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By Joseph W. Pitts and Dwight G. Moore

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CERAMIC COATINGS FOR PREVENTION OF CARBON ABSORPTION IN FOUR HEAT-RESISTANT ALLOYS

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SUMMARY

Stabilized stainless steels, when used in aircraft exhaust systems under severe operating conditions, have been shown to undergo carbon absorption with a resulting carbide precipitation at or near grain boundaries. Failures of exhaust parts have been ascribed to this cause and the prevention of the carbon absorption is therefore desirable.

In the present investigation, three ceramic coatings were applied to four heat-resistant alloys and then tested for their effectiveness in preventing carbon absorption under strongly carburizing conditions, that is, box carburizing. At 1350° F no carbon pickup occurred after the 4-hour treatment but at 1500° and 1650° F carbide precipitation was evident in the uncoated stabilized 18-8 steels extending down from the surface to a depth of as great as 0.007 inch. In most cases the ceramic coatings completely prevented the absorption.

Inconel showed no evidence of carbon absorption under the test conditions used.

INTRODUCTION

In recent years ceramic coatings have been used with success for the protection of aircraft-exhaust-system alloys. The primary purpose of the coatings is to retard the deterioration of the alloys by the various corrosive agents present in the exhaust gases.

According to Heron, Harder, and Nestor (reference 1) the most important of these corrosive agents present in the gases from internal combustion engines are lead compounds, oxygen, hydrocarbons, carbon monoxide, and free carbon. Earlier studies by the National Bureau of Standards have demonstrated the ability of ceramic coatings to protect alloys from oxygen (references 2 and 3) and lead bromide (reference 4) but there have been no studies reported relative to the effectiveness of the coatings in preventing carbon penetration.

Carbon penetration occurs when heat-resistant alloys are operated at high temperatures in the presence of carbon monoxide, carbon, or some of the hydrocarbons. That carbon is absorbed during operation of stabilized 18-8 stainless-steel aircraft exhaust systems has been demonstrated by Kahn, Oster, and Wachtell (reference 5) and by Hubbell (reference 6). The absorption is followed by carbide precipitation at grain boundaries and, according to reference 5, this carbide precipitation may be responsible for many of the failures in stainless-steel exhaust systems.

The present work was undertaken to determine whether or not the ceramic coatings as currently developed are capable of preventing or retarding carbon absorption for four heat-resistant alloys when these alloys are operated in the temperature range of 1350° to 1650° F under strongly carburizing conditions. The study constitutes part of a program on high-temperature ceramic coatings which is being conducted at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

MATERIALS

The four alloys included in the study were Inconel and three 18-8 type stainless steels - namely, AISI Types 304, 321, and 347. Composition limits of these alloys are given in table 1.

The specimens, which consisted of 1- by $1\frac{1}{2}$- inch tabs sheared from sheets of 18-gage Inconel, 14-gage Type 304, and 16-gage Types 321 and 347, were cleaned by sandblasting. Six specimens of each alloy were left uncoated and six were coated. Each of the three coatings was applied to duplicate specimens of each alloy.

The three ceramic coatings selected were prepared by the National Bureau of Standards and designated A-417, A-19H, and A-520. These coatings, which are all being used commercially, were applied to the specimen by dipping, after which they were bonded to the alloy by firing in air to the proper maturing temperatures. The average thicknesses after firing were 0.0025 inch for A-417, 0.003 inch for A-19H, and 0.0022 inch for A-520.

The compositions of the three coatings, together with the details of application, are given in table 2.

TEST PROCEDURE

The work of Kahn, Oster, and Wachtell (reference 5) indicated that carbide precipitation could be produced with Type 321 stainless steel by pack carburizing. The resulting precipitation was of a type almost identical in appearance to that noted for the same alloy that had been in operation on an aircraft exhaust. Suitable equipment for pack or box carburizing was available and hence this method of carburizing was employed for the present study.

The carburizing was done in a Globar furnace having a capacity of $7\frac{3}{4}$ cubic feet. Duplicate specimens of each alloy in both the coated and uncoated condition were first packed with a commercial carburizing compound in an alloy box with inside dimensions of 3 by 4 by 5 inches. After centering the box in the furnace chamber, the temperature was raised slowly to one of the three selected temperatures (1350°, 1500°, or 1650° F) and held at that temperature for 4 hours. At the end of the 4-hour treatment, the box was removed from the furnace and allowed to cool in air.

