CONFIDENTIAL

Copy 4
RM E57L11

UNCLASSIFIED

c. 2

NACA RM E57L11

NACA

RESEARCH MEMORANDUM

THE ADHESION OF MOLTEN BORON OXIDE TO VARIOUS MATERIALS

By W. R. Witzke

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

CLASSIFICATION CHANGED
UNCLASSIFIED
8/19/60

LIBRARY COPY

APR 1 1958

LANGLEY AERONAUTICAL LABORATORY
LIBRARY, NACA
LANGLEY FIELD, VIRGINIA

CLASSIFIED DOCUMENT

This material contains information affecting the National Defense of the United States within the meaning of the espionage laws, Title 18, U.S.C., Secs. 793 and 794, the transmission or revelation of which in any manner to an unauthorized person is prohibited by law.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

WASHINGTON

April 1, 1958

CONFIDENTIAL

UNCLASSIFIED

UNCLASSIFIED

[redacted]

4787

CV-1

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

NASA Technical Library
3 1176 01435 8932

RESEARCH MEMORANDUM

THE ADHESION OF MOLTEN BORON OXIDE TO VARIOUS MATERIALS

By W. R. Witzke

SUMMARY

The adhesion of molten boron oxide in a nitrogen atmosphere to types 304, 321, and 347 stainless steel, Inconel, Inconel X, chromium carbide, boron nitride, and graphite was studied. Contact angles and work of adhesion were obtained for drops of boron oxide at rest on the different materials by the so-called sessile-drop method. Test temperatures ranged from 860° to 1800° F. The contact angle varies linearly with temperature at temperatures just above the melting point of boron oxide. At higher temperatures the contact angle tends toward a constant value. Graphite is the least wetted by the molten oxide, followed in order by boron nitride, chromium carbide, and the metals. The metals are completely wetted above 1350° F. Adhesion was the same for each metal. At 1100° F, the work of adhesion for boron oxide - graphite is 48 dynes per centimeter. This energy is one-half that for boron oxide - boron nitride and approximately one-third that for boron oxide - metal or boron oxide - chromium carbide.

INTRODUCTION

Molten boron oxide has a strong tendency to adhere to all solid surfaces. This has been observed in the examination of engine parts following the combustion of fuels containing boron (ref. 1). The present report evaluates the amount of adhesion existing between the liquid boron oxide and various materials used in engines. Means for obtaining reduced adhesion are demonstrated by measurements involving materials other than those normally used in jet engines.

The sessile-drop method was employed to determine the contact angle formed by a drop of molten boron oxide on a horizontal surface (refs. 2 to 4). This method considers a liquid drop resting, at equilibrium, on a surface that it does not wet completely. The shape of the drop is influenced by gravity, the interfacial tension of the solid and liquid, and the surface tension of the drop. The contact angle is used in calculating the amount of adhesion between the solid and the liquid; the greater

[redacted]

UNCLASSIFIED

the angle, the less the wetting. Similar measurements have been made previously with molten boron oxide using a modification of the capillary rise method (ref. 5).

The materials examined for adhesion with molten boron oxide were types 304, 321, and 347 stainless steel, Inconel, Inconel X, boron nitride, chromium carbide, and graphite. The test temperatures ranged between 860° and 1800° F. All tests were performed in a nitrogen atmosphere.

4787

APPARATUS

The sessile-drop apparatus was composed of a combustion-tube furnace, a controlled-atmosphere system, a temperature control, and a camera. A schematic diagram of the equipment is shown in figure 1.

The combustion-tube design was similar to that used in reference 6. The tube was a 24-inch length of $1\frac{3}{4}$-inch-outside-diameter by $\frac{1}{4}$-inch-wall fused silica tubing with both ends ground to receive 45/50 standard-taper glass joints. The joints were water-jacketed. One joint was capped off by an optical flat; the other provided openings for a thermocouple tube and the controlled atmosphere. The thermocouple tube was also made of fused silica tubing (6-mm O.D. by 1-mm wall) and was connected by a graded seal to a 12/30 standard-taper joint. An Alundum plate used to support the specimen and the boron oxide drop rested on the tube walls.

The combustion-tube atmosphere was controlled by a three-way valve permitting evacuation by a vacuum pump or the bleeding in of nitrogen gas from a cylinder. A relief valve limited the system to a pressure of 2 pounds per square inch gage.

The combustion tube was mounted in a Globar tube furnace. Screws were installed on the furnace legs for leveling purposes. A 25-ampere magnetic amplifier and a temperature controller-recorder provided the necessary instrumentation to maintain the desired temperature setting. The control temperature was read by a Chromel-Alumel thermocouple situated in the fused silica tube close to the specimen.

The camera consisted of a 45-inch length of 4-inch-outside-diameter aluminum tubing fitted with a 4- by 5-inch cameraback and an f4.5 $11\frac{13}{16}$-inch E.F. Tessar Ic lens. This arrangement provided a magnification of 2.82 times with an object distance of approximately 16 inches. A 100-watt light source and an exposure of 1/25 second at f19 using Tri-X film were found satisfactory.

