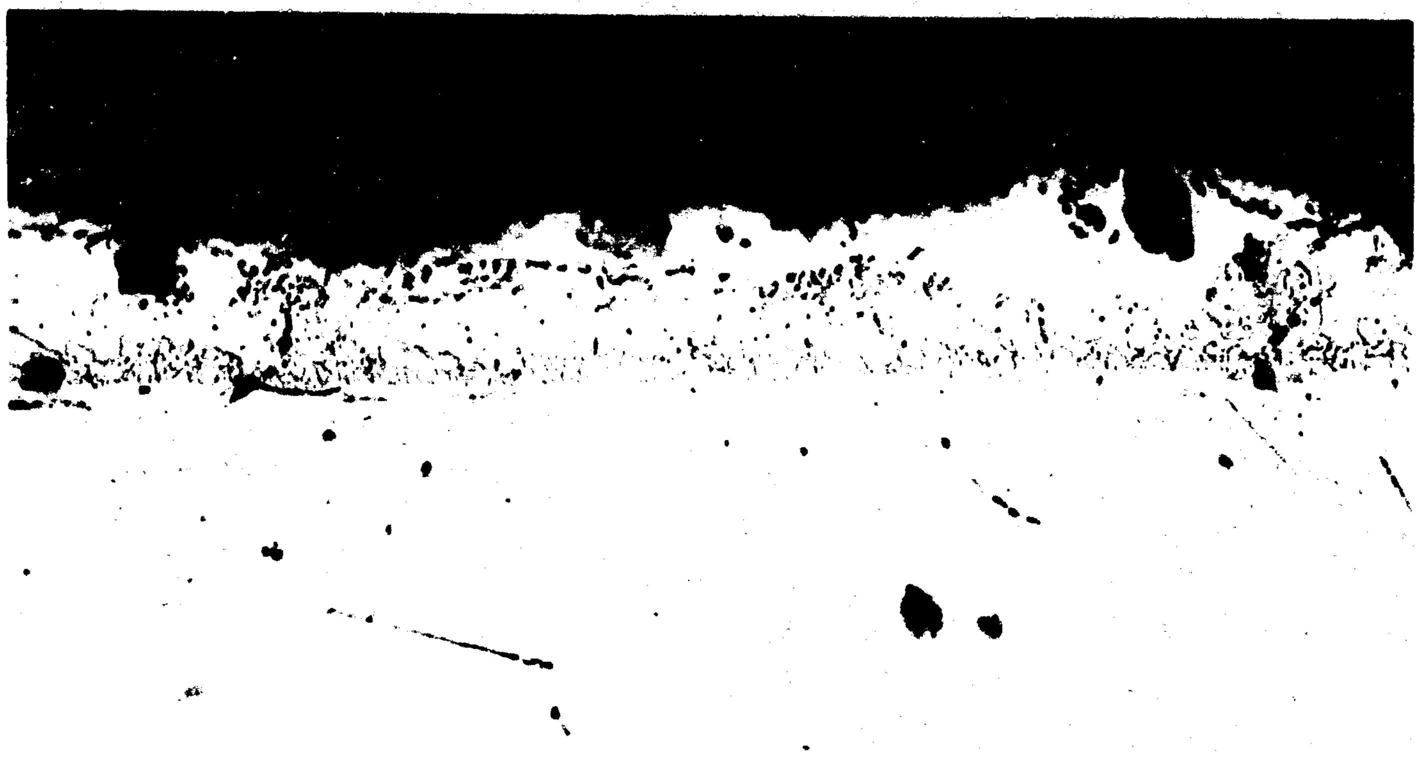
Figures 2 and 3 show the microstructure obtained using the 80Cu-20Si slurry composition. The treating times were 1 and 2 hr. respectively, at 2100°F. There is some difference in the diffusion coating thickness produced by these different times. In this case the remaining copper-base vehicle is visible on the surface above the diffusion coating. As would be expected, slurries offer excellent protection to corners and edges as seen in Figure 2.

Figure 4 shows the microstructure of the 68.5Sn-20Al-11.5Si slurry after first a 1/2 hr vacuum heat treatment at 2050°F and an additional dipping followed by a 2 hr heat treatment at 2050°F also in vacuum. The expected (V, Cb) Al_3 phase did not form. Instead small particles of (V, Cb)Si_2 are evident and apparently form a skeletal structure. It was hoped to have a heterogeneous, columnar mixture of aluminide and silicide compounds. Once again, the good corner coverage can be seen.

The microstructures in Figures 5 and 6 are of the 65Sn-25Al-7.5Cb-2.5Si after two dipping and vacuum heat treatments at 1950°F for 1/2 hr. The photomicrograph (Figure 6) taken with polarized light shows the columnar grains of (V, Cb)Al_3.

Only this last composition was oxidation tested during this period. The one specimen studied had a small edge defect before testing, but the sample survived an exposure of 8 hr at 2000°F. The sample failed at this defected region sometime between 8 and 24 hr at 2000°F.

