NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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HIGH-TEMPERATURE ATTACK OF VARIOUS COMPOUNDS ON FOUR HEAT-RESISTING ALLOYS

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SUMMARY

In the preparation of suitable protective ceramic coatings for heat-resisting alloys, indications were that certain of the common coating ingredients were reacting with the alloys and thereby limiting the life of the coated specimens at the temperatures of operation. This effect was acute in the case of Hastelloy B alloy. In order to obtain a preliminary indication of the identity of the ingredients that were causing the difficulty, a total of 61 compounds, all of which contained elements that have been or might logically be used in coatings, were tested by placing a small pulverized sample of each compound on the cleaned surface of an alloy specimen and heating in air for 17 hours at 1500° F. Visual examinations were then made to determine the degree of attack, if any. The results indicate: (1) That Hastelloy B is much more susceptible to heavy attack by corrosive coating ingredients when heated in air than the other three alloys studied (S-816, S-590, and Haynes Stellite No. 21), (2) that of the components that reacted with the alloys, the alkalies, lead compounds, and some of the alkaline earths gave the most pronounced attack, (3) that the attack of the alkalies on Hastelloy B does not occur in a carbon-dioxide or a helium atmosphere, and (4) that it should be possible to prepare coating compositions which will permit the ceramic coating of high-molybdenum alloys to prolong their life under operating conditions which now produce early deterioration.

INTRODUCTION

It is logical that some or all alloys, when protected with heat-resisting, tightly adherent, ceramic coatings might be operated safely at higher gas temperatures than can be endured for a sufficiently long period by the uncoated alloys. The potential usefulness of such a coating is, of course, greater for alloys which are readily attacked by atmospheres encountered in service.

One of the problems in the development of stable coatings for continued use at high temperature is the preparation of compositions that do not harmfully react with the alloys. The early attempts to apply ceramic coatings to Hastelloy B alloy in this study made it obvious that such reaction was occurring. The elimination of this reaction seemed possible, however, by identifying the reactive ingredients and excluding them from the coating.

The present report is concerned with a study of the attack of various compounds containing coating ingredients, or possible coating ingredients, on the high-molybdenum alloy, Hastelloy B, and also on the following alloys, which were included for purposes of comparison: S-816, S-590, and Haynes Stellite No. 21 (a Vitallium type).

MATERIALS, TEST PROCEDURE, AND RESULTS

The compositions of the four alloys included in the study are listed in table I in which the source of the alloys in each case is also indicated.

The various compounds which were tested for reaction with the alloys were procured from different sources and were not, in all cases, chemically pure. The approximate purity of most of the compounds is given in table II which also shows the results of the tests.

Specimens of Hastelloy B were prepared by cutting scrap turbine blades into sections approximately 1 square inch in area and 1/8 inch thick. The other alloys were available in sheet form, and specimens were prepared by shearing sections approximately 1 inch square.

The metal specimens were marked for identification by numbers stamped on the back and were given a light sandblast immediately before a test was started. In the first tests, the specimens were bedded in aluminum oxide on a stainless-steel rack, and approximately 1 gram of the test material was placed in a pile in the center of each specimen. In later tests the specimens were placed directly on the stainless steel without the use of any bedding material. Usually 12 or 16 specimens were tested at one time. Specimens of all four alloys were treated simultaneously with each compound.

The stainless-steel rack containing the specimens was placed in a small electric furnace, the temperature of which was maintained at $1500^{\circ} \pm 10^{\circ}$ F. At the end of the 17-hour test period, the specimens were removed and allowed to cool. They were then examined visually, with and without the aid of a binocular microscope, and any evidence of attack noted. After a light sandblast, which removed the scale produced by heating, they were again examined for pitting or any other irregularity of surface.

The attack, when it occurred, was usually more pronounced at the edges of the pile and was evidenced by excessive production of scale, discoloration, or, in severe cases, deep etching or pitting of the alloy.

Quantitative measurement of attack was not attempted because the varied forms in which it took place made it difficult to obtain comparable data and because for the purposes of this study qualitative data appeared to be adequate.

Table II summarizes the data obtained from these heating tests. Out of 61 compounds, only 23 showed no attack on Hastelloy B, while the number showing no attack on S-816 was 40; on S-590, 41; and on Haynes Stellite No. 21, 33. In general, the lead compounds and alkali salts were most corrosive on the alloys although some of the alkaline earth compounds also showed considerable attack. With 25 of the 61 compounds the attack was more pronounced on Hastelloy B than on the other three alloys, and several of the salts which attacked the Hastelloy B severely were without effect on the other alloys. Heavy attack occurred on Hastelloy B with 18 compounds, on Haynes Stellite No. 21 with 3 compounds, and on S-590 and S-816 with only 1 compound.

It will be noted from table II that some of the materials showed severe attack on Hastelloy B even though there was no evidence of melting of the compound.

Figures 1 to 5 are photographs of specimens showing the effect of five common compounds on the four alloys after heating for 17 hours at 1500° F in an air atmosphere. Four of these compounds (sodium carbonate, potassium carbonate, litharge, and lead bromide) are of a type that gave appreciable attack under the test conditions while one compound (boric acid) gave relatively no attack. All five photographs were taken at a magnification of approximately 1.5X which suitably illustrates heavy and moderate attack but which fails to bring out the discoloration and staining associated with slight attack.