PREPARATION OF MATERIALS

4787

Commercial boron oxide (B_2O_3) powder was converted to beads approximately 2 millimeters in diameter. The starting material contained 80.31 percent boron oxide, 18.96 percent water, and traces of copper, iron, zinc, sodium, silicon, and magnesium. The powder was heated in a porcelain crucible over a Bunsen flame to drive off most of the moisture. After the liquid oxide stopped bubbling, the crucible was further heated in a 2000° F furnace for 20 hours to complete the dehydration. The crucible was transferred back to the Bunsen flame. Rods of boron oxide were formed by dipping a metal wire into the melt and slowly withdrawing it. The rods were made with the melt just above the melting temperature of the oxide. Beads were prepared by melting the tip of the boron oxide rod with an air-gas torch. The liquid drop was allowed to fall about a foot through air to permit it to solidify in a spherical shape. Beads found to contain bubbles were discarded, as the shape of those beads would be distorted on heating in the sessile-drop test. Averaging 30 milligrams in weight, the boron oxide beads were stored in a desiccator until used. Spectrographic analysis indicated no significant solution of crucible materials in the B_2O_3.

The stainless-steel and Inconel specimens were cut from 1/8-inch sheet stock to form 1-inch-square plates. Following a vapor-blasting operation, the plates were stored in a desiccator until needed. The plate surfaces had an average roughness of 75 microinches.

The sample of hot-pressed boron nitride (BN) was obtained from the Carborundum Company. It was readily cut into a small plate. The test surface was made flat and smooth by rubbing on crocus cloth to give a surface roughness of about 70 microinches.

The chromium carbide (Cr_3C_2), with a surface roughness of 17 microinches, had the smoothest surface of all the test materials. This surface was cleaned with alcohol and dried before testing.

The graphite specimen was cut from a portion of electrode material. Crocus cloth was used to smooth the test surface. Being a porous material, the graphite had a rough surface averaging about 95 microinches.

PROCEDURE

A bead of boron oxide was placed on the specimen resting on the Alundum support. These items were pushed into the combustion tube to a position adjacent to the tip of the thermocouple. The apparatus was assembled, and the glass joints were lubricated and sealed with Apiezon N grease. The system was evacuated to a pressure of 0.3 millimeter of mercury, filled with nitrogen, and again evacuated. Nitrogen was then continuously fed into the system to maintain a pressure of 2 pounds per square inch gage. By viewing the specimen through the camera and using a small level, the test surface was brought to a horizontal condition. The leveling operation involved rotating the combustion tube and adjusting the furnace leg screws. Heat was applied and photographs were taken at various temperatures. After each temperature point was reached, 10 to 15 minutes were allowed for equilibrium to be established. Measurements of the magnified sessile drop were taken from 4- by 5-inch negatives using a microcomparator.

4787

DATA AND CALCULATIONS

Measured and calculated data are given in table I. The recorded dimensions of drops with either obtuse or acute contact angles are designated in figure 2. The values for the contact angle θ were computed from the drop dimensions by the procedures indicated in references 3 and 4. Obtuse contact angles involved the use of the tables of reference 7. Acute angles were determined from the equation

$$\theta = 2 \tan^{-1} (h/a)$$

where h and a are the dimensions shown in figure 2.

The relation of the surface tension σ of boron oxide in air with the temperature t has been experimentally determined (ref. 8) to be

$$\sigma = 58.2 + 0.0354(t - 300^{\circ}\ C)$$

The work of adhesion w, the energy required to separate the liquid and solid, was computed from the relation

$$w = \sigma (1 + \cos \theta)$$

RESULTS AND DISCUSSION

Values of contact angle and work of adhesion were determined for various molten boron oxide and solid specimen interfaces from 860° to 1800° F. Sessile-drop tests were performed in a nitrogen atmosphere. The effect of other atmospheres, such as oxygen, was not investigated. Measurements were taken from photographs of each interface at various temperatures. A set of photographs for a typical run is shown in figure 3.

Contact Angle

The variation of contact angle with temperature for the materials tested is shown in figure 4. The data points for the metal specimens, types 304, 321, and 347 stainless steel, Inconel, and Inconel X, group together and are therefore described by a single curve. The jog in the curve for graphite resulted because the test temperature was held constant overnight. The additional time - 16 hours over the 10 to 15 minutes normally allotted for equilibrium to be reached - produced a 3.3° difference in contact angle at the 1300° F temperature. A further decrease in contact angle occurred when the temperature was increased to 1400° F. Each curve displays the same characteristic tendencies: (1) an initial rapid decrease in contact angle as the test temperature was raised, and (2) an essentially constant contact angle above a given temperature. The initial portions of the curves for the metals and the carbide are linear.

