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**ATTACK ON METALS BY BISMUTH-LEAD-TIN
ALLOY AT ELEVATED TEMPERATURES**

Final Report—Metallurgy Program 8.2.3

**By
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January 15, 1954

**Argonne National Laboratory
Lemont, Illinois**

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ATTACK ON METALS BY BISMUTH-LEAD-TIN ALLOY AT ELEVATED TEMPERATURES

by

Walter D. Wilkinson

FOREWORD

This report covers all the unclassified work done at Argonne National Laboratory by the Metallurgy Division (mostly in the years 1949, 1950, and 1951) in investigating the attack on materials by eutectic bismuth-lead-tin alloy (nominal composition Bi-52%, Pb-32%, Sn-16% by weight) by means of static tests at elevated temperatures, in some cases up to 800°C. Specimens from several preliminary static and dynamic tests carried out by the Reactor Engineering Division were submitted to the Metallurgy Division for study. This report also covers these tests.

The metals tested included aluminum, Armco iron, cast iron, beryllium, titanium, zirconium, and various steels.

The various test procedures and types of tests employed are classified as follows.

- I. Effects of Electrical Potential and Anodized Coating on the Resistance of Aluminum to Attack by Bi-Pb-Sn Alloy.
- II. Effect of Saturation on the Resistance of Aluminum to Attack by Bi-Pb-Sn Alloy
- III. Thirty-Day Test of Vacuum-Sealed Metals at 500°C.
- IV. Eighty-Day Test of Vacuum-Sealed Metals at 500°C.
- V. Effects on Metals Dynamically Tested in Heat-Transfer Unit.
- VI. Tests with Specimens that were not Vacuum Sealed.
- VII. Tests of Chromium Steels at 600°C and 800°C with Environment Control, and of Molybdenum at 800°C.

These seven groups of tests, that is, the seven experimental procedures and the results, are described in the following section. The relationships of these results to the resistance of the various test metals to attack by Bi-Pb-Sn alloy are considered in a later section in order to facilitate interpretation of the results as a whole. In the case of metals that have been subjected to more than one type of test, the effects of differences in experimental conditions can thus be considered in a single section.

Summary of Results

Molybdenum was not attacked at 800°C. Beryllium was not attacked at 500°C. The other metals, except tungsten, which was exposed incidentally, were observably attacked. The presence of oxygen accelerates or increases the attack on iron, carbon steel, and aluminum, but limited amounts of oxygen are protective to chromium steels. Increasing the chromium content does not increase resistance to attack unless oxygen is present and may increase the solubility of the steel in the melt. Anodizing aluminum and maintaining it as an anode helps to protect it. Unprotected aluminum is readily attacked by diffusion reaction. Iron is nearly insoluble in Bi-Pb-Sn alloy at 500°C, but transgranular attack, intergranular attack, and localized attack through fissures in the reaction layer occur on Airmco iron and carbon steel. The reaction with austenitic stainless steel at temperatures up to 500°C appears to depend on the condition of the steel - particularly on factors affecting susceptibility to intergranular attack - as the transgranular diffusion reaction is not very fast.

GENERAL TEST PROCEDURES AND RESULTS

Procedure I Effects of Electrical Potential and Anodized Coating on Resistance of Aluminum to Attack by Bi-Pb-Sn Alloy

Rods of 2S aluminum, approximately 0.2" in diameter and 2.5" in length, were used as test specimens. Three of them were anodized in a 5 to 10% sulfuric acid bath. The anode coating was 1 to 2 mils thick, and its electrical resistance, measured with a Weston ohmmeter (on immersion of the specimens in mercury), was 140,000 ohms/cm² at room temperature.

Approximately 30 grams of Bi-Pb-Sn alloy were used with each of the rods tested, being sealed at a pressure of 10⁻² mm of mercury in 18-mm diameter Pyrex tubes as shown diagrammatically in Figure 1.

The tubes were heated in an aluminum block having 3/4" holes to contain them. In order to measure the temperature, a Chromel-Alumel thermocouple was placed adjacent to one of the tubes in a hole. The block and contents were heated in a muffle furnace with a Variac transformer for temperature control.

The 45-volt potential applied to one of the anodized specimens (Figure 1D) was supplied by storage batteries and the current was measured with a milliammeter.

The Bi-Pb-Sn alloy melted and closed the circuit of the milliammeter at 108°C, as measured with the thermocouple. Assuming that the Bi-Pb-Sn alloy at melting temperature immediately wetted the aluminum

specimen and the electrode sufficiently to close the circuit, there would have been an 11° maximum temperature gradient (between the thermocouple and the melt) on heating at the rate of about 1°C per minute through this temperature region. This is so because the melting point of eutectic Bi-Pb-Sn alloy is 97°C - not 108°C. If there were any delay in wetting after melting - as is probable - the temperatures, when the rate of heating was slower, must have been nearly the same as that indicated by the thermocouple measurement.

The temperature was maintained at 550°C for about 10 hours. The temperature then rose during a period of four hours to 630°C - but not quite to the fusion temperature for aluminum. The specimens were then cooled to 300°C in about one hour. During this period the direction of the current through the specimen, being maintained at a 45-volt potential, was reversed. In other words, this specimen was heated as an anode for 19 hours up to 630°C and at a potential of 45 volt. It was then cooled as a cathode nearly to 300°C in about an hour. Current and temperature readings were recorded as shown in Figure 2 and in Table I.

The aluminum specimens were removed from the still molten baths, weighed, measured, and examined metallographically (see Figures 3 through 7). The respective Bi-Pb-Sn baths were analysed chemically for aluminum.

Data from the changes in weight and dimensions and apparent solubilities obtained on the various aluminum specimens treated as in Procedure I are given in Table II. The data on apparent solubility were obtained by the chemical analysis.

An attempt to interpret these results is made in the section entitled, "Discussion of Results for Aluminum," pages 17 to 19.

Procedure II Effect of Saturation on the Resistance of Aluminum to Attack by Bi-Pb-Sn Alloy

In order to determine the effect on aluminum of Bi-Pb-Sn alloy that is saturated with aluminum, the test solution was prepared by heating 5 w/o aluminum (in the form of small lumps) with 500 grams of Bi-Pb-Sn alloy in an argon atmosphere for one week at 445°C $\pm$ 25°C. An aluminum rod was then introduced at temperature and the heating was continued for three more days. The melt was contained in a Pyrex glass beaker. Provision was made for preheating the aluminum rod and for introducing it into the melt through a seal without admitting air into the system. The rod was then removed from the melt, while still at temperature, cooled and examined for attack.

The result of this test was that pronounced diffusion penetration, evidenced by a tendency to disintegrate, had occurred at the lower end of the aluminum rod. Several aluminum lumps still floating on the surface of the alloy, however, showed only slight evidence of dissolution. The surfaces of these lumps may have gettered the oxygen in the system before the rod was introduced.

Procedure III Thirty-Day Test of Vacuum-Sealed Metals at 500°C

In all the tests with vacuum-sealed specimens (this includes also those of Procedures IV and VII. See index.) containers of cleaned Pyrex glass tubing (or quartz or Vycor for temperatures above 550°C) were formed, filled, and sealed in the following manner:

The solid specimen, usually $1/2$ " long and with a section $1/8$ " square or in diameter, was finished with 600 mesh abrasive paper. The tubing used was about one centimeter in diameter and sealed at one end. The specimen was slipped into the tube and down to the closed end, and the system was evacuated and outgassed. The tube was necked-in, so as to form a bulb about the specimen; the resultant constriction of the tubing was smaller in diameter than the specimen. (In this operation care was taken not to heat the specimen above the proposed test temperature.) With this geometry the solid specimen was retained in the bulb even though the tube was inverted.

When the system has cooled, the desired amount of eutectic alloy was added in solid form, and the specimen tube was again evacuated. It was then vacuum-sealed so as to form a second bulb enclosing the solid eutectic. (If much of the eutectic alloy melts during the sealing operation and then freezes, it may crack the tube by subsequent expansion.) The amount of eutectic alloy desired for the addition was that which can, when molten, completely fill the specimen bulb plus at least a portion of constriction in the tube. The shape of the tube, when sealed, was suggestive of an hourglass, except that the second bulb formed was ordinarily larger than the first. The dimensions of the tube depended on the apparatus in which it was to be heated, and for procedures III and IV, the length of the tube was a little less than the inner diameter of a cylindrical container which held the specimen tubes diametrically.

The tube was heated with the specimen bulb lower than the other so that the liquid metal ran down and enveloped the specimen, which was prevented by the constriction from rising to the surface. (The specimen tends to float when less dense than the liquid.)

For the thirty-day test at 500°C (Procedure III) the arrangement used for heating a number of tubes at one time is shown in Figure 8. The outer container was essentially a horizontal, 4" I.D., mild-steel tube with

an aluminum spray coating on the outside to prevent scaling. The head containing the two small diameter mild-steel tubes was welded in place before the specimens were introduced. Longitudinal guides tack-welded inside the container and glass wool cushioning were provided to hold the individual tubes in diametrical position, as shown. After the sealed specimen tubes were introduced, suitable preformed pieces of bismuth-lead eutectic alloy were carefully inserted. The amount was sufficient to fill the container more than one-half full after the alloy was molten. About 100 cc of powdered carbon was also inserted, and the cap end of the container was arc-welded in place. Thermocouples were attached by means of high-melting silver solder to the cap and to the other end. Of the two small diameter tubes at the head end, the lower one (A) was plugged and welded tight. Aluminum paint was applied to the weld area at A to help prevent scaling.

The loaded container was placed in a muffle furnace with the specimen tubes in an upright position, and brick wedges were used to keep the container from rolling. The furnace heat was then turned on, and, as the temperature increased, the carbon reacted with the oxygen in the container to form carbon monoxide. This gas, escaping from the upper tube (B) in the head, was purposely ignited. When the jet of flame began to weaken, the burner tube was plugged and welded shut. This procedure was to minimize the amount of oxygen in the container, which otherwise might form a dross with the lead-bismuth and attack the specimen tubes or the inside of the mild-steel container. The weld around the plug was painted with aluminum.