After removal from the box, the coated specimens were examined under low magnification to detect any significant alteration of the coating. All 96 specimens were then sectioned for metallographic examination. Etching was done with cupric-picral-nital reagent. This reagent, which was the same as that used by Kahn, Oster, and Wachtell (reference 5), consisted of the following:

Concentrated nitric acid, ml	0.7
Concentrated hydrochloric acid, ml	17.5
Ethyl alcohol, ml	65.0
Water, ml	16.7
Picric acid, gram	0.8
Chalcanthite $(CuSO_4 \cdot 5H_2O)$, grams	6.7

RESULTS

Low-power microscopic examination revealed that the A-19H coating on all of the alloys contained shrinkage cracks; however, all were still intact. There was occasional spalling, but exposure of the base metal was nowhere observed. The higher treatment temperatures apparently caused some flow of the coating which tended to fill the cracks and leave a smoother surface.

The A-417 coatings appeared good after the 1350° F exposure. After the 1500° and 1650° F treatments, however, they were badly blistered, with large areas of the coating having spalled off, either during treatment or on cooling. But again, spalling did not expose the metal. Those areas which blistered and later spalled revealed an underlying layer with the characteristic bright green color of the A-417 coating.

The A-520 coatings carburized at 1350° F were completely covered with a thin copper film, a result presumably of the highly reducing atmosphere on the copper oxide in the coating. Also, some spalling had occurred during cooling. The same phenomena were observed on those treated at 1500° F, but the copper film was less extensive and spalling was almost negligible. This coating presented a wavy surface, particularly in areas where no copper film had formed. The A-520 coatings treated at 1650° F had no free copper film and did not spall, but the coating surface had a pronounced wrinkled appearance. No explanation is given for the anomalous effect of the reducing atmosphere on copper oxide at the higher temperatures.

Table 3 summarizes the depth of carbon penetration as indicated by carbide precipitation at grain boundaries and the condition of the coating for Types 304, 321, and 347 stainless steels after the various pack-carburizing treatments. Inconel showed no evidence of carbide precipitation under the conditions used and hence data on Inconel have been omitted from table 3.

Figures 1 and 2 are photomicrographs of sections taken through the surface of the three stainless steels after the carburizing treatments at 1500° and 1650° F, respectively. The upper picture in each case is the uncoated alloy while the lower picture is the same alloy that has been protected with A-19H. No carbide precipitation was noted with the Type 321 and Type 347 alloys after the carburizing treatment at 1350° F. The Type 304 steel did show the type of carbide precipitation that would be expected from an unstabilized steel after a sensitizing treatment of 4 hours at 1350° F. At the same time there was no evidence of a concentration of carbides near the surface such as would be expected if there had been an absorption of carbon.

Figure 3 is a curve of case depth plotted against temperature for Type 321 stainless steel as taken from the paper by Kahn, Oster, and Wachtell (reference 5). Points representing data from the present study are included for comparison.

DISCUSSION OF RESULTS

In the present investigation the techniques of Kahn, Oster, and Wachtell (reference 5) were followed. Pack carburizing was employed to

promote carbon absorption in the alloys and the same etchant was used to bring out carbides. Figure 3 shows that only fair agreement was obtained for the Type 321 alloy which was the only alloy studied by the aforementioned authors. There is good agreement at 1350° F but at 1500° F smaller case depths were obtained in the present study although a longer carburizing time was used. The cause of this discrepancy may be due to differences in the carburizing compounds or to minor differences in the steels.

A copper plating on the surface of the Type 321 steel was studied by Kahn, Oster, and Wachtell (reference 5) as a method of preventing carbon absorption during pack carburizing. It was found that if the plating was properly applied, the steel was effectively protected and it was the belief of these authors that the carbide precipitation which occurs under service conditions could be prevented by a coating of some impervious, heat-resisting substance, properly applied.