A contact angle above 100° is shown for the graphite specimen at all temperatures. This indicates that molten boron oxide will not readily wet graphite. The metals are completely wetted (contact angle less than 5°) by the molten boron oxide above 1350° F. A material of possible intermediate properties was suggested here in the form of a metal carbide. An available specimen of chromium carbide was found to have a wettability by the molten oxide more than that of the graphite but only slightly less than the metals. Chromium carbide, however, may not be representative of other metal carbides in this property.

Boron nitride, often called "white graphite," has properties similar to graphite. Above 1300° F hot-pressed boron nitride attains a constant degree of wettability, somewhat higher than that for graphite. The contact angle for the boron oxide - boron nitride interface is constant at 40°.

On cooling to room temperature, the specimens could not be readily freed of the boron oxide, except by solution in water. The solid oxide chip could be pried away from the boron nitride and graphite surfaces, but only with the tearing away of some of the specimen material with the oxide.

Work of Adhesion

The variation of work of adhesion with temperature for molten boron oxide on various materials is shown in figure 5. Because work of adhesion is derived from the contact-angle data, the shapes of the work-of-adhesion curves are similar to the curves in figure 4. However, the quantitative measure of work of adhesion is of more use.

A comparison can be made of the amount of adhesion energy involved at temperatures known to exist at the surfaces of the turbine stator and rotor and some parts of the combustor of a jet engine. At 1100° F, the amount of energy per unit area required to separate the liquid boron oxide from graphite is 48 dynes per centimeter. At the same temperature, twice this amount of energy (99 dynes/cm) is required to remove boron oxide from boron nitride. To separate boron oxide from one of the metals under the same conditions, 132 dynes per centimeter (approx. three times the boron oxide - graphite work-of-adhesion value) is needed. At higher temperatures the work of adhesion between boron oxide and graphite tends to remain half of that between boron oxide and boron nitride.

Molten boron oxide adhered to and wet each metal tested identically.

SUMMARY OF RESULTS

The adhesion of molten boron oxide to various surfaces in an atmosphere of nitrogen was studied by the sessile-drop method. The surface materials tested included several stainless steels, Inconel, chromium carbide, boron nitride, and graphite. The results are as follows:

1. Generally, at lower temperatures, as the temperature is increased the contact angle shows a rapid linear decrease. Above a given temperature the contact angle becomes essentially constant.

2. The contact-angle studies indicated the following:

(a) Above 1350° F the metals are completely wetted by boron oxide. Molten boron oxide adhered to and wet each metal tested identically.

(b) Molten boron oxide wets chromium carbide almost as readily as it wets the metals.

(c) Above 1300° F boron nitride resists further wetting by the oxide; contact angle remains constant at 40°.

(d) Graphite is the least wetted by boron oxide, the contact angle remaining above 100°.

3. At 1100° F the work of adhesion for the boron oxide - graphite interaction is 48 dynes per centimeter. This value is half that for the boron oxide - boron nitride interaction and approximately one-third of that for the boron oxide - metal interaction.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 12, 1957

4787

REFERENCES

1. Kaufman, Warner B., Branstetter, J. Robert, and Lord, Albert M.: Experimental Investigation of Deposition by Boron-Containing Fuels in Turbojet Combustor. NACA RM E55L07, 1957.

2. Mitchell, D. W., Mitoff, S. P., Zackay, V. F., and Pack, J. A.: Measurement of Surface Tension of Glasses. Glass Industry, vol. 33, no. 9, Sept. 1952, pp. 453-457; 482; Oct., pp. 515-523.

3. Ellefson, Bennett S., and Taylor, Nelson W.: Surface Properties of Fused Salts and Glasses: I. Sessile-Drop Method for Determining Surface Tension and Density of Viscous Liquids at High Temperatures. Jour. Am. Ceramic Soc., vol. 21, no. 6, June 1938, pp. 193-205.

4. Mack, Guilford L.: Contact Angles from Dimensions of Small Bubbles and Drops. I. Spheroidal Segment Method for Acute Angles. Jour. Phys. Chem., vol. 40, Feb. 1936, pp. 159-176.

5. Cheney, S. H., Jr., Kibler, G. M., and Williamson, R. C.: Summary Report No. 4 on Combustion, Deposition and Thermal Decomposition Studies. MCC-1023-TR-143, Olin Mathieson Chem. Corp., June 30, 1955. (Dept. Navy, Bur. Aero. NOa(s) 52-1023-C.)

6. Baes, C. F., Jr., and Kellogg, H. H.: The Effect of Dissolved Sulfur on the Surface Tension of Liquid Copper. Trans. AIMME, vol. 197, 1953, pp. 643-648.

7. Bashforth, F., and Adams, J. C.: An Attempt to Test Theories of Capillarity Action by Comparing the Theoretical and Measured Forms of Drops of Fluid. Cambridge Univ. Press, 1883.

8. Shartsis, Leo, and Smock, Alden W.: Surface Tensions of Some Optical Glasses. Jour. Res. NBS, vol. 38, no. 2, Feb. 1947, pp. 241-249.