The purpose of the bismuth-lead bath was to help maintain the specimen tubes at a more nearly uniform and constant temperature than might otherwise have been practicable.

The muffle furnace was then sealed with bricks and asbestos, and the temperature was adjusted as nearly as possible to a maximum of 500°C. There was, however, at first a 40° difference in temperature between the outside surface of the ends of the container as determined by the front and rear thermocouples. It is believed that this gradient must have been reduced by further insulation of the furnace, but failure of one of the thermocouples prevented determination of the extent to which the gradient was reduced. Since convection takes place readily in molten bismuth-lead alloy, and since the distance between the front and rear specimens was less than two-thirds the length of the container, it is estimated by interpolation that the difference in temperature between the front and rear specimen was not over 20°C. The estimated temperature for the various specimens are given in Table III on the basis of a 20°C gradient.

After thirty days of heating in the muffle furnace, powered through a constant-voltage transformer, the container was rotated (by means of tongs) 180° on its axis. In this way the specimen tubes were inverted, and

the bulk of the bismuth-lead-tin alloy* in the tubes was thus enabled to flow away from the specimens while still at temperature.

The small-diameter tubes which had been plugged and welded shut (tubes A and B of Figure 8) were burned open with a cutting torch so that (after the inversion of the samples) the bismuth-lead bath could drain out through B. While still at a temperature above 200°C, the container was sectioned by means of a power hacksaw at a position two inches from the head.

The reason for sectioning at that temperature was that it was desirable to accomplish the removal of the specimen tubes while the ternary alloy in them was still liquid. Post-solidification expansion of the ternary eutectic might otherwise have prematurely broken the tubes and perhaps have caused the specimens to become mixed or lost.

It turned out that all of the tubes except one containing beryllium (Be #2) were slightly cracked at the specimen (upper) end, but otherwise sound and intact. The individual decantates were still liquid and bright, however, and showed no tendency to adhere to the inner walls of the specimen tubes, as they would have done if they had been contaminated with oxygen. The cracks at the specimen ends of the tubes presumably resulted from vibration during the power sawing.

In cases where a decantate from a specimen was to be analyzed chemically, the entire frozen decantate was used as a sample so that segregation would not be a factor. Since duplicate specimens were tested, one specimen of each metal that had been tested was examined metallographically, and the other was cleaned, when necessary, remeasured, and reweighed. In some cases it, too, was examined metallographically.

Two specimens each of beryllium, zirconium, Armco iron, and cast iron were treated by this procedure.

The surface-volume ratio for the specimens was of the order of 1 square centimeter of specimen surface to 2 to 2.5 cc of liquid alloy.

After decantation of the bulk of the alloy, attempts were made to remove any remaining traces of the alloy from specimens that were to be weighed and measured. In the removal of the eutectic alloy itself, it was

* Analysis of the alloy itself indicated that it contained the following percentages by weight: 50.8 Bi, 31.3 Pb, 16.8 Sn. It was prepared for the vacuum-sealed static tests from an alloy ingot previously formed by pouring from a graphite-covered melt in an open crucible. The initial alloy was heated in an outgassed vacuum system and vacuum-cast into a Pyrex tube, which did not appear to be wet by the alloy. The vacuum cast alloy contained less than 0.01 w/o of iron.

desirable, if possible, not to remove reaction products. In some cases, adhering particles of eutectic alloy would scale off or could be peeled off, either at room temperature or on cooling in an acetone-dry ice mixture. In other cases they would be wiped off after warming the specimens up to 150°C in paraffin oil.

For more difficult cases in which the traces of eutectic alloy could not be removed mechanically from the specimens or from reaction layers, chemical methods were tried. One method, sometimes used with aluminum and with ferrous specimens (Procedure IV), was to treat the specimens for periods from several hours to one week in warm concentrated ammonium acetate solution in the presence of air. The ammonium acetate tends to disintegrate the ternary eutectic by complexing the lead. The solution appeared not to affect the reaction layers (which were presumed to be high in tin and iron, possibly to contain some bismuth, but to be low in lead content).

A 500 ml specimen of the acetate solution was found to have removed 0.0272 gram of metal from an alloy-coated specimen.

As the acetate method was tedious, treatment with hot concentrated alkali solutions was tried on the cast iron and Armco iron specimens. A comparison of Figure 25a with Figure 25b and of Figure 19 with Figure 20, indicates that the eutectic Bi-Pb-Sn alloy was completely removed, but that a reaction layer remained. The alkali treatment in oxidizing environment results in the formation of plumbate stannate and probably a bismuthate, but apparently does not form substantial amounts of ferrate or ferrite, nor appreciably attack the iron reaction products. To check this, the Armco specimen of Figure 19 was found to have lost almost 5 mg of weight on treatment with approximately 40 cc of KOH solution, but the solution was found to contain only 0.0059 mg of iron. Likewise the KOH wash solution from the specimen of Figure 25a contained only 0.0045 mg of iron, although almost 5 mg (presumably of Bi-Pb-Sn) was removed from the specimen.

Decantates of Bi-Pb-Sn were not analyzed chemically unless there was evidence of reaction between the alloy and the specimen. When it was confirmed that the solubility of iron in Bi-Pb-Sn alloy was very slight at 500°C (of the order of 20 ppm) there appeared to be no reason for analyzing further decantates from ferrous specimens.

The results for specimens tested by Procedure III are included in Table III. The data for specimens of molybdenum treated by Procedure VII, are included in this table for comparison.

Procedure IV. Eighty-Day Test of Vacuum-Sealed Metals at 500°C

An eighty-day test in Bi-Pb-Sn alloy, similar to the thirty-day test (Procedure III), was carried out with specimens of SAE 1020 steel, 2S aluminum, Armco iron, and titanium. In this test, however, tube B (of Figure 8) terminated in Pyrex glass with a Kovar glass-to-metal connection. This facilitated sealing after the system was evacuated. It also facilitated subsequent opening of the tube for drainage of the container. An atmosphere of argon (instead of carbon monoxide) was introduced.

These modifications of procedure had, however, no effect on the specimens, which were sealed, as before, in Pyrex glass tubes. The furnace insulation and controls were adjusted so that the temperatures of the specimens ranged between 470°C and 500°C, the variations being due chiefly to fluctuations in line voltage.

After the container was inverted at the end of eighty days, the bath metal that was drained off appeared clean and bright. When the container was cut open, all the specimen tubes were removed intact.

Except in the case of the aluminum (which was obviously attacked) specimens were weighed and measured as in Procedure III. The results did not justify analysis of the decantates.

The results for specimens treated by Procedure IV are included in Table III.

The Armco iron specimen was cleaned with ammonium acetate, as described on page 8, before measuring and weighing.

Procedure V. Effect on Metals in a Heat-Transfer Test Unit

In some heat-transfer experiments by S. Untermeyer of the Reactor Engineering Division, Bi-Pb-Sn alloy was circulated in a test system for periods of time up to more than 1000 hours and at temperatures up to at least 400°C. Parts of the system were submitted to the Metallurgy Division for examination. Since the system was designed for heat-transfer tests, it is evident that the information obtainable on metal reactions is somewhat incomplete and perhaps not ideal for the evaluation of liquid-metal attack. The results, however, are the only data available from ANL for attack by dynamic Bi-Pb-Sn alloy.

The alloy was circulated by means of a cast iron pump in a housed system that was filled with argon from cylinders (believed to have been charged with argon in 1948*). The alloy was heated in a steel heater tube

* Before present high-purity argon was available commercially.

by passage of an AC current introduced by means of electrodes at each end, as shown in Figure 34a. Some of the current thus presumably flowed from an electrode through the tube wall into the liquid metal and out through the tube wall at the other electrode; but a fraction of the current (depending on the relative cross-sections and the resistance) flowed in the tube wall parallel to the current conducted by the liquid metal. The return pipe consisted of stainless steel tubing. This tubing was welded at the ends to mild-steel tubing.

The rate of flow through a 1/4" I.D. tube was calculated to be 7 feet per second.

Circulation of the Bi-Pb-Sn alloy resulted in the formation of a considerable amount of dross. This occurred despite attempts to provide an inert environment through the use of an argon atmosphere. A sample of the dross was submitted to the Metallurgy Division for examination.

During an attempt to thaw some Bi-Pb-Sn alloy that had frozen in the cast iron pump, the pump was broken (presumably by expansion of the alloy) and had to be replaced. Portions of the broken pump casting were also submitted to the Metallurgy Division for examination.

Tensile specimens were cut from the cast iron pump housing and were found to have normal strength and ductility for a cast iron. The respective values for three specimens were: Tensile strength, 16,000, 17,000, and 17,000 psi; elongation, 10, 10, and 0.9% in two inches. Figures 26a and 26b, respectively, show micrographs of the pump casting sectioned in a region where failure did not occur and also in a failure area.

After slightly over 1000 hours of service with Bi-Pb-Sn alloy the heater pipe was submitted to the Metallurgy Division for examination.

At the time of the dynamic test, the steel used for the heater pipe was supposed to have been made of ordinary low-carbon steel. Subsequent chemical analysis, however, showed it to contain 0.168% S and 0.17% C. It was therefore made of a high-sulfur, free machining steel. The heater tube was fabricated by machining a 27/64" rod of this steel and drilling it out axially with a 1/4" drill. A sketch of the heater pipe, as well as micrographs taken from it after failure, are shown in Figures 34 and 35. Sulfide inclusions could be seen on examination of the specimen under the microscope (Figure 35b).

The system was subsequently used for circulating bismuth-lead alloy, but after about 12 hours service with this alloy, the return pipe failed. It was submitted to the Metallurgy Division for examination. Since

the failure was presumably due primarily to the previous 1000-hour service with Bi-Pb-Sn alloy, rather than to Bi-Pb alloy, the examination* of the specimen is included in this report.