Table 3 and figures 1 and 2 indicate that ceramic coatings qualify for this purpose. Of the three coatings studied, A-19H proved to be the most effective in preventing carbon absorption under all test conditions, but it should be pointed out that pack carburizing represents an extremely severe carburizing condition. In operation, carburizing gases from high fuel-air ratios are common in aircraft exhaust systems, especially during take-off and during flight at high altitudes. However, even under the highest fuel-air ratios encountered, the carburizing conditions would probably never reach the severity encountered in pack carburizing. Also, in aircraft exhaust systems, high gas velocities may cause flow of the coated material if the coating lacks sufficient refractoriness. For both of these reasons, the pack-carburizing treatment cannot be considered as a suitable test for coating selection and, at the present time, it is believed that the only reliable criterion for establishing the superiority of one coating over another is by the service testing of coated exhaust parts.

No evidence of carbon pickup was noted for Inconel at any of the three carburizing temperatures when the specimens were examined after the cupric-picral-nital etch. Inconel is not susceptible to carbide precipitation and was included in the present study only to demonstrate its resistance to the test conditions.

The Type 304 steel, which is unstabilized, showed carbide precipitation throughout its entire structure at all three carburizing temperatures. However, at 1500° and 1650° F there was evidence of carbon absorption into the steel surface and this was evidenced by a greater amount of carbide formation. As shown in figures 1 and 2, the line of demarcation representing the case depth due to carbon absorption was poorly defined, but the photomicrographs nevertheless illustrate that some carbon absorption has occurred with the uncoated steel. The same

figures show that this absorption has been prevented when the steel was protected with the A-19H coating.

According to Hubbell (reference 6) the corrosion resistance of stainless steels used in exhaust systems is not materially reduced by the heavy network of carbides that forms under severe operating conditions. This view is not in keeping with the findings of Rosenberg and Darr (reference 7), Kahn, Oster, and Wachtell (reference 5), Promisel (reference 8), nor with a 1948 report of the American Society for Metals Subcommittee on Wrought Heat-Resisting Alloys (reference 9). The mass of evidence therefore seems to be that once the austenitic steel becomes sensitized, whether by carbon absorption or by improper stabilization, the alloy is subject to intergranular attack by the corrosive influences that are present in the exhaust gases. With properly stabilized steels, the present study indicates that a ceramic coating can be expected to inhibit carbon absorption and thereby prolong the life of the alloy by retarding intergranular corrosion.

It is also possible that the ceramic coatings might permit the use of an unstabilized steel in exhuast-system service. With an unstabilized steel, a carbide network would form from the temperature treatment alone, but the coating would tend to seal the surface and thus prevent corrosion of the sensitized grain boundaries. Clark and Freeman (reference 10) have pointed out that sensitization, of itself, does not necessarily have an adverse effect on the unstabilized stainless steels used in the petroleum industry. It is not too improbable, therefore, that these same steels might be suitable for exhaust service if they could be protected from intergranular corrosion at grain boundaries caused by the corrosive components present in the exhaust gases. The more serious of these corrosive components are believed to be lead compounds and that intergranular attack can be induced by the deposition of lead compounds has been reported by Buck (reference 11). An earlier investigation by the National Bureau of Standards (reference 4) demonstrated that lead bromide in a vapor state can be highly corrosive on heat-resisting alloys and also demonstrated that ceramic coatings are effective in preventing the attack. Thus, it seems possible that an unstabilized steel, such as Type 304, when protected with a suitable ceramic coating might give service in an exhaust system that would be equally as good as the more expensive stabilized alloys. Service tests would of course be necessary to establish whether comparable service from the coated unstabilized steel could, in fact, be achieved.

It is not the purpose of the present paper to point out the need for protecting 18-8 steels against carbon absorption but only to demonstrate the feasibility of protecting against such absorption by use of a ceramic coating. The fact that ceramic coatings have been applied to exhaust parts and have performed satisfactorily indicates that they can be expected to withstand the operating conditions. Therefore, if

in any given application carbon absorption appears to be contributing to early failures of the stainless-steel parts, the use of a suitable ceramic coating might reasonably be expected to prolong its life.

CONCLUDING REMARKS

It has been demonstrated that the application of a ceramic coating can inhibit the carbon absorption that occurs when both stabilized and unstabilized austenitic stainless steels are box carburized for 4 hours at temperatures above 1350° F. The ceramic coating apparently seals the surface of the steel from the carburizing gases and thus prevents carbon pickup and the resulting precipitation of carbides at or near the grain boundaries.