TABLE I. - SESSILE-DROP DATA

Specimen	Boron oxide drop weight, mg	Temperature, °F, (±5° F)	Drop dimension (fig. 2), cm (±0.00005 cm) x	z	a	h	Contact angle, θ, deg	Work of adhesion, W, dynes/cm
304 Stainless steel	30.8	865	0.1730	0.1572	0.1275	0.2570	146.0	11.0
		900	.1796	.1611	.1556	.2400	128.8	24.1
		940	.1924	.1649	.1852	.2102	110.8	42.2
		980	-----	-----	.2147	.1852	81.6	75.6
		1025	-----	-----	.2452	.1518	63.5	97.0
		1060	-----	-----	.3173	.0980	34.3	124
		1095	-----	-----	.3672	.0633	19.6	133
		1155	-----	-----	.4141	.0505	13.9	137
		1200	-----	-----	.4283	.0343	9.2	140
		1250	-----	-----	.4460	.0314	8.1	142
		1305	-----	-----	.4399	.0205	5.3	145
		1350	-----	-----	.5306	.0176	3.8	147
321 Stainless steel	28.7	860	0.1707	0.1540	0.1287	0.2524	146.6	10.6
		900	.1758	.1605	.1540	.2341	125.0	27.5
		940	.1868	.1671	.1833	.1710	97.2	57.3
		980	-----	-----	.2228	.1610	71.7	87.0
		1025	-----	-----	.2583	.1254	51.1	109
		1065	-----	-----	.2982	.0944	35.1	123
		1100	-----	-----	.3560	.0650	20.7	133
		1150	-----	-----	.4058	.0453	12.7	137
		1200	-----	-----	.4078	.0352	9.9	140
		1250	-----	-----	.3644	.0289	9.1	142
		1300	-----	-----	.3862	.0210	6.2	145
		1350	-----	-----	.3567	.0092	3.0	147
347 Stainless steel	31.6	860	0.1728	0.1580	0.1333	0.2513	139.6	15.2
		900	.1794	.1635	.1633	.2332	120.8	31.5
		940	.1964	.1754	.1850	.2059	100.0	54.0
		975	-----	-----	.2268	.1781	76.3	81.6
		1020	-----	-----	.2675	.1377	54.5	108
		1055	-----	-----	.3142	.1004	35.4	123
		1100	-----	-----	.3655	.0640	19.9	133
		1150	-----	-----	.3816	.0394	11.8	138
		1200	-----	-----	.3978	.0344	9.9	140
		1250	-----	-----	.3722	.0216	8.6	143
		1300	-----	-----	.2841	.0234	9.4	144
		1350	-----	-----	.3152	.0138	5.0	147
Inconel	32.9	860	0.1690	0.1571	0.1257	0.2602	143.0	12.8
		900	.1848	.1658	.1706	.2352	119.9	32.4
		940	.1942	.1614	.1905	.2054	108.8	44.3
		980	-----	-----	.2306	.1576	68.7	90.3
		1015	-----	-----	.2530	.1179	50.0	110
		1060	-----	-----	.3044	.1234	44.1	117
		1100	-----	-----	.3478	.0949	30.5	128
		1150	-----	-----	.4229	.0804	21.5	134
		1195	-----	-----	.4556	.0585	14.6	139
		1250	-----	-----	.5222	.0540	11.8	141
		1300	-----	-----	.5408	.0403	8.5	144
		1355	-----	-----	.6104	.0292	5.5	147
Inconel	27.6	860	0.1736	0.1574	0.1479	0.2538	128.7	24.0
		940	.1885	.1516	.1860	.1918	107.8	45.4
		980	-----	-----	.2160	.1638	74.4	84.0
		1055	-----	-----	.2755	.0902	38.3	122
		1100	-----	-----	.3118	.0645	23.4	131
		1150	-----	-----	.3364	.0475	16.1	136
		1300	-----	-----	.3967	.0134	3.9	145
Inconel X	28.6	865	0.1709	0.1544	0.1318	0.2448	140.7	14.5
		900	.1774	.1558	.1624	.2246	123.6	28.8
		940	.1876	.1670	.1887	.2069	107.6	45.7
		980	-----	-----	.2226	.1829	72.4	86.1
		1020	-----	-----	.2560	.1385	56.8	104
		1055	-----	-----	.3005	.1040	38.2	121
		1100	-----	-----	.3398	.0801	28.5	130
		1155	-----	-----	.3855	.0618	15.3	137
		1200	-----	-----	.4599	.0416	10.8	140
		1250	-----	-----	.4836	.0298	7.1	142
		1300	-----	-----	.4941	.0304	7.0	145
		1350	-----	-----	.5522	.0219	4.7	147
Chromium carbide	39.7	865	0.1853	0.1322	0.1357	0.2302	171.0	0.8
		890	.1796	.1726	.1406	.2511	126.3	26.3
		1000	.2086	.1816	.2086	.2188	98.8	56.4
		1050	-----	-----	.2714	.1582	60.5	101
		1090	-----	-----	.3470	.1089	34.8	125
		1140	-----	-----	.3866	.0836	24.4	133
		1190	-----	-----	.3867	.0630	18.5	137
Boron nitride	62.5	905	0.2317	0.1947	0.1988	0.2998	139.3	16.7
		1000	-----	-----	.2818	.2896	91.7	64.6
		1095	-----	-----	.3258	.2194	68.0	94.2
		1205	-----	-----	.3755	.1674	48.1	118
		1305	-----	-----	.4127	.1497	39.9	128
		1405	-----	-----	.4270	.1536	39.6	132
		1505	-----	-----	.4372	.1620	40.7	135
		1610	-----	-----	.4246	.1628	41.9	137
		1710	-----	-----	.4371	.1590	40.0	142
Graphite	31.4	940	0.1910	0.1877	0.1665	0.2257	130.2	23.2
		975	.2044	.1705	.1918	.2209	118.0	37.2
		1020	.2014	.1728	.1954	.2138	108.4	45.8
		1060	.2204	.1817	.2100	.2164	109.4	45.5
		1090	.2138	.1740	.2155	.2094	107.0	48.4
		1200	.2085	.1695	.2101	.2048	107.6	49.2
		1300	.2174	.1780	.2103	.2128	107.8	50.3
		[a]1295	.2151	.1732	.2133	.2117	104.5	54.3
		1400	.2133	.1792	.2151	.2037	100.5	60.9
		1510	.2201	.1934	.2157	.2165	101.2	61.4
		1610	.2028	.1813	.2087	.2111	101.7	62.6
		1705	.2182	.1836	.2180	.2088	100.6	65.7
		1800	.2099	.1820	.2147	.2155	103.9	62.5

