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HIGH-TEMPERATURE
OXIDATION PROTECTIVE COATINGS
FOR VANADIUM-BASE ALLOYS

Contract N600(19)59182

Department of the Navy
Bureau of Naval Weapons
Washington 25, D. C.
Attention: Code RRMA-222

ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
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HIGH-TEMPERATURE
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FOR VANADIUM-BASE ALLOYS

Contract N600(19)59182
(Bimonthly Report No. 3)
January 13, 1963 - March 12, 1963

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April 8, 1963

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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ABSTRACT

Basic pack siliconizing processing variables such as time, temperature, edge and surface preparation, activator concentration, and powder size are being investigated to optimize oxidation life and coating adherence for thin sheet material.

Fifteen vanadium-columbium alloy compositions have been pack siliconized and oxidation tested. Minimum life has been established at about 150 hr at 2200°F for each of the alloys.

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I. INTRODUCTION

This is the third bimonthly progress report under Contract N600(19)59182, summarizing the work performed on ARF Project B6001 during the period January 13, 1963 to March 12, 1963.

Efforts are being devoted to optimizing the highly-promising silicide coatings for vanadium-columbium alloys. The reliability of these coatings on several of the higher-strength alloys will be evaluated in detail after a study of coating processing variables has been completed. Vanadium alloy specimens will also be coated for evaluation by aerospace and other organizations participating in the data-exchange program under Contract NOW 62-0101c, "Pilot Evaluation of Vanadium Alloys."

To date, two of the most promising vanadium-columbium alloys are V-1Ti-60Cb and V-20Cb-4Ti-1Zr-0.075C*, and 100-pound ingots of these compositions have been fabricated to sheet under the pilot evaluation program. Other compositions studied include additions of tantalum, hafnium, tungsten, titanium, molybdenum, and zirconium in varying amounts. Fifteen of these alloys have been siliconized and oxidation tested. When selection is established, a third large ingot will be made for pilot evaluation.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Silicide-Base Coatings

1. Investigation of Processing Variables

Previous pack variable studies on 0.050 inch thick sheet were made to establish the parameters necessary for producing siliconized

* Compositions are reported in weight per cent.

alloys having maximum oxidation resistance. Processing for 16 hours at 2200° F in small retorts using a 10:1 Si:NaF ratio, with the activator in a separate container, under a static argon atmosphere. (1) However, when coating thin sheet (20-30 mils), or using large retorts, several problems were encountered. The pack sintering that occurs during a continuous 16 hour siliconizing treatment causes excessive warpage and distortion of this thin material. Furthermore, the thick coatings that are produced on thin stock have relatively poor adherence and fail by laminar separation during plastic bending. These factors have led to the investigation of processing variables adaptable to the coating of thin sheet.

In this study, pack and retort design, activator species, and atmosphere were kept constant while silicon powder size, edge and surface preparation techniques, activator concentration, time, and temperature were varied. The influence of these processing variables on coating adherence and static oxidation life is under investigation.

Preliminary results indicate that double pack processing may not increase the reliability coatings and that sixteen hours of treatment is not necessary for maximum life. The static air oxidation life of V-1Ti-60Cb alloy specimens siliconized for 8, 16 and for a double 8 hour coating cycle is shown in Table I. Of the four specimens of V-60Cb-1Ti that lasted the longest, two were produced by processing for only eight hours, and the others were given two eight-hour treatments. Furthermore, only one other specimen received a single eight-hour treatment, and this specimen shows no sign of failure after twenty-one hours. However, it was determined that there is less sintering of the pack with two eight-hour runs than with one sixteen-hour run, and consequently less specimen distortion.

Investigation of edge and surface preparation techniques has also been made. Samples were prepared by barrel tumbling for 100 hours

(1) J. J. Rausch and F. C. Holtz, "High-Temperature Oxidation Protective Coatings for Vanadium-Base Alloys," Final Report, Contract NOW 61-0806-c, August, 1962.

TABLE I
STATIC OXIDATION LIFE OF V-60Cb-1Ti SPECIMENS
SILICONIZED FOR 8, 16, and DOUBLE-8 HOUR CYCLES

Processing, hrs	Run*	Static Oxidation Life at 2200°F, hrs	Mode of Failure, Type of Oxidation
8	13	255	edge
Double-8	13	255	edge
Double-8	B	>255	
8	16	230	edge
Double-8	16	>210	
Double-8	B	160	defect
Double-8	16	155	edge
Double-8	17	154	edge
Double-8	L-1	>126	
Double-8	L-1	>126	
Double-8	17	118	general
16	18	> 68	
Double-8	16	55	edge and defect
16	18	52	edge
Double-8	15	50	edge
Double-8	L-2	50	defect
16	14	25	defect
8	13	> 21	
Double-8	L-2	18	defect

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in a water-alumina grit slurry, hand finishing on a rubber bonded grinding wheel, and hand finishing on a surface grinder using a fine silicon carbide belt. All of the samples were degreased and etched in 25 HNO₃-5 HF-70 H₂O with a subsequent water and acetone rinse. There apparently is no great difference in oxidation life due to the three techniques investigated as long as the edges are uniformly round and free from saw or shear cuts introduced during sizing, and the surface is clean and free of oxide. Table II shows the static oxidation life of tumbled and non-tumbled (hand finished) V-60Cb-1Ti and V-20Cb-5Ti specimens. The barrel tumbling technique, however, produces the most apparently uniform specimens. A specimen prepared in this manner may be seen in Figure 1.