Chemical analyses were carried out to determine the type of stainless steel used in the return pipe of the heat transfer system. The results indicated that the steel was Type 347 stainless, since the specimen was reported to contain the following weight percentages: 0.09 - C, 11.65 - Ni, 17.92 - Cr, 0.88 - Nb. The return pipe from the heater tube was completely filled with Bi-Pb at the time of failure. For illustrations of failure and of a reaction zone in the specimen, see Figures 36a and 36b.

The system therefore contained at least three solid metals: cast iron, free-machining high-sulphur steel, and Type 347 stainless steel (18-8Nb). A further complicating factor was that additions of magnesium and titanium had been made to the Bi-Pb-Sn alloy to determine their effect on heat transfer.

Concerning the dross taken from the system for examination, it was of interest to estimate the composition of oxide in the dross and thus to determine whether oxidation caused any shift in the ratio of Bi to Pb to Sn.

The oxide in the sample of dross was removed from the unoxidized metal by extraction with pretreated zinc chloride. The extraction was carried out by B. Blumenthal in accordance with a procedure outlined by A. J. Phillips.⁽¹⁾ The zinc chloride for the extraction was held above fusion temperature for two hours before addition of the dross. This procedure ensured absence of moisture. The metal collected in the bottom of the container (a Pyrex glass beaker was used). The fusion was cast into an assay cone mold made of graphite. The oxides either dissolved in the zinc chloride phase or were suspended in it.

Three oxide-free metallic buttons obtained by zinc chloride treatment of three 20-g samples of dross constituted 95.61%, 96.28%, and 95.10%, respectively, of the original dross. The average of these values is 95.66%. Subtracting this from 100 gives 4.3 as the percentage of oxide in the dross.

The dross treated as described had been crushed to -60 mesh in a Pyrex mortar and was further prepared by rolling and quartering. A representative portion of it was found by chemical analysis to contain the following percentages by weight: 50.3 - Bi, 29.8 - Pb, 18.3 - Sn, 0.05 - Mg, 0.01 - Fe, 0.01 - Ca, and less than 0.01 each of Ag, Al, As, B, Be, Co, Cr, Cu, Mn, Na, Ni, P, Sb, Si, Ti, Zn, and Zr.

* A substantial amount of work on this specimen was done by F. L. Brown, ANL, Metallurgy Division.

The metal separated from the oxides by the zinc chloride treatment was found by chemical analysis to contain the following percentages by weight: 50.8 - Bi, 30.5 - Pb, 17.2 - Sn, 0.01 - Fe, 0.05 - Mg, and less than 0.01 of any of the trace elements listed in the analysis of the dross.

Since 100 g of dross would contain 50.3 g of Bi (metal plus metal in oxide) and 95.7 (the average per cent of metal in the dross) grams of metal would contain 50.8 w/o of Bi, or 48.6 g of metallic Bi, the dross would contain $50.3 - 48.6 = 1.7$ g of Bi as an oxide.

Similarly, 100 g of dross would contain.

$$\begin{aligned} 29.8 - 95.7 \times 0.305 &= 0.6 \text{ g of Pb as oxide, and} \\ 18.3 - 95.7 \times 0.172 &= 1.8 \text{ g of Sn as oxide,} \end{aligned}$$

Assuming the formation of Bi_2O_3 , Pb_2O , and SnO :

1.7 g Bi would correspond to	1.89 g of oxide
0.6 g Pb would correspond to	0.62 g of oxide
1.8 g Sn would correspond to	2.07 g of oxide
Total: 4.1 g metal would correspond to	4.58 g of oxide
	in 100 g dross

Assuming the oxide formulas to be as indicated, the total calculated percentages of oxides, 4.58, is close to the actual percentage of oxides, 4.34, extracted by the zinc-chloride. This is evidence that the oxide compositions formed were approximately those assumed.

Of the metals in the dross as oxides, 14.6% was lead, 41.5% was bismuth, and 43.9% was tin. Also present were traces of iron and magnesium (probably added as a wetting agent).

This showed that eutectic Bi-Pb-Sn alloy becomes depleted most rapidly in tin in oxidizing conditions prevail.

Procedure VI Tests with Specimens that Were Not Vacuum Sealed

Several static tests were carried out by the Reactor Engineering Division in which specimens were heated in the presence of Bi-Pb-Sn alloy. The resulting specimens were turned over to the Metallurgy Division for examination. In these tests, which were of an exploratory nature, no particular care was exercised in preparing the alloy, sampling, heating, or in controlling the atmosphere.

In one test, which will be called the semi-oxidizing test, a 7/8" I.D., 4" long tube of low-carbon steel was three-quarters filled with eutectic Bi-Pb-Sn alloy; the tube was plugged with an 18-8 type stainless steel plug (which was welded to the tube around the edge) and was heated for seven days in a furnace at about 570°C with the tube on its side.

Micrographs of a portion of the carbon steel container that was in contact with the Bi-Pb-Sn alloy are shown in Figures 29a, b, and c. Figure 38 shows a reaction layer on the stainless steel plug.

The question as to whether any metal from the carbon steel container or the stainless steel plug had passed into the Bi-Pb-Sn, in addition to having formed reaction layers, may be illuminated to a slight extent by Figures 40 and 41. Figure 40 is typical of the Bi-Pb-Sn alloy before use and shows simply a eutectic field. Figure 41 shows "foreign islands" in the Bi-Pb-Sn alloy that had been heated in the carbon steel container in contact with the stainless steel plug.

In the other test, which will be called the oxidizing test, a specimen of stainless steel and a specimen of Armco iron immersed in Bi-Pb-Sn alloy in an open porcelain container were heated for 16 days at about 500°C.

Micrographs of the Armco iron specimen are shown in Figures 23 and 24. The stainless steel specimen is shown in Figures 39a and b.

Procedure VII Tests of Chromium Steels at 600°C and 800°C with Environment Control, and of Molybdenum at 800°C

The effects of environment and of chromium content on the resistance of high-chromium (Types 430 and 446) stainless steels to attack by Bi-Pb-Sn alloy were the principal subjects of the investigations of Procedure VII, although molybdenum was also tested in Bi-Pb-Sn at 800°C.

In these tests, weighed and measured specimens were vacuum-sealed at 10^{-4} mm or mercury (much as for Procedure III, pages 6 to 9) into hourglass specimen tubes containing vacuum-cast Bi-Pb-Sn alloy, which, however, in alternate cases had been hydrogen treated. (Hydrogen was bubbled through the alloy only for a short time, in these cases, because of the formation of tin hydride which, if removed as dross, would reduce the amount of tin remaining.) The hydrogen-treated alloy was then heated at about 200°C in a vacuum in order to outgas the alloy (that is, to remove any moisture, excess hydrogen, and carbon dioxide, which is commonly present). In order to bring to light any effect of orientation, sets of specimens were cut parallel to and transverse to the direction of grain. (See Figure 42.) The specimen tubes were made of quartz, and a pair of similar specimens were sealed in each tube, except in the case of a blank specimen.

In these tests the mild-steel containers for the specimen tubes, and the surrounding Bi-Pb baths - about 70 cc in volume - consisted of bombs in tilting furnaces as shown in Figure 43. These bombs were constructed with tubes at the upper end, which were maintained sealed with rubber tubing and pinch clamps during the heating period. The molten Bi-Pb baths were normally drained out of the bombs on tilting the furnace after the seals were removed.

All specimens were prepared by polishing on 600-grit emery paper and cleaning with acetone, carbon tetrachloride, 200-proof alcohol, and petroleum ether before being sealed.

In the set of 600°C tests one pair of longitudinally cut specimens and one pair of transversely cut specimens were each vacuum-sealed in respective quartz tubes with vacuum-cast Bi-Pb-Sn; corresponding pairs of specimens were vacuum-sealed with hydrogen-treated Bi-Pb-Sn alloy. In addition, one metallographically examined transverse specimen (Figure 45b) was sealed with purified argon (but with no Bi-Pb-Sn alloy). At the end of the heating period the Bi-Pb bath was readily drained from the quartz specimen tubes.

The bomb from the 600°C test was opened at the drain tube and the Bi-Pb alloy was readily drained off by tilting the furnace. When the bomb was cut open, the quartz specimen tubes were intact and the Bi-Pb-Sn was found to have been effectively decanted from the specimens.

The decantates of Bi-Pb-Sn from the 600°C specimens were weighed and then analyzed chemically. One specimen from each pair was examined metallographically, and the other specimen was treated with 12 N nitric acid. Treatment continued until the weight change in one hour was insignificant and no globules of ternary eutectic alloy could be seen on the specimens. The specimens cleaned in this manner were then weighed and measured.

In the first set of tests at 800°C, the tube (3/16" wall thickness) extending into the bomb scaled off during the test, and the bomb itself acquired a 1/4" to 3/8" thick layer of scale. (The scaling is believed due to failure to aluminize the outside of the bomb.) Consequent to failure of the tube, the surface of the Bi-Pb-bath was extensively oxidized so that the Bi-Pb could not at first be drained out. It was therefore necessary to section the bomb beyond the scale level of the bath.

In a second set of tests at 800°C two pairs of the specimens consisted of Type 430 stainless steel sealed with Bi-Pb-Sn plus additions of lead monoxide (PbO). To one pair 0.0001 g of PbO was added, which would supply enough oxygen to correspond to approximately 35 layers of oxygen atoms if all were concentrated on the surface of the specimen. In the other case 0.0100 g of PbO was added, which would correspond to about 3500 layers of oxygen atoms if all were concentrated on the surface of the specimens.

Before being heated at 800°C, the bomb containing the specimens was heated for two days at 400°C to provide opportunity for the protective oxide film-forming reaction to occur on the specimens below the temperature at which Bi-Pb-Sn is believed to attack Type 430 steel.