[a]A 16-hr interval occurred between this reading and the previous one.

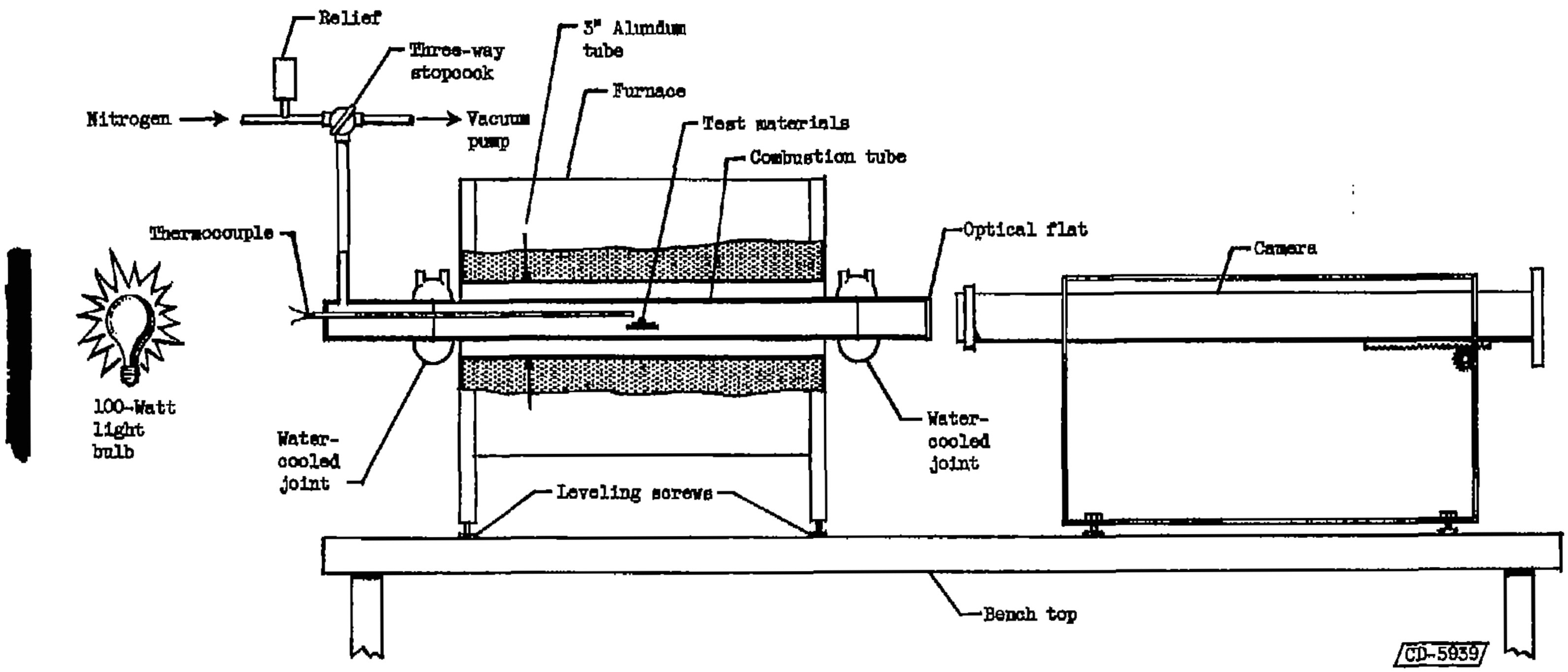
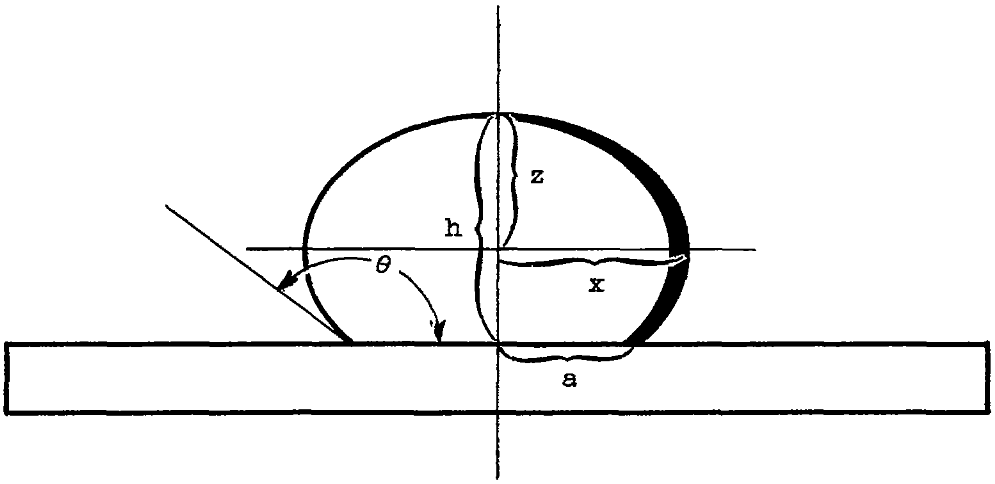
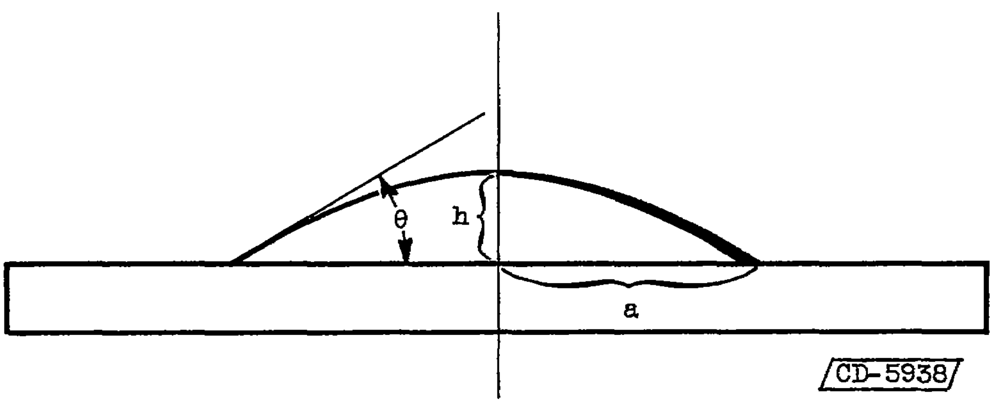