It is certainly worth noting that most failures occurred because of edge oxidation. A typical failure is shown in Figure 2. It is believed that edge failures are caused by seams or laps in the alloy specimens which result in non-uniform distribution of the silicide layers. Some of the samples were found to contain laminations which were smeared over during cutting and subsequent edge preparation. Many of these laminations were the result of excessive cold rolling, without intermediate anneals, to produce the thin (0.020 to 0.030 inch) sheet.

Silicon powder size and activator concentration are being studied at the present time. Pack runs are being made using -325, -200 + 325, -100 + 200, and -30 + 100 mesh high-purity (99.999+) silicon powder.

Previously, activator concentration was determined by the size of the pack. However, the amount of activator used is probably more dependent on the volume of the retort than on the weight of the pack. Current pack runs are being made using 2 to 6 grams of activator per liter of retort. This is the range of activator concentration that was used in previous work with small retorts.

2. Oxidation Behavior of Additional Siliconized Alloys

Alloys which are currently being developed under Contract NOw 62-0101-c, "Pilot Evaluation of Vanadium Alloys", are being siliconized to determine the protective capabilities. The alloys which have

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Neg. No. 24708

Mag. $\times 10X$

Fig. 1

V-60Cb-1Ti specimen tumbled for 100 hours in a water-alumina grit slurry and etched in $25\text{HNO}_3-5\text{HF}-70\text{H}_2\text{O}$.

TABLE II
STATIC OXIDATION LIFE OF ALLOYS WITH DIFFERENT TYPES
OF SURFACE PREPARATION

Run	Edge and Surface Preparation	Static Oxidation Life at 2200° F, hrs	Mode of Failure, Type of Oxidation
<u>V-60Cb-4Ti</u>			
B	Not tumbled	>255	
16	Tumbled	230	edge
16	Tumbled	>210	
B	Not tumbled	160	defect
18	Not tumbled	135	edge
17	Tumbled	134	edge and general
L-1	Tumbled	>126	
L-1	Tumbled	>126	
17	Tumbled	118	general
18	Tumbled	> 68	
16	Not tumbled	55	edge and defect
18	Tumbled	52	edge
L-2	Tumbled	50	defect
13	Tumbled	> 21	
L-2	Tumbled	18	defect
<u>V-20Cb-5Ti</u>			
16	Not tumbled	>223	
16	Tumbled	180	edge
18	Tumbled	108	edge
14	Not tumbled	23	edge
16	Tumbled	23	edge

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TABLE II(continued)

Run	Edge and Surface Preparation	Static Oxidation Life at 2200°F hrs	Mode of Failure, Type of Oxidation
18	Tumbled	>23	
18	Not tumbled	18	defect
13	Not tumbled	6	defect
16	Not tumbled	6	general
18	Not tumbled	2	edge and defect

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Neg. No. 24709

Mag. 10X



Neg. No. 24315

Mag. 20X

Fig. 3

Edge oxidation failure which occurred in sample 1305, after exposure for 20 hours at 2200° F.

been coated include:

V-70Cb-5Ta-1Ti	V-60Cb-1Hf
V-70Cb-5W-1Ti	V-40Cb-30Ta-1Hf
V-60Cb-10Ta-1Hf	V-20Cb-10Ta-5Ti
V-60Cb-5W-1Hf	V-20Cb-5W-5Ti
V-60Cb-2.5Mo-1Ti-0.5Ru	V-20Cb-4Ti-1Zr
V-60Cb-1Hf-0.40	V-20Cb-4Hf-0.025O
V-60Cb-2Ti-0.075C	V-20Cb-4Ti-1Zr-0.07C
V-10Cb-10W	

Small test coupons, approximately 20-25 mils thick and 1/2 inch square, were coated by pack siliconizing at 150° F for various times. The static air oxidation life of the coated alloys is reported in Table III.

In general, all of the alloys produced satisfactory coatings with life times greater than 150 hours at 200° F. Some coated alloys, such as V-60Cb-10Ta-1Hf and V-10Cb-10W, appear to have greater oxidation resistance than others. However, a sufficient number of tests have not been run to draw definite conclusions. The major hindrance preventing determination of the best alloys is that most of the specimens were cut from laminated stock which may have caused premature failures. The excessive amount of laminations may be due to the fact that most of the stock for these studies originated as edge trimmings from 0.050 sheet used for tensile evaluations. Subsequent cold rolling to 0.020 or 0.025 inch stock, without an intermediate anneal, may have been excessive for some of the more difficult-to-work alloys.