Two other pairs of specimens in the second set of 800°C tests consisted of the higher chromium Type 446 steel, longitudinal and transverse, and a fifth pair of specimens consisted of molybdenum (see Figure 33).

All the specimens of Procedure VII were roughly $1/8" \times 1/8" \times 1/2"$ (their exact initial weights and dimensions were recorded). The time of heating for these specimens was approximately one month - 30 days for the 600° test and 32 days for the 800° tests including the two days at 400°.

Although some of the Bi-Pb-Sn alloy was decanted from the high-chromium steel specimens, an aggregate of crystals, which weighed about $3/4$ gram, remained with some undecanted Bi-Pb-Sn alloy in the upper part of the inverted specimen tube. The crystals had apparently been in part dispersed in the melt and in part attached to the specimen. These crystals were vacuum filtered from most of the Bi-Pb-Sn and treated with 12N nitric acid to remove adhering traces of Bi-Pb-Sn. The acid does not attack the crystals. Chemical analysis indicated the crystals to contain the following percentages by weight: 1.5 - Sn, 15.1 - Cr, 82.6 - Fe, 0.01 - Pb, less than 0.01 - Bi (see crystals in Figure 54).

Specimens to be weighed and measured were treated with 12N nitric acid at room temperature for 18 hours (or until the weight change in one hour was insignificant and no globules of ternary eutectic alloy could be seen on the specimens).

Specimens for metallographic examination were not treated with the acid.

Both molybdenum specimens were treated for 24 hours in concentrated HCl at 60°C to 80°C.

The results of the tests showing the effects on Type 430 steel of orientation, hydrogen in the bath, and temperature are given in Table IV. The results of the testing showing the effects of chromium content in ferritic stainless steel, and of oxygen content in the system are given in Table V.

DISCUSSION OF RESULTS

Discussion of Results for Aluminum

Von Kremann,⁽²⁾ among others, has shown that passage of an electric current through a molten alloy can sometimes effect a differential transport of material just as passage of a current through an aqueous solution sometimes can effect transport, resulting in anodizing, for example, or in plating, as well as in local changes in solution concentration. The current might be expected to influence (increase or decrease) the tendency of a component of the molten alloy to migrate out of the alloy and react with a metal electrode, which might, if desired, be the container itself. It might further be expected that such a current could be used to protect an anodized aluminum electrode against the attack of a liquid metal. The current might actually repair and preserve the anodized coating, in the event that temperature changes should cause local cracking or flaking of the coat, or in the event that the alloy might otherwise tend to penetrate the coating and attack the base metal, particularly when at elevated temperatures.

Differential transport has not been commonly observed in molten alloy because the DC sources available have not always been adequate to maintain the current densities required for the cross sections involved.

If, however, a current of a few milliamperes were caused to pass through incipient pinholes in an anodized coating, it is conceivable that the current density at the pinhole might easily be high enough to exert an effect, the nature of the effect depending on the direction of the current.

Protective Potential and Anodized Coating

From the meager experimental work that has been carried out by Procedure I, pages 4 to 5, there is evidence that a potential of 45 volts does tend to protect an anodized aluminum anode at temperatures nearly up to the melting point of aluminum, and that an anodized coating retards the attack by Bi-Pb-Sn to some extent, even in the absence of an electric current.

In considering the protective action of an anodized coating per se, it is believed that the results obtained with Specimen C (see Figure 1 and 7, and Table II) are apt to be typical and that Specimen A (Figures 1 and 5) is not typical. It is probable that the presence of the tungsten wire had no direct effect on the results, but that some leakage of air occurred into container A, probably around the seal at the broken tungsten wire.

The electric current perhaps tended to preserve the anodized coat on Specimen D, and may have tended to deplete the ternary alloy of tin and possibly of bismuth in the locality of the anodized coat. The lead, which presumably tends to remain in that region, apparently is not as aggressive in its attack on the aluminum and on the anodized coat.

Specimen C (Figure 7) which was simply anodized and then exposed to B-Pb-Sn alloy gained less than D (Figure 4) in dimensions and lost less in weight. In some places C lost no dimensions. In the case of Specimen C, chemical analysis showed the apparent solubility of aluminum in the bath to correspond to a loss of 0.27 gram of aluminum from the specimen. Since the actual loss of weight (0.0004 gram) is comparatively insignificant almost 0.27 gram of metal from the melt must have been picked up by the specimen in exchange for the aluminum that was lost. Figure 4 shows the reaction zone on this specimen.

A comparison of Specimens C and D verifies the fact that an anodized coating by itself was not as protective as when a specimen with such a coating was also maintained as an anode with respect to the melt. The potential difference is presumed to have reduced the amount of metal dissolving into the specimen.

Diffusion Reaction

In the event that the diffusion reaction between B-Pb-Sn and aluminum were to result in a compound that would act as a diffusion barrier it would be expected to slow down or stop the reaction. Incompleteness of attack on a small aluminum specimen during the test of Procedure IV which involved heating aluminum in B-Pb-Sn at 500°C for eighty days showed that there is probably some protective action due to the formation of a diffusion barrier. At the test temperature 500°C the attack was nevertheless too severe for unprotected aluminum to be considered as a container for B-Pb-Sn (see Figure 30).

The metallographic section of Specimen B Procedure I (Figure 6) shows the reaction zone that occurred.

Effect of Temperature

The proximity to the melting temperature of specimens treated by Procedure I constitutes a drastic test of aluminum and anything that tends to inhibit attack at this temperature range may be considered for application at lower temperatures.

Evidence that lowering the test temperature increases the resistance, even of unprotected 2S aluminum, as might be expected for a comparison of Specimen B (Procedure I) which was heated in B-Pb-Sn for only 16 hours at 550°C to 650°C to the aluminum specimen (Procedure IV) which was heated for 80 days at 500°C. The latter specimen appeared no more badly attacked than the former. Further data for temperatures lower than 500°C would be needed to complete a study of the effect of temperature.

Solubility in Melt

From the aluminum-tin diagram^(3,4) the solubility of aluminum in eutectic Bi-Pb-Sn alloy in the temperature range of 550°C to 630°C should lie between 3 and 4 w/o if the solubility to aluminum in lead and bismuth is essentially nil. This value, estimated from the dilution ratio, is a little more than was found experimentally (Procedure I, Specimen B), as the amount of aluminum actually found in the melt by analysis was 1.46 w/o.

It appears that, except by dilution, lead and bismuth do not markedly affect the tendency of aluminum to dissolve in tin, but may have some secondary inhibiting effect. In application of the dilution factor to the solubility indicated in the phase diagram, aluminum would appear to have poor resistance to solution attack by Bi-Pb-Sn alloy at temperatures as low as 300°C.

In contrast to this is the solubility of the specimens of anodized aluminum maintained at a potential of 45 volts with respect to the melt. With this protection the apparent solubility was only 0.14 w/o of aluminum (instead of 1.46 w/o).

The relative weight losses of Table II are, on account of pick-up from the bath, of no significance by themselves, but should be considered in the light of other data in the table and of the metallographic results and the appearance of the specimens (see Figures 3 to 7). The apparent solubilities of Specimens B, C, and D give some indication of the relative solution attack although any aluminum oxide formed and removed, as presumably with Specimen A, would be included in the analysis on which the apparent solubility is based.

Direction of Current

The cooling indicated by a portion of the curve of Figure 2 was carried out with the direction of the current reversed. At 330°C the current on heating was 1000 times greater than the reversed current at the same potential, on cooling. It can be conjectured either that a film with a rectifying action was present or that a change in resistance occurred as the result of reaction after the anodic measurement was made and before the cathodic measurement was made.

Since the anodic current minimized attack on the specimen, the cathodic current may have had the opposite effect. Its time of application was only 5% of the total, and the current was much weaker. Its effect would therefore be minor. It may, nevertheless, have been responsible for part of whatever attack did occur on Specimen D.

Discussion of Results for Beryllium

As indicated in Table III, and in Figures 9 and 10, Bi-Pb-Sn does not attack beryllium at 500°C. When tested as in Procedure III, no beryllium was detected in the decantate, there was no reaction zone, and the specimens did not appear to have been wetted by the molten alloy.

Appreciable attack by Bi-Pb-Sn alloy on beryllium at 500°C would probably occur only if enough oxygen or other material such as nickel, capable of reacting with beryllium, were present in the test system.

Discussion of Results for Titanium

The thirty-day test specimen of titanium (Figure 31) did not appear to the eye to have a reaction zone, but Figure 32 and the data of Table III leave no doubt that titanium is slightly attacked by Bi-Pb-Sn alloy in the neighborhood of 500°C under the test conditions of Procedure IV, page 10. The rate of attack 2.5 mils in eighty days is not great. The stock from which the titanium specimens were taken was reported to contain a trace of manganese. Because of the small amount it is doubtful that this appreciably influenced the reaction.

Discussion of Results for Zirconium

Although Table III and Figures 11, 13, 15, and 17 indicate that Bi-Pb-Sn alloy at 500°C may slightly attack zirconium, impurities in the zirconium appear to be a factor. Although no zirconium was found in the decantate, measurement of the specimens showed a slight decrease in their weight and volume, and reaction zones of 0.5 and 1 mil were observed. Since no measurable zirconium was removed, loss in weight must be due chiefly to a removal of impurities.

It was observed that the greater penetration occurred on the specimen having the smaller grains and the greater number of plate-like crystals. Orientation and grain size may be co-factors influencing the rate of attack.

Discussion of Results for Armco Iron, Cast Iron, and Steel

The phase diagram^(3,4) for iron and tin shows that the solubility of iron in tin at 500°C is about 2 w/o, so one might expect the solubility of iron in eutectic Bi-Pb-Sn alloy (a 16 w/o tin alloy) to be about 0.3 w/o. Actually, however, less than 0.01 w/o of iron was found in any of the eutectic alloy specimens used in test Procedures III, IV, or VI (see Table III). In the case of the thirty-day tests at 500°C, only 0.002 w/o Fe was found in the Bi-Pb-Sn decantate from an Armco iron specimen, and 0.0025 w/o Fe was found in the Bi-Pb-Sn decantate from a cast iron specimen. These percentages would include any particulate iron or iron compound in suspension as well as the iron that was dissolved.