Figure 1. - Arrangement of sessile-drop apparatus.



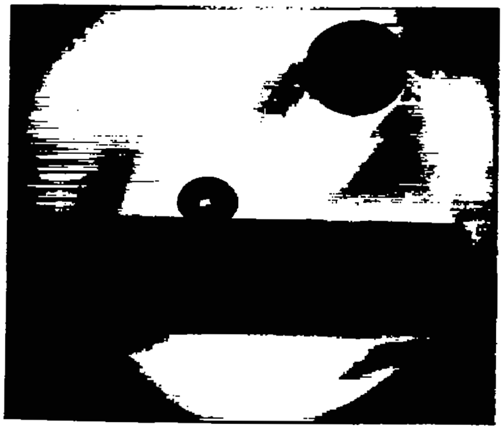
(a) Contact angle $\theta > 90^{\circ}$.



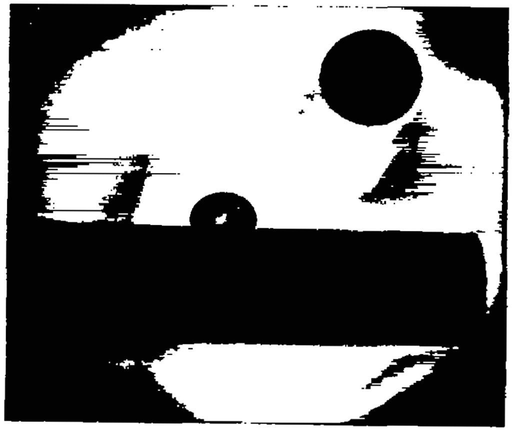
(b) Contact angle $\theta < 90^{\circ}$.

Figure 2. - Measurements taken from photograph of sessile drop depending on contact angle.