All the data listed in table II were obtained in an air atmosphere. In order to determine whether similar attack would occur under the same heating conditions in atmospheres other than air, tests were made with 16 compounds on Hastelloy B in atmospheres of carbon dioxide and of helium. When making these tests, the specimens with the compound in position were placed in a gastight coated-steel muffle, $2\frac{1}{8}$-inch inside diameter by 23 inches long. This muffle was then positioned in a small electric furnace so that one end of the muffle protruded several inches from the furnace door. Before heating, the muffle was first flushed with the gas after which a steady flow was maintained under a pressure of 2 inches of water throughout the heating period. After raising the specimens to 1500° F and holding for 17 hours at that temperature, they were cooled in the furnace, removed, and examined. The results, summarized in table III, indicate that (1) the alkalies do not attack Hastelloy B in atmospheres of helium or carbon dioxide, (2) the litharge, lead oxide (red lead), and barium carbonate are corrosive in both atmospheres, and (3) the calcium carbonate, cobalt oxide, and sodium aluminate are corrosive in carbon dioxide but not in helium.

ANALYSIS AND DISCUSSION

Table II shows that most of the alkali salts are strongly corrosive toward the alloys at 1500° F in an air atmosphere. Normally, ceramic coatings contain substantial amounts of alkali and the results of this study suggest that by omitting the offending ingredients coatings which do not attack Hastelloy B and other alloys can be compounded.

One of the more important observations in the present study is the finding that the alkalies do not attack Hastelloy B at 1500° F in an atmosphere of carbon dioxide or helium. This fact, together with the observation that the attack in air is more pronounced near the edge of the pile where air is most readily available to the compound-alloy interface, indicates that the reaction of many of the compounds with the alloys occurs primarily by a reaction not with the alloy itself but with the oxide film which normally forms when the alloy is heated in air. These oxide films consist of complex combinations of the oxides of the various metals present in the alloy and the tightness of the oxide layer may be very much altered by reaction with other materials with which they come in contact. In this connection, Pheil (reference 1) states that the protective scale which forms on chromium-containing alloys for heating elements may be destroyed if any alkalies are present in the refractories, and this mechanism may easily bring about destruction of the element.

The finding that little or no attack by the alkalies occurs in the absence of air indicates that if the ceramic coatings were quite impermeable the alkalies might then be incorporated into them without ill effects. However, the smallest break in the coating would, under these conditions, permit the beginning of serious attack. Also rapid attack might be expected at any point of junction of coated and uncoated surfaces, such as at the end of a coated turbine blade. In view of these dangers, it appears preferable to have, in all cases, coatings which are substantially inert toward the oxide films which form on the alloys.

Table III shows that, even in an inert atmosphere of pure helium, litharge, red lead, and barium carbonate still attacked the Hastelloy B. The mechanism of the attack for these compounds, however, was different from that of the alkalies and alkaline earths. Inspection of specimens treated with litharge and red lead after heating in the helium atmosphere showed evidence of free lead. The attack was therefore believed to have been caused by reduction of the lead compound by the alloy, followed by an alloying of the free lead thus formed with some or all the phases present in the Hastelloy B. Barium carbonate is believed to have caused attack by some similar mechanism.

One immediate application of the results of the present study would be in stressing the importance of appropriate fuel selection for gas-turbine installations. Indications are that even traces of alkali in the fuel oil might prove corrosive on the alloy parts operating at high temperature and highly so on alloys of the Hastelloy B type. It is, of course, recognized that the possibility of alkali in kerosene is not great but it could conceivably be present on occasion if poor refinery practices were followed. Also if heavier fuels were used at some time in the future, there would be a definite danger of contamination by alkali.

Table II shows that the attack obtained with two sulfides, cadium sulfide and chalcopyrite, was moderately heavy at least in the case of Hastelloy B. The effect of sulfur gases on heat-resisting alloys has already been described in an earlier report (reference 2) and the importance of maintaining the sulfur content of kerosene at the lowest possible value is believed obvious.

Table II shows the lead compounds as a rule to be very corrosive on the alloys. Small quantities of lead bromide are normally present in leaded aviation fuels, and when using a fuel of this type in a gas turbine an accelerated scaling rate might well be expected. If lead oxide were formed during combustion the attack, as is indicated in table II, would in most cases be even more rapid.

CONCLUSIONS

The following conclusions may be drawn from a study of the attack of various compounds on Hastelloy B, S-816, S-590, and Haynes Stellite No. 21 alloys when heated at 1500° F for 17 hours:

1. Of four alloys tested, Hastelloy B was found to be the most susceptible to heavy attack by the more corrosive coating ingredients when heated in air.

2. In general, the compounds most corrosive toward the four alloys tested were the alkalies, lead compounds, and some of the alkaline earths.

3. The attack on Hastelloy B by alkalies, which was very pronounced in an air atmosphere at 1500° F, did not take place under the same heating conditions in atmospheres of carbon dioxide or helium.