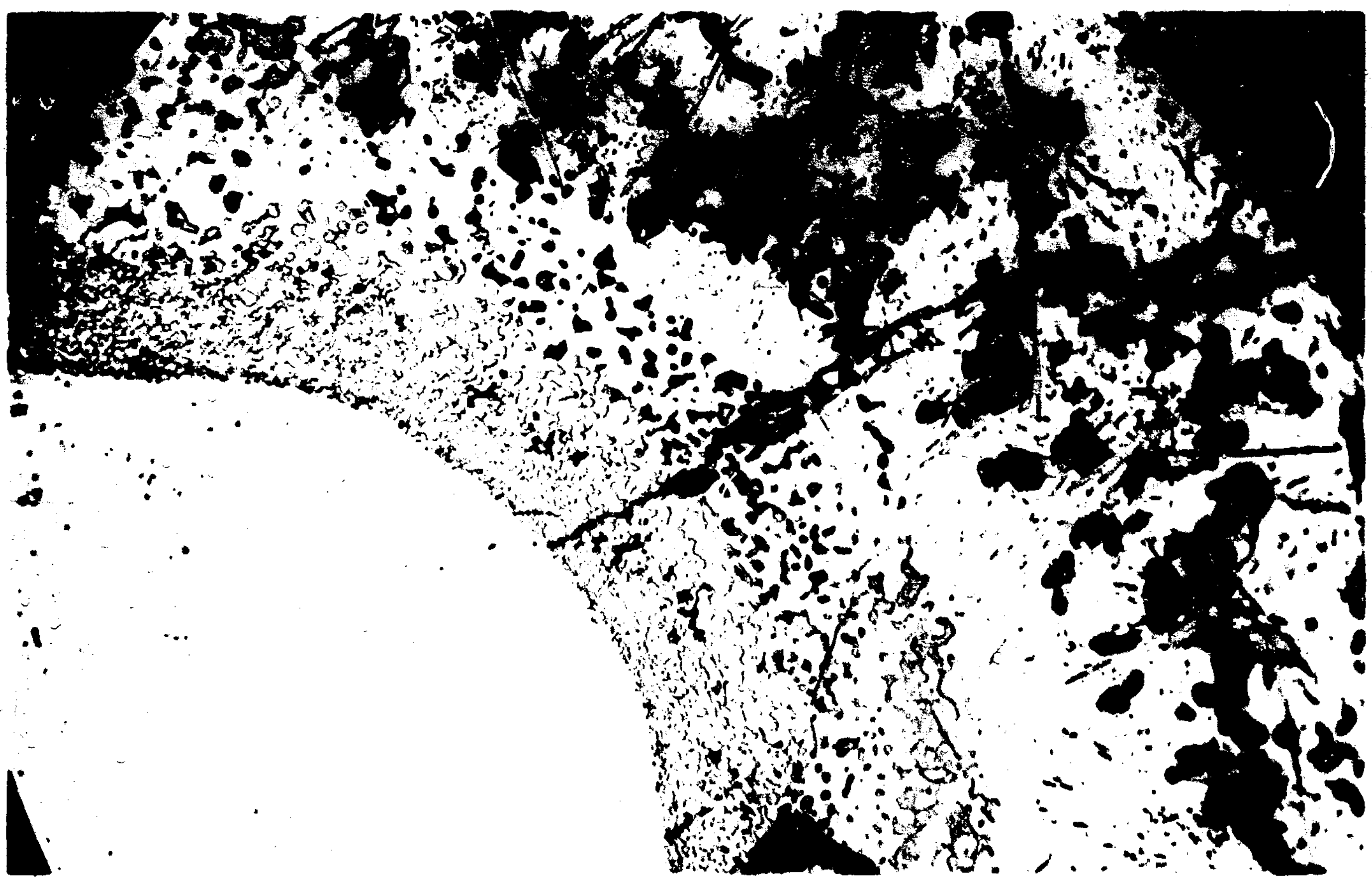
Work has been initiated to study these same slurry compositions, using an argon atmosphere for heat treatment rather than vacuum. Initial experiments were made with the 75Ag-25Si, 75Sn-25Si, and 80Cu-20Si compositions, all on 20-mil V-60Cb-1Ti. Heat treatment was for 4 hr at 1800°F in flowing argon. The silver and tin base alloy coatings both had a loose powdery coating indicating an incomplete alloy reaction between the coating constituents as well as a reaction with impurities in the argon. Samples are being prepared for treatment at higher temperatures (2000°-2300°F) in a pure static argon atmosphere.



Neg. No. 26447 X500

Fig. 3

80 Cu-20Si Slurry on V-60Cb-1Ti. Vacuum diffused for 2-hr at 2100°F.



Neg. No. 26450 X400

Fig. 4

68.5Sn-20Al-11.5Si slurry on V-60Cb-1Ti. Vacuum diffused for 1/2 hr at 2050°F.

Neg. No. 26452

X400
(Bright Field)

Fig. 5

65Sn-25Al-7.5Cb-2.5Si slurry on V-60Cb-1Ti. Vacuum diffused for 1/2 hr at 1950°F. Recoated and given the same heat treatment.

Neg. No. 26454

X400
(Polarized Light)

Fig. 6

Same field of view as in Figure 5 except that this photomicrograph was taken with polarized light.

III. FUTURE WORK

Major efforts during the forthcoming period will be divided into two areas: (1) continued evaluation of the effect of the coating and coating process in the substrate material; and (2) continued development of a slurry coating process. Mechanical properties will be determined for coated alloys in the as-coated condition and after selected combined stress-oxidation exposures. Slurry coating development will continue by studying metal coating systems containing Ag, Cu, and Sn as vehicles for silicide-type coatings.

IV. LOGBOOKS AND PERSONNEL

Data for this report are recorded in IITRI Logbook No. C14234 and C14387.

The following personnel have been the principal contributors to the planning and execution of the work.

F. C. Holtz . . . . . . Project Consultant
L. I. Kane . . . . Project Engineer
D. D. Lawthers . . . . Project Engineer
J. J. Rausch . . . . . . Project Supervisor
R. C. Vanderjack. . . . Project Technician

Respectfully submitted,
IIT RESEARCH INSTITUTE

Larry I. Kane,
Assistant Metallurgist

John J. Rausch, Manager
Coatings Research

Approved by:

R. J. Van Thyne, Asst, Director
Metals and Ceramics Research