This would rule out solution attack as an important consideration insofar as solution of iron at 500°C is concerned. If the phase diagram is correct the lead and bismuth or one or the other evidently tend to reduce the solubility of iron in liquid tin.

The solubility results mentioned do not rule out the possibility of solution attack or intergranular material such as carbides. Tin need not be held responsible for this type of attack so much as bismuth.* For example the Bi-Pb constant temperature baths of Procedure III and IV attack the mild steel coritainers intergranularly but lead in the absence of oxygen is less reactive intergranularly with steel than is bismuth. Bi-Pb-Sn is more aggressive in its attack however than is Bi-Pb because tin readily reacts with the iron of the exposed grain once an avenue of intergranular invasion is open (see Figure 20).

Iron-Tin Compound Formation

As is known iron and tin form various compounds but there is no unanimity as to the ranges of stability of their respective structures.^(3,4,5) FeSn_2 which is tetragonal (or hexagonal) is unstable above 450°C or 496°C. When it breaks down on rise in temperature excess tin should form around islands of hexagonal (or monoclinic) Fe_3Sn_2 which is stable to 600°C (or from 0 to 800°C). At 760°C there is a tendency to form hexagonal Fe_2Sn (or Fe_2Sn) which is stable to 900°C. None of these compounds is isomorphous with ferritic iron. The reaction layers are therefore unlikely to be uniformly protective and adherent particularly during temperature changes that involve changes in the compounds or that involve differential expansion.

Loosely adherent compound particles can be cracked by the expansional stresses of freezing and thawing of the Bi-Pb-Sn and dislodge during dynamic testing. Fissures in the compound layer would be ideal sites for localized attack such as occurred in the dynamic test of Procedure V, pages 10 to 12. This when it occurs makes the rate of attack faster than if it depended on simple diffusion.

Any ferritic specimen (see for example Figures 21b, 27, and 29) that has experienced appreciable attack will exhibit evidence of both intergranular envelopment and of transgranular attack and the localized attack just mentioned is not uncommon (see Figures 25a and 34b). In the case of Armco iron as compared with SAE 1020 steel (see Figures 24 and 29) limitation in the amount of intergranular material may in that sense retard intergranular attack but because of grain growth and the initial relative size of the grains in Armco iron any intergranular attack that does occur on Armco iron is apt to be relatively destructive. Another form of attack can occur on relatively weak and brittle containers. For example containers of cast iron, which is relatively weak and brittle may perhaps be damaged by the expansion

*However as will be shown such attack is negligible at these temperatures unless oxygen is present.

of Bi-Pb-Sn on freezing although this was not observed, but fracture of the container has occurred when frozen Bi-Pb-Sn was being warmed to the melting point (see Figure 26). It is interesting that the graphite of cast iron is relatively resistant to attack by Bi-Pb-Sn at 500°C (Figure 25), particularly in the inert environment of Procedure III. The weight loss experienced by the companion to this specimen (vacuum-sealed with Bi-Pb-Sn at 500°C for one month) would correspond to an average penetration of 4.5 mils.

Effect of Oxygen

The presence of oxygen in a system increases the rate of attack by Bi-Pb-Sn on iron or carbon steel although, as later discussion will show, oxygen sometimes helps to protect stainless steel against such attack.* For example, a 2-mil reaction zone appeared on the mild-steel specimen vacuum-sealed with Bi-Pb-Sn at 500°C for eighty days (Procedure IV, Figure 27), whereas uneven penetration of one to two mils occurred in only seven days on a specimen heated in the neighborhood of 570°C in the presence of a limited amount of oxygen (Procedure VI, Figure 29). The increase in the rate of attack, based on the average increase in depth of reaction zone per month, is of the order of ten-fold for the latter specimen. (It would not be accurate to attribute the increased rate of attack entirely to the presence of oxygen, since the respective test temperatures were not strictly comparable.)

The tests with Armco iron specimen heated for only 16 days in Bi-Pb-Sn alloy at 500°C in the presence of air had a 5-mil reaction zone (Procedure VI, Figure 23). Vacuum-sealed specimens heated in Bi-Pb-Sn alloy at approximately the same temperature for 30 days (Figures 19 and 20) and 80 days (Figure 21) had fairly uniform reaction zones averaging 0.8 mil and 1.05 mil, respectively, although Figure 21 shows a non-typical part of the reaction zone which is abnormally deep.

Depth of Penetration

From the depth of the reaction zone one can roughly calculate and compare depths of actual penetration in the following way. The enveloping of some of the outer grains by the reaction zone is evidence of intergranular

*In the long run this statement probably holds regardless of whether the oxygen is dissolved in steel, is present in intergranular segregate, is present as surface oxide, is present as dross in the melt, or is present in the atmosphere. If the temperature is high enough, it may also hold for oxide segregated or dissolved within the grains. The present tests are compatible with this statement, although much more needs to be done to test it in all its ramifications. One exception would be if the only oxygen were present as highly stable oxides, as in aluminum-killed steel, and if no dross capable of reacting with the stable oxides were present in the melt.

attack, although these grains also show obvious transgranular attack. Since solution attack is not a factor, and tin is the most aggressive of the elements in the ferrary electrode (6) the depth of penetration by transgranular attack will depend on which iron-tin compound has formed. Assuming that the average composition of the reaction compound corresponds to FeSn ,* the penetration of the Armstrong diffusion compound formation would be approximately one-half the depth of the transgranular reaction zone. This is because the atomic volumes referred for the compound are of the same order as for iron. No intergranular attack is in this case assumed.

Since however, a study of the specimens indicates that intergranular attack predominates the development of surface grains - at least, initially - these grains are attacked transgranularly from all directions. The initial rate of transgranular attack in a single direction would, therefore, be of the order of one-half the apparent penetration rate, i.e. $(1/2) \cdot (1/2)$ times the depth of the observed transgranular reaction zone formed in a given unit time. This is, of course, a rough approximation whose validity decreases with the grain size.

Should the intergranular form of attack diminish with time, or be initially absent, the transgranular penetration would then be from a single direction, and the penetration rate would approach, or equal, $1/2$ times the depth of the observed transgranular reaction zone formed in a given time.

*In support of the assumption that FeSn is the principal compound formed by the reaction of iron with Bi-Pb-Sn at 500°C is the fact that the average gain in dimension of 1 x 80-day Armstrong specimen was approximately equal to half depth of the reaction zone. (This specimen was chosen to minimize the effect of accumulation of oxygen.)

The measured gain of one mil in dimension corresponds to 0.5 mil build-up on each of two opposite surfaces. The mean measured reaction penetration is the depth of the reaction zone minus the build-up on a surface, i.e., $1.1 - 0.5 = 0.6$ mil.

It is assumed here that FeSn is hexagonal and parameters $a = 4.23\text{\AA}$, $c = 5.12\text{\AA}$, and has a NiAs structure. This results in the average volume referred per atom of FeSn being $18\text{\AA}^3$ as compared to about $12\text{\AA}^3$ for ferrite. Consequently, if X = the average depth of penetration, the build-up in the case of FeSn formation would be $(18/12)^{1/3} X = 1.1 X$. Hence, if the build-up is 0.5 mil, the depth of penetration would be 0.46 mil, or approximately 0.5 mil. Hence, in view of the roughness of the measurements, this agrees as closely as can be expected with the measured value.

If the formation of Fe_2Sn or FeSn_2 would have resulted in 1.1 mil or 1.6 mil calculated penetration for the same build-up. Formation of FeSn_2 would have resulted in twice the build-up for the same penetration.

Now Figures 21 and 27 suggest that intergranular attack does not progress rapidly beyond the surface grains of these specimens - even though it was an important factor in creating the reaction zones that have been observed.

In the case of the vacuum-sealed specimens an initial intergranular attack which eventually slows down and nearly stops can be explained by the presence of traces of oxygen, perhaps on the surface or in the surface zone of the specimens or dispersed in the Bi-Pb-Sn. (Unless the system were subjected to a strongly reducing environment prior to the test, it is difficult to see how all traces of oxygen could have been eliminated.) These traces can promote and accelerate incipient intergranular attack but apparently are not sufficient to maintain it. Otherwise the region of intergranular attack would have progressed farther beyond the region of transgranular attack and one should see additional partially enveloped grains farther within the reaction zone. These remarks apply to reactions at about 500°C.

On the basis of this explanation one can predict that a reaction modulus, k , for a 30-day test on a vacuum-sealed specimen would (because of the presence of trace amounts of oxygen*) be slightly greater than that obtained for an 80-day test on a corresponding specimen. One can likewise predict that k for a specimen tested in the presence of gross amounts of oxygen would be greater. These predictions have been confirmed.

For transgranular reactions that are purely diffusion dependent, the reaction modulus should be the same for every specimen in the same environment, regardless of the duration of the test. Differences in k must be attributed to the presence of oxygen (not necessarily to different amounts of oxygen if the testing periods differ), since oxygen seems to be the chief, if not the only, factor present capable of complicating the reaction.

The diffusion formula $x = k(t)^n$, where x = depth of transgranular penetration in mils, t = time, and $n = 1/2$, gives (for Armco iron):

$k = 0.015$ for the 30-day test in vacuum; ($x = 0.4$; $t = 720$)

$k = 0.014$ for the 80-day test in vacuum; ($x = 0.6$; $t = 1920$)

$k = 0.064$ for the 16-day test in the presence of air; ($x = 1.3$; $t = 384$)

The k 's for the vacuum-tested specimens were calculated on the basis that the transgranular penetration was $1/2$ the depth of the reaction.