4. From the results obtained it should be possible to prepare coating compositions and techniques of application which will permit the ceramic coating of high-molybdenum alloys to prolong their life under operating conditions which now produce early deterioration.

National Bureau of Standards
Washington, D. C., September 25, 1947

REFERENCES

1. Pheil, L. B.: Practical Aspects of the Oxidation and Scaling of Nonferrous Alloys. P. 95 in Review of Oxidation and Scaling of Heated Solid Metals, Great Britain Dept. of Sci. and Ind. Res., His Majesty's Stationery Office, Adastral House (Kingsway, London), W.C.2., 1935.

2. Harrison, W. N., Moore, D. G., and Richmond, J. C.: Review of an Investigation of Ceramic Coatings for Metallic Turbine Parts and Other High-Temperature Applications. NACA TN No. 1186, 1947.

TABLE I.- COMPOSITION, SOURCE, AND FORM OF FOUR ALLOYS

Alloy	Source	Form (a)	Chemical composition (percent) (b)									
			Cr	Ni	Co	Mo	W	Cb	Fe	C	Mn	Si
S-816	Allegheny Ludlum Steel Corp.	0.050-in. sheet	20.26	19.90	43.45	4.16	4.65	3.63	2.58	0.30	0.50	0.45
S-590	Allegheny Ludlum Steel Corp.	0.050-in. sheet	19.15	19.13	19.63	3.95	4.10	4.19	[c]27.93	.47	.69	.76
Hastelloy B	Haynes Stellite Company	$\frac{1}{8}$-in. slabs cut from turbine blades	-----	65.1	-----	28.6	----	----	4.7	.05	.59	.19
Haynes Stellite No. 21	Haynes Stellite Company	0.050-in. sheet	25.0	-----	69.0	6.0	----	----	-----	.24	----	----

[a] The S-816 and S-590 materials were hot-rolled at 2150° to 2200° F, annealed 25 min at 2180° F, air-cooled, sandblasted, scrubbed, cold-rolled one pass, buckled, and sheared. Hastelloy B was cut from surplus cast turbine blades. Information regarding preparation and treatment of Haynes Stellite No. 21 sheet was not available.

[b] Compositions of S-816 and S-590 are for heats supplied by manufacturer. Compositions of Hastelloy B and Haynes Stellite No. 21 are not for actual heats used but are typical of these alloys. Analysis in each case was supplied by the manufacturer.

[c] By difference.