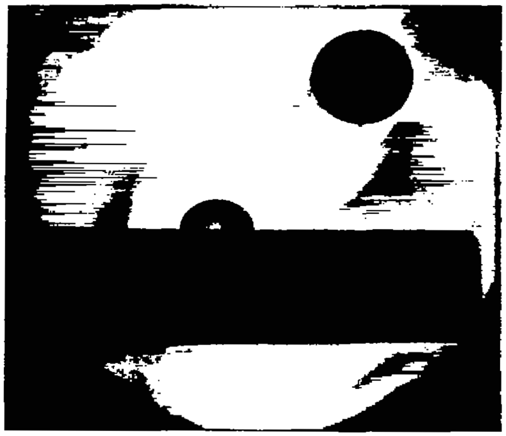
[redacted]



(a) 865° F.

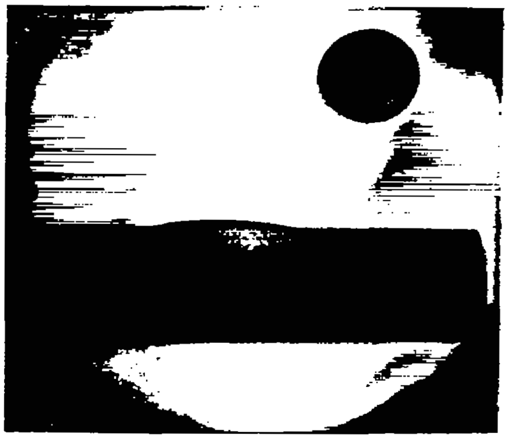


(b) 940° F.

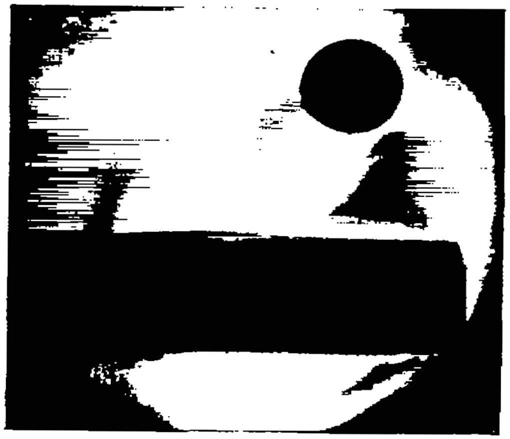


(c) 980° F.

(d) 1060° F.



(e) 1155° F.



C-46721

(f) 1250° F.

Figure 3. - Photographs of a boron oxide drop on type 304 stainless steel at various temperatures.

[redacted]