Alloy and coating development indicates that the third 100 pound ingot will have a composition of V-60Cb-1Zr with a minor addition of carbon.

Other efforts under this program include the siliconizing of bend, tensile, stress-rupture, and other specimens prepared from sheet fabricated from the 100-pound ingots of V-1Ti-60Cb and V-4Ti-20Cb-1Zr-0.075C. This work is also being coordinated under Contract N0w 62-0101-c. Specimens up to 8 inches long are currently being coated and will

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TABLE III
STATIC OXIDATION LIFE OF VARIOUS VANADIUM ALLOYS

Run	Static Oxidation Life at 2200° F, hr	Mode of Failure, Type of Oxidation
V-40Cb-30Ta-1Hf		
14	55	edge
14	23	defect
17	13	edge and defect
V-20Cb-10Ta-5Ti		
15	> 270	
17	117	edge
V-70Cb-5W-1Ti		
15	225	edge
25	205	general
V-60Cb-5W-1Hf		
15	105	edge
17	6	edge
V-60Cb-2.5Mo-1Ti-0.5Ru		
13	180	edge
15	90	edge
V-60Cb-10Ta-1Hf		
17	> 320	
14	265	general
14	185	defect

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TABLE III (continued)

Run	Static Oxidation Life at 2200° F, hr	Mode of Failure, Type of Oxidation
V-10Cb-10W		
18	> 360	
18	> 70	
16	34	edge
14	24	edge
13	9	edge
V-70Cb-5Ta-1Ti		
14	115	general
15	105	general
17	68	edge
V-60Cb-1Hf		
13	265	edge
16	> 223	
13	44	general
17	6	edge
V-20Cb-5Ti-5W		
16	> 205	
14	74	general
13	20	defect
V-20Cb-4Ti-1Zr		
15	255	general
15	255	general
13	180	edge

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TABLE III (continued)

Run	Static Oxidation Life at 2200° F, hr	Mode of Failure, Type of Oxidation
18	108	general
18	50	defect
13	6	general
	V-20Cb-1Hf	
15	31	edge

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be forwarded to the aerospace and other organizations participating in the data-exchange portion of the pilot evaluation program. Results of these evaluations of coated specimens will be presented in reports issued under NOW 62-0101-c, and pertinent information will also be discussed in reports under this oxidation-protective coatings program.

III. SUMMARY

Major effort during this period has been divided into optimizing the pack siliconizing process for coating large batches of V-1Ti-60Cb and V-5Ti-20Cb alloys and determining the coatability or oxidation life of vanadium alloys which are currently being developed under Contract NOW 62-0101-c.

Silicon powder size, edge and surface preparation, activator concentration, time, and temperature are the parameters under study. Their effect on static oxidation life and coating adherence during elastic and plastic bending is being determined. The type of surface preparation appears to be unimportant if specimens are clean and free from surface and edge defects. The other parameters are still under investigation.

Fifteen different vanadium alloys have been pack siliconized and tested to determine their static oxidation resistance. The samples (approximately 1 x 1 x .020in) were oxidized at 2200° F; a minimum life of 150 hours can be expected of all the alloys. Some alloys such as V-60Cb-10Ta-1Hf and V-10Cb-10W have potential lives of over 300 hours at this temperature.

Mechanical test specimens of V-60Cb-1Ti are being pack siliconized under the contract mentioned above for distribution to the organizations participating in our data exchange program. Alloy development studies indicate that the third 100-pound ingot will have the composition V-60Cb-1Zr-0.075C. The life of siliconized coatings on this composition is being investigated.

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IV. FUTURE WORK

Determination of the oxidation and mechanical property behavior of V-20Cb-4Ti-1Zr-0.075C, V-60Cb-1Ti, and V-60Cb-1Zr-0.075C after siliconizing will continue. These determinations will be made under static and dynamic conditions.

Investigation of processing variables will continue with major emphasis on determining the influence of these variables on oxidation life and coating adherence during elastic and plastic bending.

Work on the evaluation of Ag-Si slurry coatings has been initiated. Diffusion studies of Ag-TiSi₂, Ag-VSi₂, and Ag-CbSi₂ mixtures into V-60Cb-1Ti and V-20Cb-5Ti will be made. Specimens will be prepared and subjected to some of the tests given the pack-siliconized specimens.

V. LOGBOOKS AND PERSONNEL

Data for this report are recorded in ARF Logbooks C-13008, C-13172, C-13280, and C-13294.

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

F. G. Holtz	-	Project Leader
L. I. Kane	-	Technical Assistant
J. J. Rausch	-	Silicide-Base Coatings
R. C. Vanderjack	-	Project Technician

Respectfully submitted,

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