TABLE II.- ATTACK ON FOUR HEAT-RESISTING ALLOYS BY VARIOUS COMPOUNDS AFTER 17 HOURS HEATING IN AIR AT 1500° F

Compound	Chemical symbol	Purity	Fusibility at 1500° F (a)	Attack after 17 hr in air at 1500° F (b)			
				S-816	S-590	Hastelloy B	Haynes Stellite No. 21
Aluminum oxide	Al_2O_3	^{c}99%	3	N	N	N	N
Aluminum phosphate	$AlPO_4$	Tech.	2	M	S	H	N
Arsenous oxide	As_2O_3	Tech.	1	N	N	N	N
Barium carbonate	$BaCO_3$	Tech.	2	N	N	H	S
Barium chloride	$BaCl_2 \cdot 2H_2O$	C.P.	2	S	S	M	M
Barium hydroxide	$Ba(OH)_2 \cdot 8H_2O$	C.P.	1	S	S	S	S
Barium nitrate	$Ba(NO_3)_2$	C.P.	1	N	N	N	N
Barium sulfate	$BaSO_4$	C.P.	3	S	S	M	M
Beryllium oxide	BeO	C.P.	3	N	N	N	N
Bismuth trioxide	Bi_2O_3	C.P.	1	M	M	S	M
Bone ash	Impure $Ca_3(PO_4)_2$	Com.	3	N	N	N	N
Borax	$Na_2B_4O_7 \cdot 10H_2O$	Tech.	1	N	N	H	S
Boric acid	H_3BO_3	C.P.	1	S	S	M	S
Cadmium acetate	$Cd(C_2H_3O_2)_2 \cdot 3H_2O$	C.P.	1	N	N	M	-
Cadmium sulfide	CdS	C.P.	1	N	N	M	N
Cadmium tungstate	$CdWO_4$	C.P.	1	N	N	H	H
Calcium carbonate	$CaCO_3$	C.P.	3	S	N	H	N
Calcium chloride	$CaCl_2$	C.P.	1	M	S	S	H
Calcium sulfate	$CaSO_4 \cdot 2H_2O$	C.P.	3	N	N	N	N
Chalcopyrite	$CuFeS_2$	Com.	3	H	M	H	S
Chromic oxide	Cr_2O_3	C.P.	3	N	N	M	S
Cobalt oxide	CoO	C.P.	2	N	N	H	N
Cryolite	Na_3AlF_6	Com.	1	S	S	H	M
Cupric oxide	CuO	C.P.	1	N	N	S	N
Derry spar	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	Com.	3	N	N	N	N
Ferric oxide	Fe_2O_3	C.P.	3	S	S	N	S
Fluorspar	CaF_2	Com.	2	S	N	M	N
Lanthanum nitrate	$La(NO_3)_3 \cdot 6H_2O$	C.P.	1	N	N	N	N
Lanthanum oxide	La_2O_3	C.P.	3	N	N	N	N
Lead bromide	$PbBr_2$	C.P.	2	S	M	N	S
Lead carbonate (white lead)	$2PbCO_3 \cdot Pb(OH)_2$	C.P.	2	M	S	M	M
Lead chromate	$PbCrO_4$	C.P.	1	N	N	H	N
Lead oxide (red lead)	Pb_3O_4	C.P.	2	M	M	H	H
Litharge	PbO	Tech.	2	M	M	H	S
Lithium carbonate	Li_2CO_3	U.S.P.	1	M	M	M	S
Magnesium carbonate	$MgCO_3$	Tech.	3	N	N	N	N
Magnesium oxide	MgO	Tech.	3	N	N	H	N
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	C.P.	1	N	N	N	N
Manganese dioxide	MnO_2	C.P.	3	N	N	N	N
Molybdenum trioxide	MoO_3	C.P.	1	N	S	N	N
Nepheline seyenite	$0.75Na_2O \cdot 0.25K_2O \cdot 1.1Al_2O_3 \cdot 4.5SiO_2$	Com.	3	N	N	N	S
Nickel oxide	NiO	C.P.	3	N	N	M	N
Oxford crystal spar	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	Com.	3	N	N	N	N
Potassium alum	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	C.P.	1	N	N	H	N
Potassium carbonate	K_2CO_3	A.C.S.	1	M	M	H	S
Potassium dichromate	$K_2Cr_2O_7$	Reagent	1	N	N	S	N
Silicon dioxide	SiO_2	Com.	3	N	N	N	N
Sodium aluminate	$NaAlO_2$	Reagent	1	M	H	H	M
Sodium antimonate	$2NaSbO_3 \cdot 7H_2O$	C.P.	3	N	N	S	S
Sodium carbonate	Na_2CO_3	Tech.	1	N	M	H	S
Sodium pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	C.P.	1	M	S	H	S
Sodium tungstate	Na_2WO_4	C.P.	1	N	N	H	S
Strontium carbonate	$SrCO_3$	C.P.	3	N	N	H	N
Strontium sulfate	$SrSO_4$	C.P.	1	N	N	M	N
Thorium oxide	ThO_2	C.P.	3	N	N	N	N
Tin oxide	SnO_2	C.P.	3	N	N	N	N
Titanium dioxide	TiO_2	C.P.	3	S	N	S	S
Wollastonite	$CaSiO_3$	Com.	3	N	N	N	N
Zinc oxide	ZnO	Tech.	3	N	N	N	N
Zinc phosphate	$Zn_3(PO_4)_2$	C.P.	3	N	N	S	-
Zirconium dioxide	ZrO_2	C.P.	3	N	N	N	N

[a] Numbers refer to degree of fusibility. Number 1 indicates compound has melted or sublimed during test; while 2 refers to a sintering action only; and 3 indicates that neither melting nor sintering occurred at the test temperature. Fusing with oxide scale may in some cases have caused greater fusibility than might otherwise be expected from reported melting points.

[b] Letter symbols refer to degree of attack. N refers to no visible attack; S, to a slight attack as evidenced by discoloration or staining; M, to moderate attack as distinguished by somewhat more scale formation than normal with some shallow pitting; and H, to heavy attack as evidenced by excessive scale formation accompanied by deep pitting and etching of alloy surface.

[c] Aluminum Ore Co. number A-1. Contains 0.6 percent sodium oxide (Na_2O).

TABLE III.- ATTACK OF 16 COMPOUNDS ON HASTELLOY B IN AIR, CARBON-DIOXIDE, AND HELIUM ATMOSPHERES AFTER 17 HOURS HEATING AT 1500° F

Compound (1)	Atmosphere (2)		
	Air	Carbon dioxide	Helium
Barium carbonate	H	M	S
Borax	H	N	N
Calcium carbonate	H	M	N
Cobalt oxide	H	S	N
Cryolite	H	N	N
Fluorspar	M	N	N
Lead chromate	H	N	N
Lead oxide (red lead)	H	M	M
Lepidolite	H	N	N
Litharge	H	M	M
Magnesium oxide	H	N	N
Potassium alum	H	N	N
Potassium carbonate	H	N	N
Sodium aluminate	H	S	N
Sodium carbonate	H	N	N
Sodium tungstate	H	N	N

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[1] See table II for composition and purity.

[2] Attack designations same as table II - that is, H, heavy; M, moderate; S, slight; and N, none.