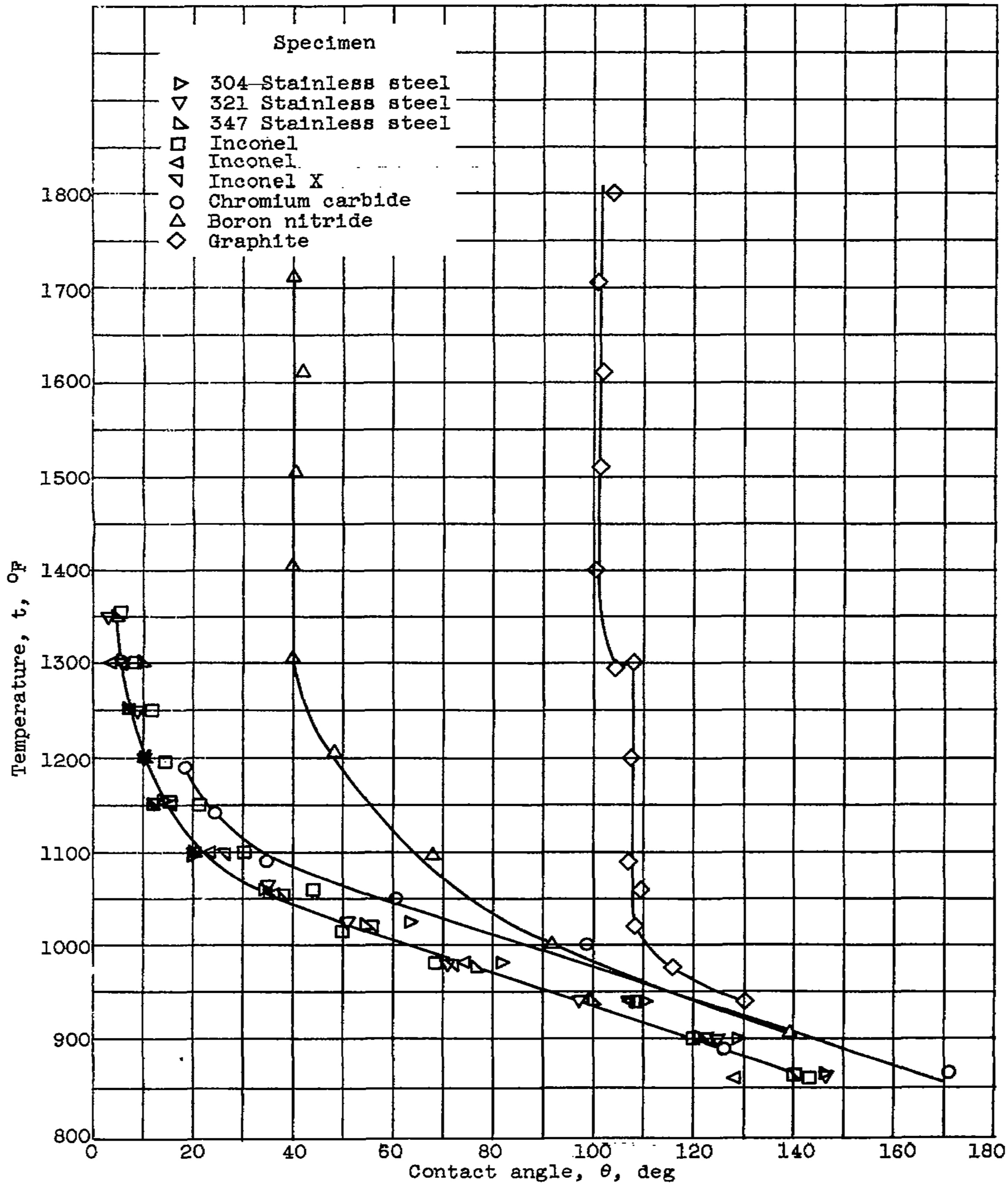


Figure 4. - Variation of contact angle with temperature for molten boron oxide on various materials.

[redacted]

4787

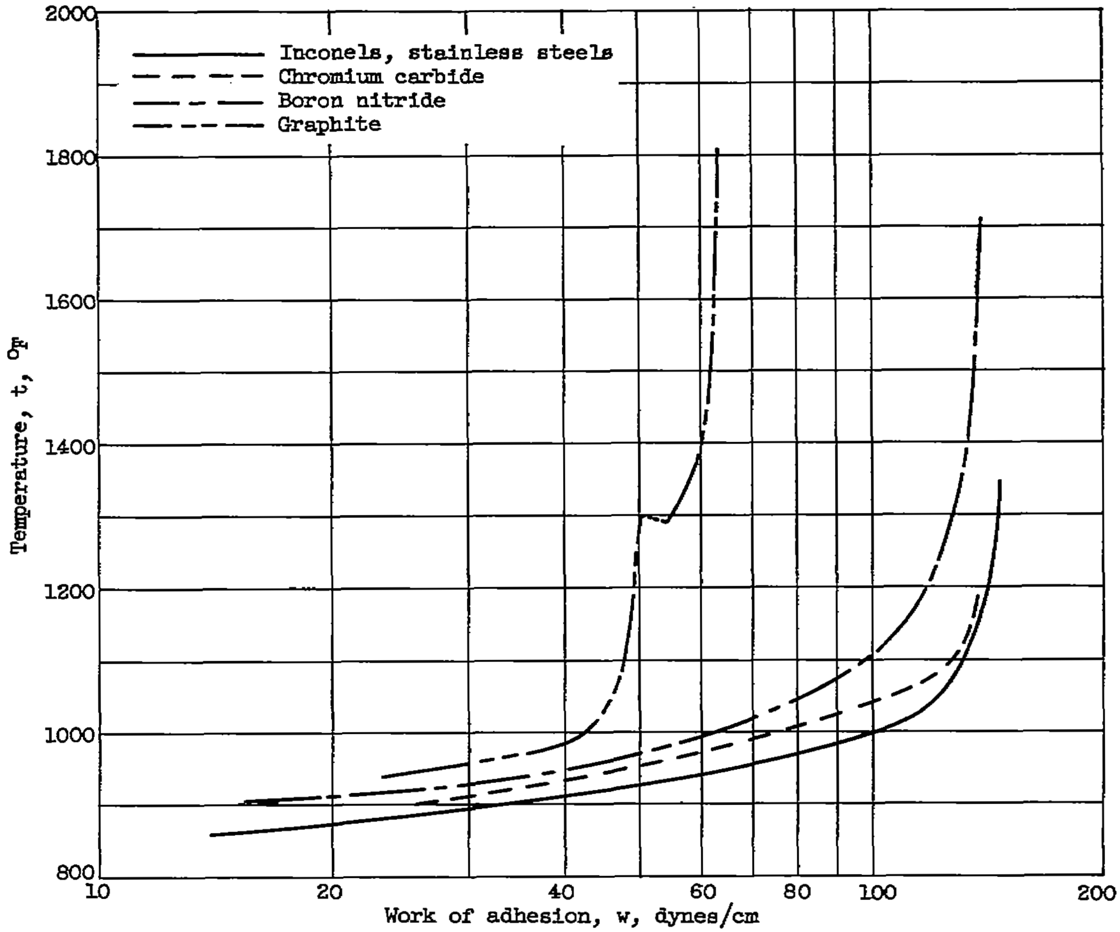


Figure 5. - Variation of work of adhesion with temperature for molten boron oxide on various materials.

NACA - Langley Field, Va.

[redacted]

NASA Technical Library
3 1176 01435 8932

[redacted]