The k for the specimen tested in the presence of air was calculated on the basis that the uni-directional transgranular penetration was $1/2 \times 1/2$ the depth of the reaction zone (to allow, as before, for the composition FeSn and also for intergranular attack leading to transgranular envelopment). Thus, the 5-mil reaction zone corresponded to 1.25-mil uni-directional penetration.

*Which would encourage intergranular attack and thus permit transgranular envelopment of grains.

This k value, for a system from which no attempt was made to exclude air, is thus approximately 5 times the k values obtained for outgassed systems. If the effect of intergranular penetration were not excluded, the k value for the specimen tested in the presence of air would obviously be 8 to 10 times that for the vacuum-sealed specimens. This latter ratio is a more realistic measure of the effect of air on the corrosion rate, since intergranular penetration actually does take place.

The data for cast iron are also indicative of enhanced corrosion by Bi-Pb-Sn when in the presence of oxygen. A portion of the pump casting submitted by S. Untermeyer has a 3-mil reaction zone (see Figure 26). Some replacement of the graphite veins near the surface and the presence of dross indicated an oxidizing environment. The Bi-Pb-Sn in contact with the pump casting was in the temperature range of only 120°C to 250°C, while cast iron tested in an evacuated system was at 500°C.

The indicated rate of attack for the pump casting was, nevertheless, in terms of mils per month, five times the rate observed for the relatively oxide-free system in which the 30-day test specimen had a 1-mil reaction zone. Although the relatively oxide-free system was static and the other was dynamic, the rate of movement of Bi-Pb-Sn through the pump body was slow, and extensive erosive action was therefore improbable.

In the case of the free-machining high-sulfur steel heater tube of Procedure V, the fluid flow was fast enough to be turbulent (therefore erosive to loosely adherent iron-tin compounds). Resulting voids in the compound layer may have been a factor in the localized pit-type attack that occurred. Little can be said as to any effect due to heating by alternating current or to the presence of sulfur, or of any resulting lead sulfide. In view of the effect of an anodized coating on aluminum, one cannot immediately rule out the possibility of some local insulating, protective, or rectifying action of a sulfur compound.

The slight weight loss recorded for an Armco iron specimen treated at 500°C for one month was probably due to abrasion losses incurred during the removal of adherent Bi-Pb-Sn prior to weighing, despite a correction for material found in the ammonium acetate leach solution. The analytical results show that the loss could not have been due to solubility.

Exposure of iron and steel to Bi-Pb-Sn at temperatures below 450°C, instead of, say, 500°C, might lead to the initial formation of FeSn_2 instead of FeSn . This perhaps should minimize attack by increasing the thickness of the reaction zone for a given amount of penetration.

Discussion of Results for Stainless Steel

The only specimens of austenitic (18-8 type), chromium-nickel stainless steel tested in Bi-Pb-Sn alloy were two static-test specimens and one dynamic-test specimen submitted by the Reactor Engineering Division. The

object of these tests (Procedures V and VI) was, insofar as they are germane to this report, to evaluate the resistance of these steels to attack by Bi-Pb-Sn alloy. The results did not appear to justify additional tests with austenitic stainless steel, and little is known about the factors influencing attack.

Although a sample taken from the eutectic alloy used for the one-week semi-oxidizing test at 570°C contained less than 0.01 w/o each of nickel, chromium, and iron (spectrographic analysis), the sampling procedure did not take account of segregation in the melt, and the analysis does not necessarily indicate the true contents.

The reason for the failure at 300°C of the dynamically tested niobium-bearing, chromium-nickel (Type 347) stainless steel tube is presumed to be a local defect in the steel - perhaps an inclusion, a cold shut, or an incipient crack resulting from welding stresses or embrittlement. Most of the inner surface away from the weld area was relatively unaffected.

The magnesium and titanium added to promote wettability of the Bi-Pb-Sn may have reduced oxides which might otherwise have had a protective action on the stainless steel.

A comparison of the statically tested austenitic stainless steel specimens* (Figure 38, for example) with the plain carbon steel specimens (Figure 29) shows less envelopment of grains in the case of the stainless steel.

Of the stainless steel specimens tested at ANL most were of straight high-chromium types of steels (Procedure VII). Data from American Smelting and Refining Company⁽⁷⁾ had suggested that chromium steels have good resistance to attack by Bi-Pb-Sn alloy, and that increase in chromium content increased this resistance. High-chromium steel, such as Type 430 (16 w/o Cr, 0.12 w/o C), was reported to have had good resistance to attack at 648°C. Various higher chromium steels were somewhat more resistant and had, according to the report, good resistance at temperatures up to about 760°C. The tests at ANL were to check these indications and to determine what factors might affect the results.

The tests at ANL were at 600°C and at 800°C, thus bracketing the temperatures used for most of the tests at American Smelting and Refining Company (A. S. and R.) that appeared to be relevant. It is significant that the A. S. and R. results were obtained with specimens in a Bi-Pb-Sn bath protected only by a graphite blanket, while the specimens at ANL were sealed with Bi-Pb-Sn in quartz capsules (either evacuated, or with known additions of oxygen). Moreover, the effect of pretreating the melt with hydrogen was studied at ANL, and also the effect of grain orientation - but the latter turned out to be unimportant.

*Examined by S. Hugh Paine.

The higher chromium Type 446 (25 w/o Cr - 0.35 w/o C) steel had poor resistance to attack by Bi-Pb-Sn alloy at 800°C (see Figure 55). At this temperature the iron-chromium alloy was sufficiently soluble in the eutectic alloy to form crystals - at least when the system was oxygen free (see Figure 53). No opportunity was provided for comparing Type 446 steel with Type 430 steel or for investigating the effect of oxygen additions on Type 446 steel - other than comparison of a test with a hydrogen-treated melt with one containing ordinary amounts of oxygen.

In the tests with Type 430 steel in a system to which some oxygen was deliberately added as lead oxide the oxygen presumably formed a rather uniformly protective coating by oxidizing the surface of the specimens. The conditions of these tests apparently approximated the A, S, and R, conditions to the extent that the attack was less than in the oxygen-free systems. The A, S, and R, tests however permitted the continual ingress of limited amounts of oxygen perhaps as carbon monoxide or dioxide* during the entire period of the test. The rate at which this occurred was not enough to form a gross (of undetermined corrosive potentialities), but the continual migration of oxygen to the specimens might be expected to help maintain a protective layer on them.

In the tests at ANL no oxygen (other than that initially sealed in the system) could enter. Hence there was no inward migration of oxygen to maintain a protective layer once it was penetrated. The limited amounts of oxygen that were present however appeared to be progressively protective in accordance with the amounts added. Table IV and Figures 44, 47, 48, 49, 50, 51, and 52 show that attack on Type 430 steel in a system containing hydrogen-treated Bi-Pb-Sr was greater than in a system containing normal vacuum-melted Bi-Pb-Sr at 600°C but not at 800°C and attack in the normal system was greater at 800°C than in one containing a minute addition of lead oxide and attack in this system was greater than in one containing an addition of one hundred times as much lead oxide.

Discussion of Results for Molybdenum and Tungsten

Since molybdenum underwent no significant changes in weight nor in dimensions, nor exhibited any metallographic evidence of reaction, despite treatment for one month in Bi-Pb-Sn alloy at 800°C molybdenum ranks high above other metals tested for resistance to attack by eutectic Bi-Pb-Sn (see Figure 33).

*A gas is evolved from commercial lead when it is heated in a vacuum. O. C. Shepard Stanford University School of Mineral Science, had verbally reported that such a gas has been identified as carbon dioxide. This would indicate the solubility of such a gas and its ability to diffuse through the melt.

Considerations of ordinary chemistry would suggest that molybdenum would getter oxygen in the system, and that the resulting molybdenum oxide would volatilize at the higher test temperatures. Instances in which attack has been observed on molybdenum that has been heated in Bi-Pb-Sn alloy or in Bi-Pb can, perhaps, be explained in this way.

The same suggestion might apply to tungsten in Bi-Pb-Sn. Although no formal test of tungsten was made in the work covered by this report, the fine tungsten wire used in connection with a test on aluminum (Procedure I) did not appear to have been attacked.

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TABLE I

Effect of Temperature on Values of Current and Resistance when Heating and Cooling Anodized Aluminum in Eutectic Bi-Pb-Sn While Maintaining a Potential Difference of 45 Volts Between the Aluminum and the Eutectic Bath

Temp. °C	Time of Reading hours	Polarity of Specimen	Heating or Cooling	Current,* Milliamp/cm ²	Resistance,* ohms x 10 ³ cm ²
20	0	Positive	-	0.026 (inHg)	140
108	1.2	Positive	Heating	0.003	1290
150	-	Positive	Heating	0.22	17
200 to 250	-	Positive	Heating	0.14	26
275	3.25	Positive	Heating	0.22	17
300	-	Positive	Heating	0.3 to 1.7	13 to 2.1
330	5	Positive	Heating	260.0	0.014
600	19	Negative	Cooling	30.0	.13
550	-	Negative	Cooling	3.0	1.3
500	-	Negative	Cooling	0.66	5.7
450	-	Negative	Cooling	0.43	8.6
400	-	Negative	Cooling	0.3	13
350	-	Negative	Cooling	0.3	13
330	20	Negative	Cooling	0.26	14

* Based on 3.5 square centimeters as the value for the area of interface between the melt and the specimen.

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TABLE II

Measurements on Aluminum Specimens Treated by Test Procedure I at 540° - 630°C in Bi-Pb-Sn

Specimen	Length, In.	Diameter, In.	Weight, g.	Al Found in Bi-Pb-Sn	Remarks
A. Anodized No Current before test after test difference	2.5053 <u>2.5043</u> -0.0010	0.1732 <u>0.1725</u> -0.0007	2.6788 <u>2.6609</u> -0.0190	3.10 w/o	W wire intended for use as an electrode broken. Possible air leak at seal. See Figs. 3A and 5.
B. 2S No Current before test after test difference	2.5122 - large, negative	0.1874 - large, negative	3.0652 - large, negative	1.46 w/o	See Figs. 3B and 6.
C. Anodized No Current before test after test difference	2.5113 <u>2.5129</u> +0.0016	.1810 to .1852 <u>.1818 to .1861</u> +0.0008 to +.0009	2.9352 <u>2.9348</u> -0.0004	0.94 w/o	Dia. not uniform. See Figs. 3C and 7.
D. Anodized 45 V applied During Test before test after test difference	2.5121 <u>2.5361</u> +0.0240	0.1876 <u>0.2115</u> +0.0239	3.0533 <u>3.0369</u> -0.0164	0.14 w/o	Anodized specimen maintained as anode in Bi-Pb-Sn. See Figs. 3D and 4.