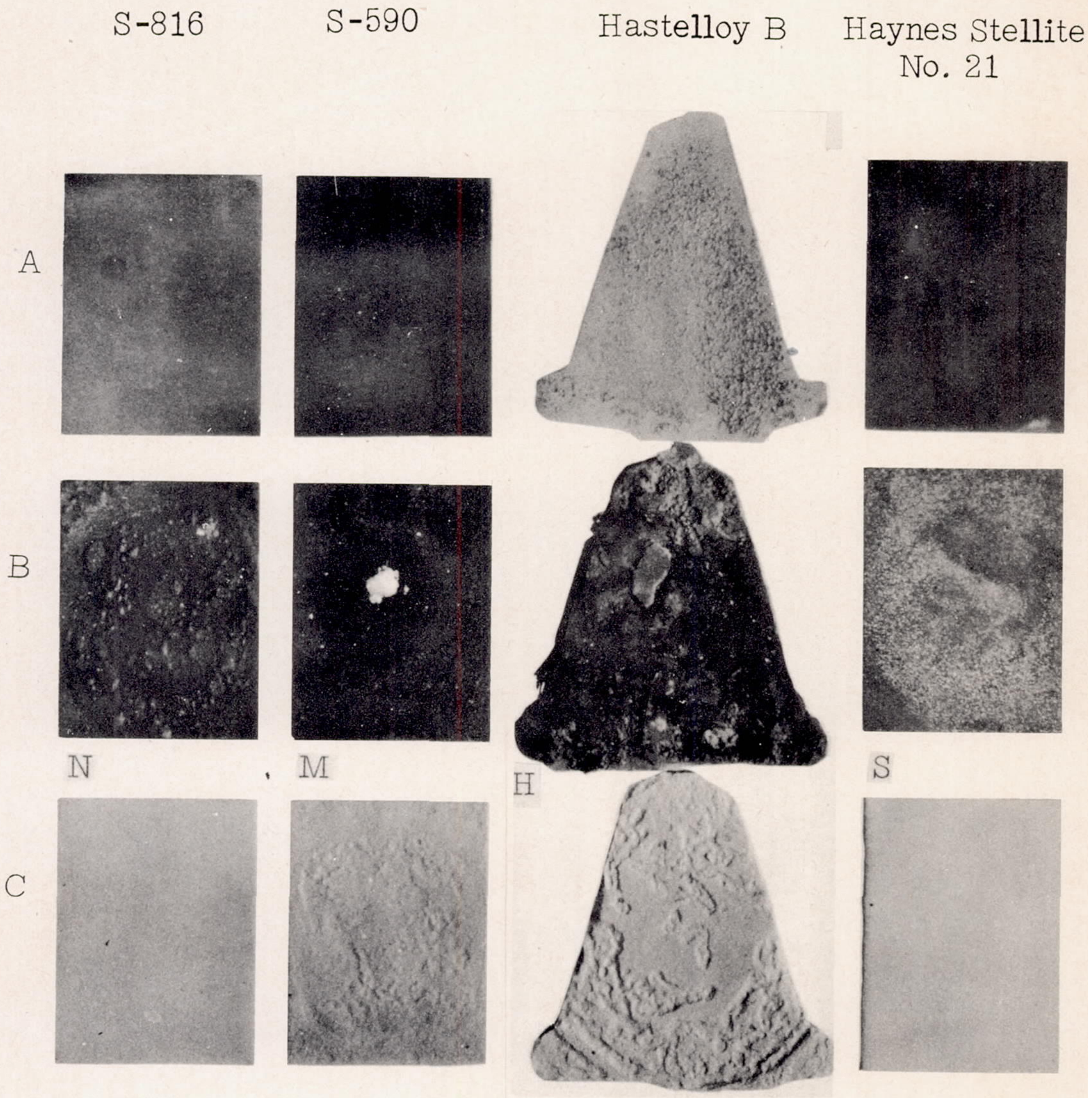

Figure 1.- Specimens after heating for 17 hours in air at 1500° F. Row A, specimens heated without added material. Row B, specimens on which 1 gram of sodium carbonate was placed before heating and not disturbed after removal from furnace. Row C, specimens treated same as row B except for light sandblasting to remove scale. Letters between two bottom rows indicate attack ratings as described in table II. (Magnification, 1.5X.)