In exhaust systems, the coating may be expected to perform a dual function with respect to carbon. First, it tends to prevent carbon from being absorbed into the steel and, second, if sensitization of the steel should occur during operation because of improper stabilization of the carbon initially present, the coating tends to prevent intergranular corrosion by sealing the sensitized grain boundaries from contack with the corrosive components present in the exhaust gases.

National Bureau of Standards
Washington, D.C., March 13, 1951

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TABLE 1.- COMPOSITION LIMITS OF THREE STAINLESS STEELS AND INCONEL

Alloy	Percent by weight of -							
	C (a)	Mn (a)	P (a)	S (a)	Si (a)	Cr	Ni	Other
AISI Type 304	0.08	2.00	0.040	0.030	1.00	18.0-20.0	8.0-11.0	
AISI Type 321	.08	2.00	.040	.030	1.00	17.0-19.0	8.0-11.0	Ti[b](5 × C)
AISI Type 347	.08	2.00	.040	.030	1.00	17.0-19.0	9.0-12.0	Cb[b](10 × C)
Inconel	.15	1.0	-----	.02	.5	12.0-15.0	[b]75.0	Fe, [a]9.0 Cu, [a]0.5

[a]Max.
[b]Min.

TABLE 2.- COMPOSITION AND APPLICATION DATA FOR CERAMIC

COATINGS A-19H, A-417, AND A-520

(a) Coating compositions

Ingredient	Parts by weight in -		
	A-19H (2)	A-417	A-520
Frit 11	100.0	----	------
Frit 331	------	70.0	90.0
Chromic oxide	------	30.0	------
Cupric oxide	------	----	10.0
Black cobalt oxide	1.0	----	------
Calcined alumina[1]	25.0	----	------
Enameling clay	10.0	5.0	6.0
Citric acid	.05	----	------
Sodium nitrite	------	----	.025
Water	50.0	48.0	45.0

[1]Obtained from Aluminum Ore Co., East St. Louis, Ill., A-1 grade.

[2]Differs from regular A-19 in that none of the softer frit (no. 1) is used.

(b) Application data

Specifications	Coating		
	A-19H	A-417	A-520
Milling fineness[1]	1.0	0.4	0.3
Specific gravity of slip for dipping	1.60-1.62	1.78-1.82	1.85-1.90
Recommended fired thickness, mils	2-3	1.5-2.5	1.5-2.5
Firing temperature, °F	1650	1850	1750

[1]Grams on a No. 200 U. S. Standard Sieve using a 50-ml sample of slip.

(c) Computed oxide composition of frits

Oxide	Percent by weight in -	
	Frit 11	Frit 331
SiO_2	49.2	38.0
Al_2O_3	7.7	----
B_2O_3	17.4	6.5
Na_2O	15.2	----
K_2O	4.5	----
BaO	----	44.0
CaO	2.9	4.0
ZnO	----	5.0
BeO	----	2.5
F_2	.4	----
CoO	.6	----
NiO	.7	----
MnO_2	1.4	----
	100.0	100.0

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TABLE 3.- DEPTH OF CARBON PENETRATION AND CONDITION OF COATINGS FOR AISI TYPES 304, 321, AND 347 STAINLESS STEELS AFTER PACK CARBURIZING FOR 4 HOURS AT 1350°, 1500°, AND 1650° F

Coating	Carburizing temperature (°F)	AISI Type 304		AISI Type 321		AISI Type 347	
		Case depth (in.) (a)	Condition of coating (b)	Case depth (in.) (a)	Condition of coating (b)	Case depth (in.) (a)	Condition of coating (b)
None	1350	0	---	0	-----	0	---
A-19H		0	C	0	C	0	C
A-417		0	I	0	I	0	I
A-520		0	M,S	0	M,S	0	M,S
None	1500	[c]0.020	---	0.003	-----	0.003	---
A-19H		0	C	0	C	0	C
A-417		[c].015	B,S	0	B,S	[d].003	B,S
A-520		[c].015	M,W	0	M,S,W	.001	M,W
None	1650	[c]0.030	---	0.004	-----	0.007	---
A-19H		0	I	0	C	0	C
A-417		0	I	0	I	0	I
A-520		[c].015	W	.001	W	0	W

[a]Represents average depth to which alloy showed carbide precipitation at grain boundaries. Determined microscopically after etching with cupric-picral-nital reagent.