TABLE III

Results for Specimens Tested in Bi-Pb-Sn at 500°C by Procedures III and VII, and for Molybdenum Tested in Bi-Pb-Sn at 800°C by Procedure VI

Specimen	Temp., °C	Duration, Days	Length, Inches	Width or Dia., In.	Thickness, Inches	Weight, g	Bi-Pb-Sn, g used	Remarks
<u>Be #1</u> Before After	500	30	0.3754 0.3756	0.1231	-	0.1323	47.74	Appearance and metallographic behavior same as for Be #2. No attack observed.
<u>Be #2</u> Before After	500	30	0.3758 0.3758	0.1247 0.1247	-	0.1367 0.1367	42.53	See Figs. 9 and 10. No Be found in decantate. No attack observed.
<u>Zr #1</u> Before After	495	30	0.3916 0.3785	0.1286 0.1286	- -	0.5039 -	44.15	See Figs. 11, 13, 15 and 17. No Zr found in decantate. Slight attack.
<u>Zr #2</u> Before After	495	30	0.3995 0.3695	0.1284 0.1294	- -	0.5146 0.5064	32.23	See Figs. 12, 14, 16 and 18. Slight attack.
<u>Armco #1</u> Before After	490	30	0.3707 0.3742	0.1268 0.1270	0.1247 0.1255	0.7389 -	28.63	See Fig. 20. Specimen wiped. No other attempt to clean. 0.002-w/o Fe in decantate.
<u>Armco #2</u> Before After	490	30	0.3614 0.3616	0.1269 0.1270	0.1253 0.1266	0.7231 0.7146	30.35	See Fig. 19. Specimen KOH treated. Weight corrected for Fe in KOH.
<u>Armco #3</u> Before After	485±15	80	0.6237 -	0.2034 -	- -	1.5718 -	21.32	See Figs. 21 and 22. Slight attack.
<u>Armco #4</u> Before After	485±15	80	0.6286 0.6301	0.2013 0.2023	- -	1.4229 1.4235	29.20	Specimen cleaned with ammonium acetate.
<u>Cast Iron #1</u> Before After	485	30	0.4965 0.4982	0.1880 -	0.1751 0.1729	1.8346 -	47.45	See Fig. 25. Specimen wiped only. Slight attack.
<u>Cast Iron #2</u> Before After	485	30	0.5006 0.5035	0.1842 0.1862	0.1920 0.1931	1.9854 1.9739	40.15	0.003-w/o Fe in decantate. Specimen KOH treated. Weight corrected for Fe in KOH.
<u>Aluminum #1</u> Before After	485±15	80	0.60 -	0.19 -	- -	0.73 -	21.82	Specimen severely attacked. See Fig. 30.
<u>Aluminum #2</u> Before After	485±15	80	0.64 -	0.19 -	- -	0.77 -	24.09	Specimen severely attacked.
<u>1020 Steel #1</u> Before After	485±15	80	0.6154 0.6164	0.1876 0.1895	- -	2.1754 2.1775	26.25	Specimen NaOH treated.
<u>1020 Steel #2</u> Before After	485±15	80	0.5896 -	0.1877 -	- -	2.0863 -	20.02	See Figs. 27 and 28. Slight attack. Specimen wiped only.
<u>Titanium #1</u> Before After	485±15	80	0.5038 0.5039	0.1951 0.1961	0.1985 0.1991	1.4229 1.4235	22.92	Very slight attack.
<u>Titanium #2</u> Before After	485±15	80	0.5166 -	0.1955 -	0.2080 -	- -	21.47	See Figs. 31 and 32. Slight attack on some areas.
<u>Molybdenum #1</u> Before After	800	30	0.4366 0.4367	0.2364 0.2359	0.1119 0.1119	1.8736 1.8732	52.5	Specimen not wet. No attack observed.
<u>Molybdenum #2</u> Before After	800	30	0.4315 0.4314	0.2490 0.2490	0.1124 0.1125	1.9521 1.9520	52.3	See Fig. 33. No attack observed.

TABLE IV

Thirty-Day Tests of Type 430* Stainless Steel in Bi-Pb-Sn Alloy at 600°C and 800°C
(Showing Effects of Orientation, Hydrogen in Bath, and Temperature)

Specimen	Temp., °C	Grain Direction	Treatment of Bi-Pb-Sn	Length, In.	Width, In.	Thickness, In.	Weight, gram	Grams of Bi-Pb-Sn	Remarks
<u>430 SS I</u> Before After Difference	600	transverse	vac.-cast	0.6173 0.6174 +0.0001	0.1373 0.1373 -0-	0.1110 0.1106 -0.0004	1.1372 1.1338 -0.0034	39.1	See Figure 44b for micro of companion specimen in same bath. Companion specimen parallel to grain.
<u>430 SS II</u> Before After Difference	600	parallel	H ₂ -treated	0.6176 0.6173 -0.0003	0.1665 0.1665 -0-	0.1065 0.1063 -0.0002	1.3306 1.3269 -0.0037	42.8	See Figure 44a for micro of companion specimen in same bath. Companion specimen transverse to grain.
<u>430 SS III</u> Before After Difference	800	transverse	vac.-cast	0.6147 - -	0.1744 - -	0.1093 - -	1.4351 0.6277 -0.7629	42.9	See Figure 47a for micro of companion specimen in same bath. Companion specimen transverse to grain.
<u>430 SS IV</u> Before After Difference	800	transverse	H ₂ -treated	0.6163 - -	0.1778 - -	0.1081 - -	1.4626 0.7816 -0.6810	42.1	See Figure 47b for micro of companion specimen in same bath. Companion specimen parallel to grain.

*Type 430 SS: 23 to 27 w/o Cr, 0.35 max. w/o C.

TABLE V

Thirty-Day* Test of Types 430 and 446** Stainless Steels in Bi-Pb-Sn Alloy at 800°C with and without Lead Oxide (Showing Effects of Chromium Content of the Steel and of Oxygen Content of the System)

Specimen	PbO Added, gram	Length, In.	Width, In.	Thickness, In.	Weight, gram	Grams of Bi-Pb-Sn	Remarks
<u>430 SS V</u>	0.0001					52.4	Reaction zone of companion specimen 6 to 10 mils. See Figure 51.
Before		0.4452	0.1943	0.1238	1.3109		
After		<u>0.4466</u>	<u>0.1955</u>	<u>0.1240</u>	<u>1.2895</u>		
Difference		+0.0014	+0.0012	+0.0002	-0.0214		
<u>430 SS VI</u>	0.0100					52.7	Reaction zone of companion specimens 1 to 6 mils. See Figure 52.
Before		0.4259	0.2112	0.1366	1.5318		
After		<u>0.4259</u>	<u>0.2113</u>	<u>0.1365</u>	<u>1.5126</u>		
Difference		-0-	+0.0001	-0.0001	-0.0192		
<u>430 SS VII</u>	nil					52.5	Irregular solution attack and greater reaction penetration on companion specimen than on 430 SS V or SS VI or their companions. See Figure 49. Specimen cut longitudinal to grain.
Before		0.4177	0.1625	0.1474	1.2282		
After		<u>0.4200</u>	<u>0.1628</u>	<u>0.1535</u>	<u>1.0185</u>		
Difference		+0.0023	+0.0003	+0.0061	-0.2097		
<u>430 SS VIII</u>	nil					52.1	Reaction zone of companion specimen 10 to 15 mils. Mean penetration greatest on this specimen. See Figure 50.
Before		0.3791	0.1817	0.1000	0.8374		
After		<u>0.3788</u>	<u>0.1817</u>	<u>0.1000</u>	<u>0.8188</u>		
Difference		-0.0003	-0-	-0-	-0.0186		
<u>446 SS I</u>	nil					53.5	0.22 g of Fe-Cr alloy crystals found in Bi-Pb-Sn. Penetration of companion specimen twice that of Type 430 SS. See Figures 55a and b. Specimen was back to back with companion.
Before		0.4301	0.2594	0.1185	1.6174		
After		<u>0.4360</u>	<u>0.2683</u>	<u>0.1271</u>	<u>1.3725</u>		
Difference		+0.0059	+0.0089	+0.0086	-0.0449		
<u>446 SS II</u>	nil					52.5	0.189 g of Fe-Cr alloy crystals found in Bi-Pb-Sn. Penetration of companion specimen twice that for Type 430 SS. See Figures 55c and d.
Before		0.4767	0.2604	0.1183	1.7730		
After		<u>0.4716</u>	<u>0.2638</u>	<u>0.1171</u>	<u>1.4902</u>		
Difference		-0.0051	+0.0034	-0.0012	-0.2828		

*Plus two days at 400°C (before heating to 800°C) to establish equilibrium.

**Type 430 SS: 14 to 18 w/o Cr, 0.12 max. w/o C.

Type 446 SS: 23 to 27 w/o Cr, 0.35 max. w/o C.

Because of broken
W wire, specimen
was tested as shown
without application of
current.