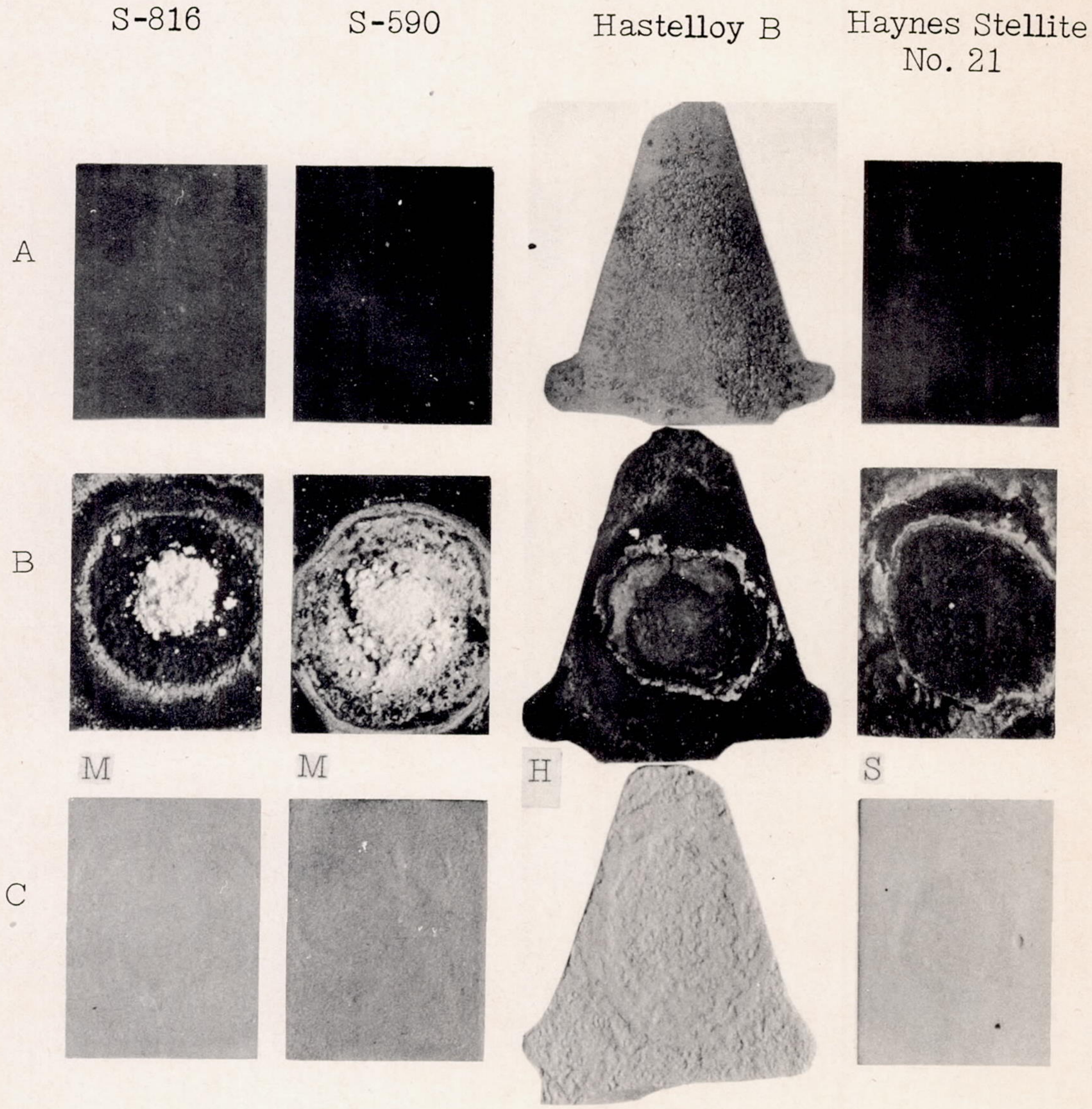

Figure 2.- Specimens after heating for 17 hours in air at 1500° F. Row A, specimens heated without added material. Row B, specimens on which 1 gram of potassium carbonate was placed before heating and not disturbed after removal from furnace. Row C, specimens treated same as row B except for light sandblasting to remove scale. Letters between two bottom rows indicate attack ratings as described in table II. (Magnification, 1.5X.)