[b]Letter symbols denote following coating conditions:

- I coating intact; no major change in appearance
- B coating blistered
- M metallic copper at coating surface
- C cracks in coating but not extending to alloy surface
- S coating spalled but did not expose alloy surface
- W wrinkled appearance of coating surface

[c]Carbide precipitation occurred throughout structure of AISI Type 304 alloy at 1500° and 1650° F but was more intense near surface. Because of gradual change in degree of precipitation inward from surface, case depth is rough approximation only.

[d]Localized.

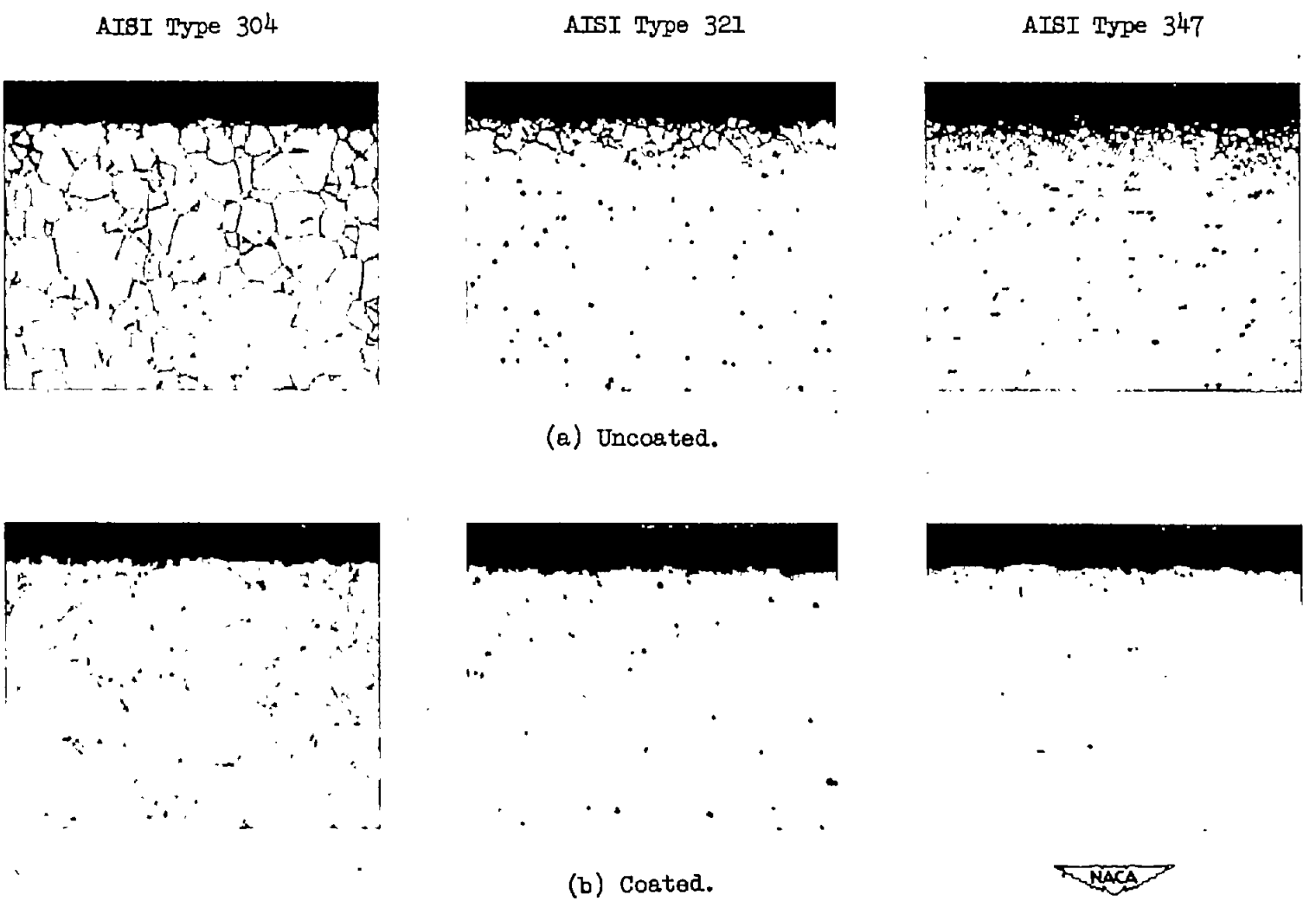

Figure 1.- Photomicrographs (X100, cupric-picral-nital etch) of sections through the surface of both coated (A-19H) and uncoated stainless-steel specimens after box carburizing for 4 hours at 1500° F.