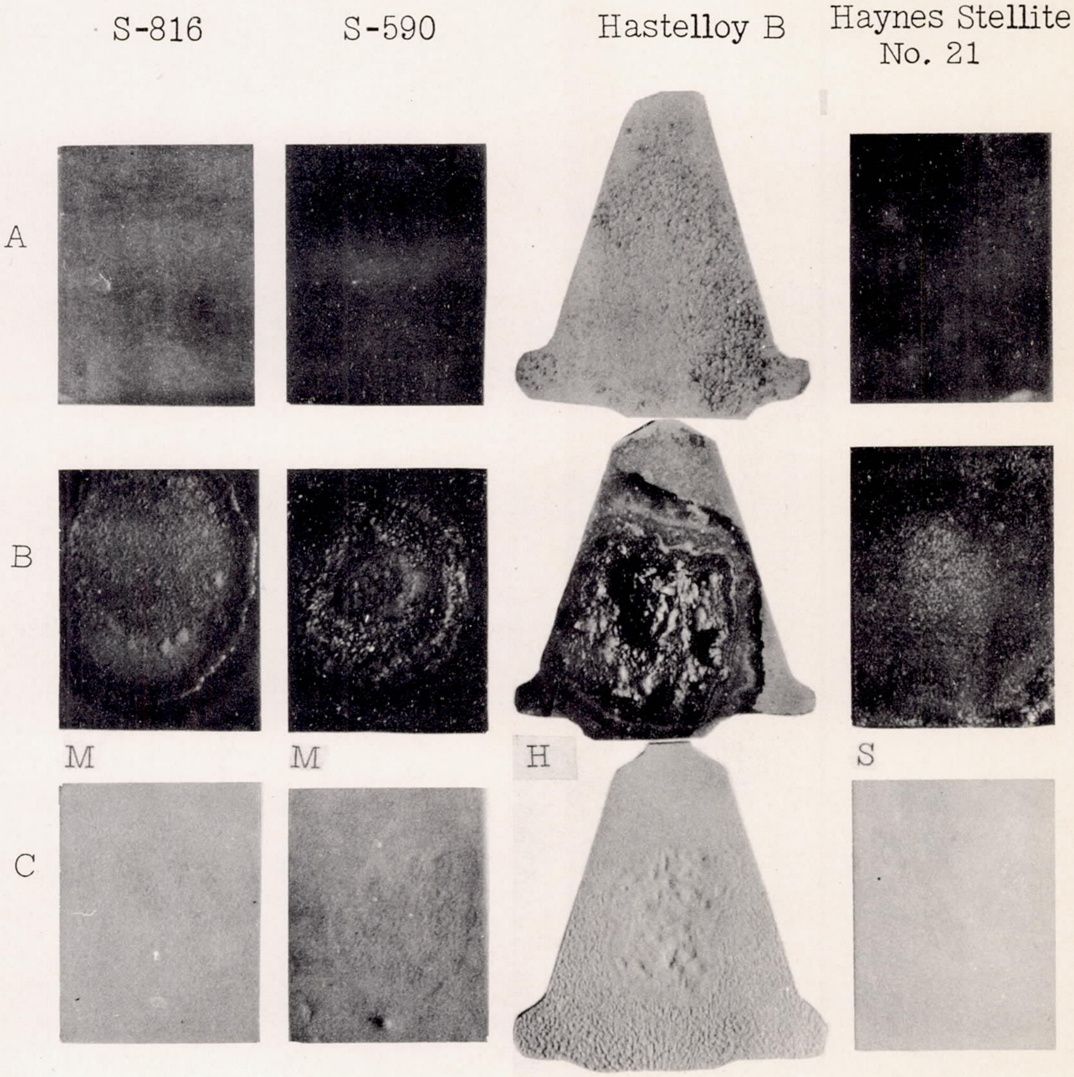

Figure 3.- Specimens after heating for 17 hours in air at 1500° F. Row A, specimens heated without added material. Row B, specimens on which 1 gram of litharge was placed before heating and not disturbed after removal from furnace. Row C, specimens treated same as row B except for light sandblasting to remove scale. Letters between two bottom rows indicate attack ratings as described in table II. (Magnification, 1.5X.)

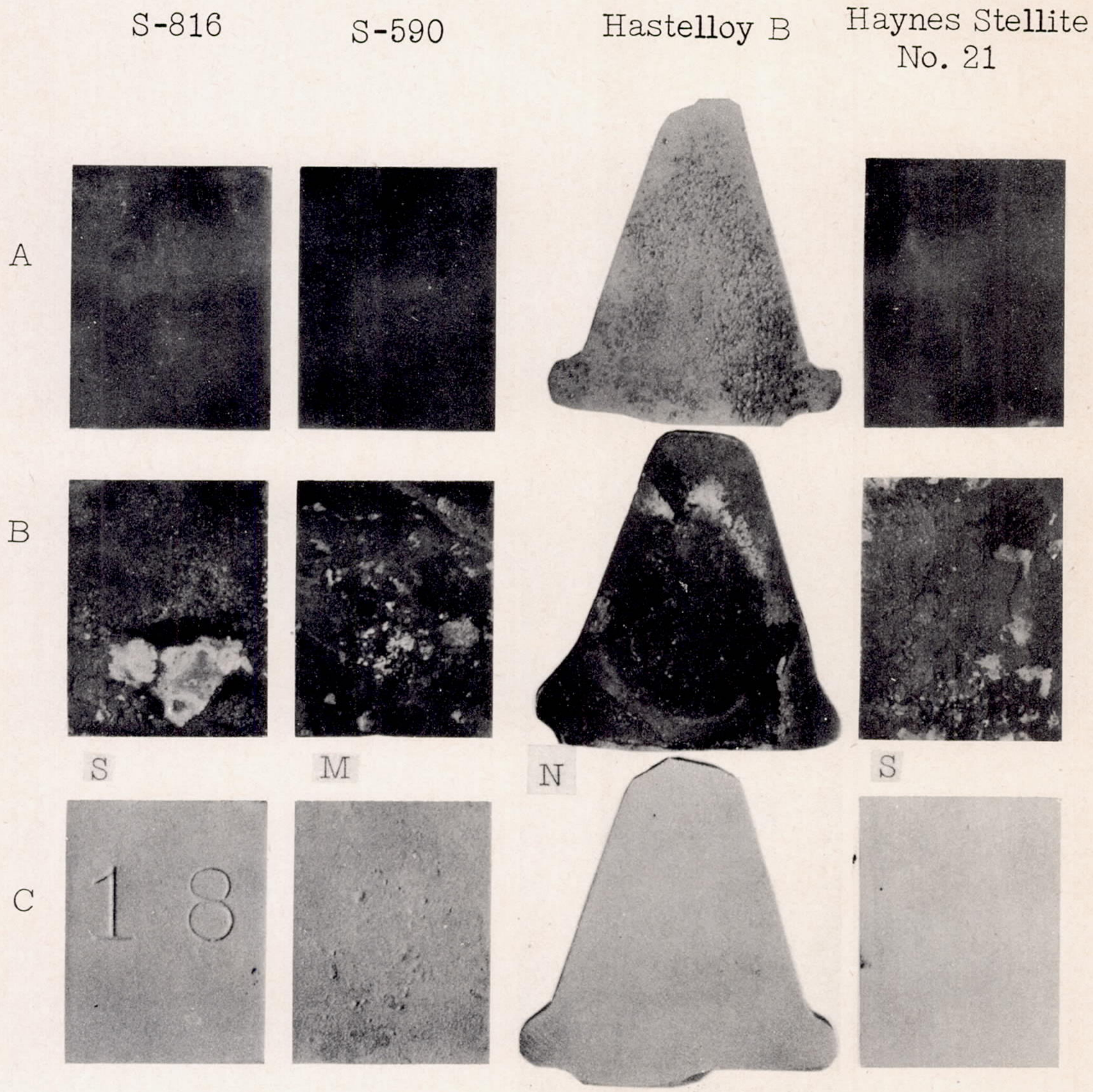

Figure 4.- Specimens after heating for 17 hours in air at 1500° F. Row A, specimens heated without added material. Row B, specimens on which 1 gram of lead bromide was placed before heating and not disturbed after removal from furnace. Row C, specimens treated same as row B except for light sandblasting to remove scale. Letters between two bottom rows indicate attack ratings as described in table II. (Magnification, 1.5X.)

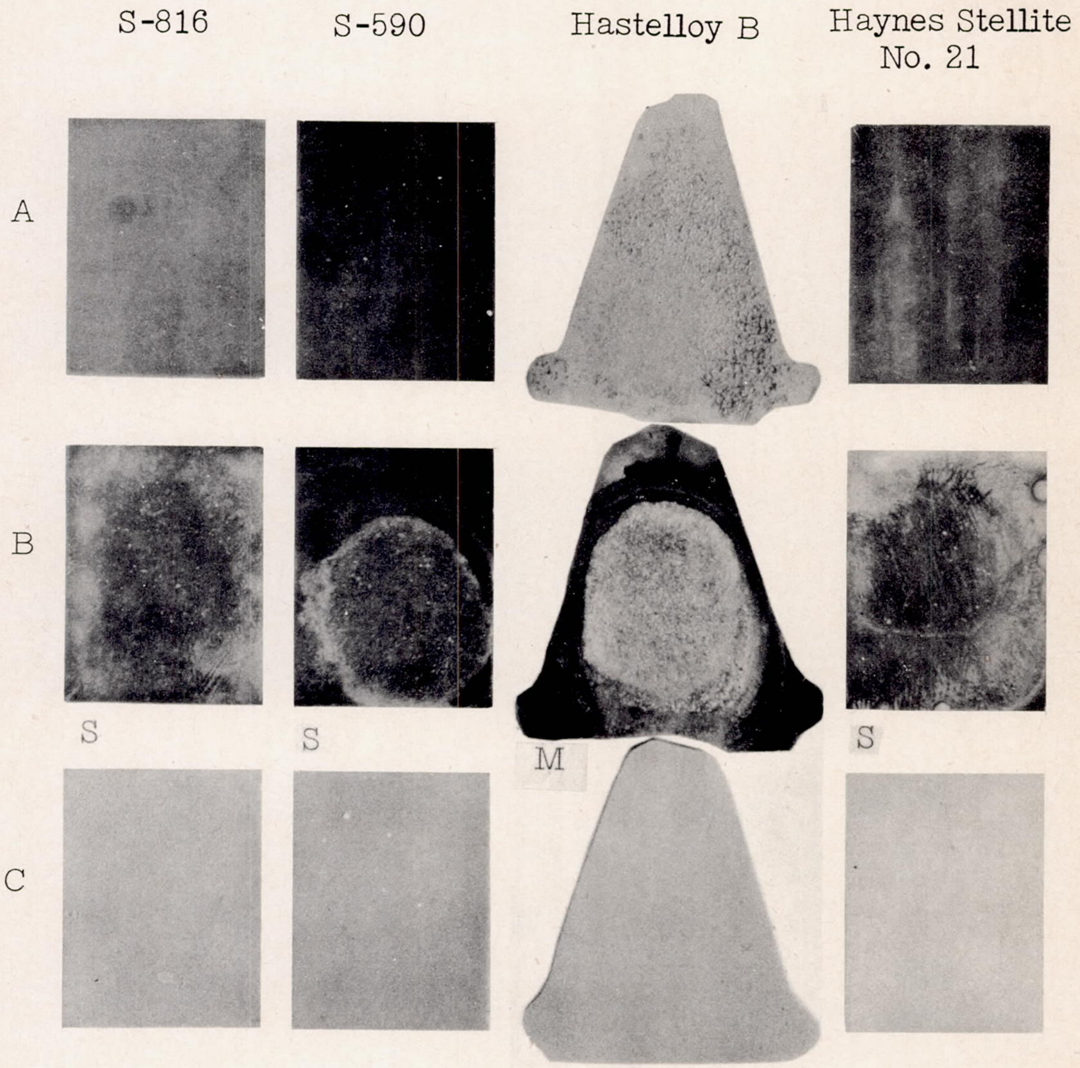

Figure 5.- Specimens after heating for 17 hours in air at 1500° F. Row A, specimens heated without added material. Row B, specimens on which 1 gram of boric acid was placed before heating and not disturbed after removal from furnace. Row C, specimens treated same as row B except for light sandblasting to remove scale. Letters between two bottom rows indicate attack ratings as described in table II. (Magnification, 1.5X.)