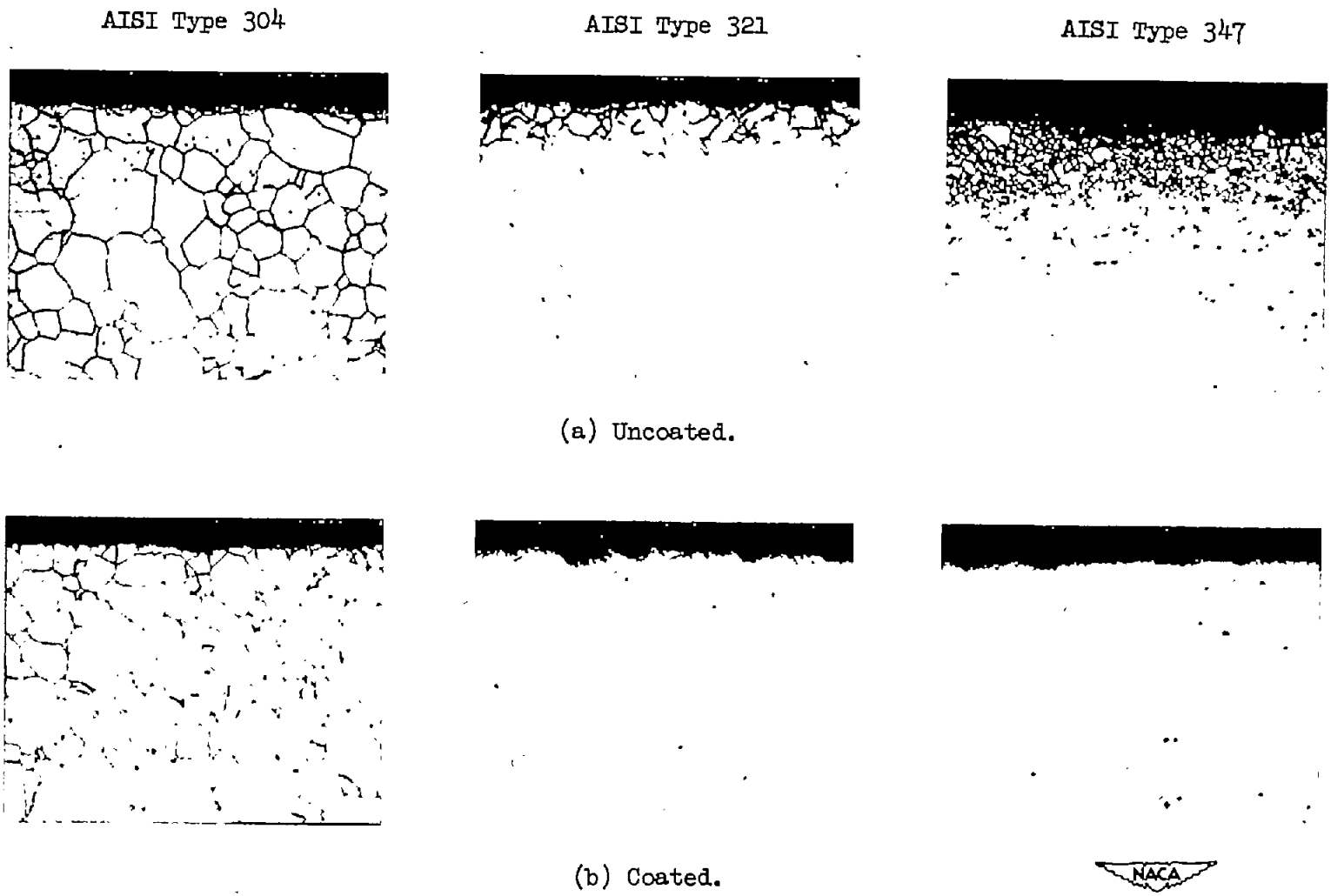

Figure 2.- Photomicrographs (X100, cupric-picral-nital etch) of sections through the surface of both coated (A-19H) and uncoated stainless-steel specimens after box carburizing for 4 hours at 1650° F.

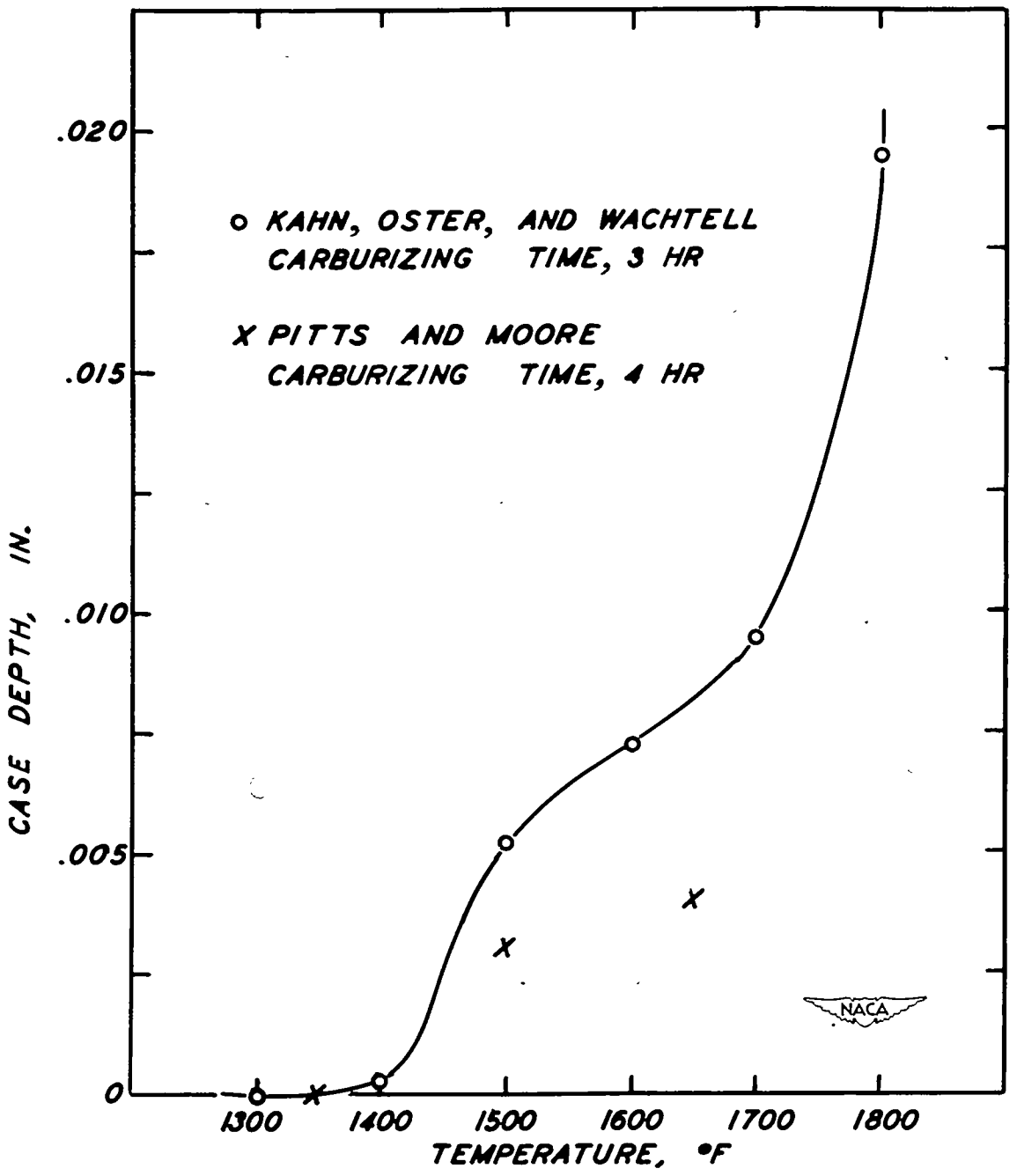

Figure 3.- Case depth plotted against temperature for AISI Type 321 stainless steel after box carburizing for the times indicated. Case depth represents average depth to which alloy showed carbide precipitation at grain boundaries.

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