FIG. 1 DIAGRAM SHOWING SPECIMENS AS VACUUM-SEALED IN PYREX TUBES FOR TESTS SHOWING THE EFFECTS OF ELECTRICAL POTENTIAL AND ANODIZED COATINGS ON THE RESISTANCE OF ALUMINUM TO ATTACK BY Bi-Pb-Sn ALLOY

FIG. 2 VALUES FOR CURRENT AT 45 VOLTS THROUGH ANODIZED ALUMINUM IN Bi-Pb-Sn EUTECTIC ALLOY AT VARIOUS TEMPERATURES

Figure 3. Aluminum Specimen Rods

Macro 4465

Approx. 2X

Macro 4466

Approx. 2X

Side views and end views of 2S aluminum rods after partial immersion in Bi-Pb-Sn alloy at 540°C to 630°C (near the melting temperature of aluminum) for 16 hours. "A" was anodized and a tungsten wire was in the melt. "B" was unprotected aluminum. "C" was anodized. "D" was anodized and maintained as an anode at 45 volts during most of the test. The specimen appears to have been partially upset by its own weight.

Figure 4. Anodized Al Maintained as Anode in Bi-Pb-Sn

Sections of "Specimen D" of Figure 3: Left top, section of portion maintained above Bi-Pb-Sn; right top, section through swollen portion near surface of Bi-Pb-Sn; bottom, section through portion of specimen immersed in Bi-Pb-Sn at 540°-630°C for 16 hours.

Figure 5. Anodized with W

2 mils

Micro 6918

250X

Section of anodized Al heated in Bi-Pb-Sn in presence of W wire. "Specimen A" of Fig. 3.

Figure 6. Unprotected 2S

2 mils

Micro 6917

250X

Section of unprotected ^{aluminum} 2S heated in Bi-Pb-Sn at 540-630°C for 16 hours. "Specimen B" of Fig. 3.

Figure 7. Anodized

1 mil

Micro 6915

500X

Section of anodized Al heated in Bi-Pb-Sn for 16 hours at 540-630°C. "Specimen C" of Fig. 3.

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ROTATE CHAMBER 180° ON AXIS TO DECANT Bi-Pb-Sn FROM SPECIMENS. BURN OFF WELDED-IN PLUGS TO DRAIN MOLTEN Bi-Pb FROM CHAMBER AT END OF TEST. SAW OFF END OF CHAMBER AND REMOVE SPECIMEN TUBES WHILE Bi-Pb-Sn IS STILL MOLTEN.

FIG. 8 STEEL CHAMBER CONTAINING CONSTANT-TEMPERATURE Bi-Pb BATH FOR VACUUM-SEALED QUARTZ TUBES CONTAINING SPECIMENS IN Bi-Pb-Sn ALLOY

Figure 9. Beryllium Before and After 30-Day Test at 500°C

a. End of Be Rod Before Test

Micro 6432

25X

End of 1/8" diameter beryllium rod before test. The test consisted in heating specimen in Bi-Pb-Sn alloy for 30 days at 500°C.

b. End of Be Rod After Test

Macro 7187

25X

End of same specimen as in Figure 9a after test. The low-melting alloy did not wet the beryllium which exhibits many of the original polishing scratches.

Figure 10. Section of Be Rod After Test

Micro 7282

Polarized Light

500X

This is a cross section of the beryllium rod (see Fig. 9) after the specimen had been heated in Bi-Pb-Sn eutectic alloy for 30 days at 500°C. There is no evidence of reaction between the alloy and the beryllium.

Figure 11. End of Zr Specimen 1

Macro 6419

Figure 12. End of Zr Specimen 2

25X Macro 6420

25X

Two different zirconium specimens are shown in the above photographs. Each shows an end of an 1/8" diameter zirconium rod before exposure to Bi-Pb-Sn alloy.

Figure 13. Zr Specimen 1 After Test

Macro 7184

Figure 14. Zr Specimen 2 After Test

25X Macro 7185

25X

These photographs show the same ends of zirconium specimens 1 and 2 after immersion in Bi-Pb-Sn alloy at 495°C for 30 days. Both specimens were wetted, but specimen 1 still shows some of the original polishing scratches.

Figure 15. Section of Zr Specimen 1.

1 mil

Micro 7278 Bright Field

500X

Figure 16. Section of Zr Specimen 2.

1 mil

Micro 7279 Bright Field

500X

Observe the difference in depth of reaction zone between zirconium specimen No. 1 and zirconium specimen No. 2. Both specimens had been immersed in Bi-Pb-Sn eutectic alloy at 495°C for 30 days.

Figure 17. Section of Zr Specimen 1.

Micro 7277 Polarized Light

250X

Figure 18. Section of Zr Specimen 2.

Micro 7280 Polarized Light

250X

The chief difference between zirconium specimen No. 1 and zirconium specimen No. 2 revealed by polarized light is that the latter exhibits a greater number of plate-like inclusions in the grains. This difference may be related to the difference in resistance of the two specimens to attack by Bi-Pb-Sn at 495°C.

Figure 19. Armco Iron (Specimen 2) 30-Day Test

Micro 6783 2% Nital Etch 250X

Cross-section of Armco iron, Specimen 2, after 30 days in Bi-Pb-Sn alloy at 490°C. Adhering alloy was removed by treatment in KOH solution and possibly by the nital etch. Erosion was slight.

Figure 20. Armco Iron (Specimen 1) 30-Day Test

a.

b.

Micro 6784 2% Nital Etch 250X Micro 6785 2% Nital Etch 250X

Cross-section, showing most severely attacked areas of Armco iron, Specimen 1, after 30 days in Bi-Pb-Sn alloy at 490°C. Adhering alloy was wiped off. Many parts of the specimen exhibited little, if any, evidence of attack.

Figure 21. Armco Iron After 80-Day Test.

a.

Micro 7264

2% Nital Etch

100X

b.

2mils

Micro 7265

As-Polished

250X

Sections of Armco iron after 80 days in Bi-Pb-Sn alloy at approximately 485°C. The attack appears to have been initially intergranular by solution, and subsequently by diffusion reaction.

Figure 22. Armco Iron in Specimen Tube

Macro 4572-D

2X

Specimen tube containing Armco iron specimen and Bi-Pb-Sn alloy, which was decanted at 485°C after 80 days of heating.

Figure 23. Attack on Armco Iron by Bi-Pb-Sn Exposed to Air

Micro 6567

Dark Field

100X

Section of Armco iron heated 16 days in Bi-Pb-Sn alloy at 500°C in an open porcelain dish. The micrograph was taken in a dark field with a stage micrometer superimposed so as to indicate the depth of the reaction zone. Each fine division on the scale represents 0.4 mil. The average depth of the reaction zone is therefore about 5 mils, much more than was observed after 80 days in the absence of air.

Figure 24.

Micro 6376

2% Nital Etch

250X

Section of the same specimen as in Fig. 23, but shown in bright field after etching. Observe the finer grains in the reaction zone.

Figure 25. Cast Iron After 30 Days in Bi-Pb-Sn

a. No KOH Treatment (Specimen 1)

Micro 6897

2% Nital Etch

500X

b. Treated in KOH Solution (Specimen 2)

Micro 6900

2% Nital Etch

500X

These sections of two similar cast iron specimens after 30 days in Bi-Pb-Sn alloy at 485°C show that cementite and ferrite are attacked but that graphite is relatively unaffected. Specimen "b" shows that KOH treatment removed the eutectic alloy but not the reaction layer.

Figure 26. Cast Iron Pump Casting After Failure

a. Interface with Bi-Pb-Sn Showing Slight Attack

Micro 6445

As-Polished

25X

b. Interface at Failure Zone Showing no Reaction

Micro 6418

As-Polished

75X

Sections of a gray iron casting of a pump used to circulate Bi-Pb-Sn alloy at 120°C to 250°C for 6 days in an oxidizing environment. The casting failed while the frozen alloy was being remelted. Microsection "a" shows a high rate of attack compared to that in an air-free system (see Fig. 25); but microsection "b" suggests that failure was due to fracture rather than to erosion or corrosion, which would have rounded the sharp edges characteristic of a fresh fracture. Bi-Pb-Sn is shown in the fracture zone, but no evidence of reaction.

Figure 27. Mild Steel, 80 Day Test (Specimen 2)

a.

Micro 7262

2% Nital Etch

100X

b.

2 mils

Micro 7263

As-Polished

250X

Section of SAE 1020 mild-steel specimen after being heated in Bi-Pb-Sn at 485°C for 80 days. Initial solution attack, either along surface cracks or intergranular, appears to have been followed by diffusion reaction. The nital tends to etch the reaction zone out of focus.

Figure 28. Mild Steel in Specimen Tube

Macro 4572-C

2X

Most of the Bi-Pb-Sn was decanted away from the mild steel, but some of the alloy remained adhering to the lower part of the specimen.

Figure 29. Mild Steel Tested in Bi-Pb-Sn in Presence of Air

a.

1 mil

Micro 6466

As-Polished

1000X

b.

1 mil

Micro 6465

As-Polished

1000X

c.

Micro 6468

2% Nital Eten

250X

Sections of a mild-steel specimen heated in Bi-Pb-Sn alloy for 7 days at about 570°C without attempting to exclude air. The maximum penetration (shown in "b" and "c") was more than one-half that occurring in 80 days at 500°C with the exclusion of air although many portions of the specimen, as shown in "a", were not badly attacked.

Figure 30. Aluminum in Specimen Tube.

Macro 4562-A

2X

Specimen tube containing severely attacked 2S aluminum specimen, and Bi-Pb-Sn alloy, which was decanted at 485°C after 80 days of heating.

Figure 31. Titanium in Specimen Tube.

Macro 4572-B

2X

Specimen tube like that of Fig. 30 but containing titanium. The Bi-Pb-Sn alloy drained readily from most portions of the specimen.

Figure 32. Titanium (Specimen 2) from 80-Day Test

a.

Micro 7340

5% HF Etch

100X

b.

Micro 7341

5% HF Etch

250X

Sections of titanium specimen treated for 80 days in Bi-Pb-Sn alloy. Section "a" shows no evidence of attack. Section "b" which was more lightly etched, shows evidence of wetting and reaction.

Figure 33. Molybdenum after 30 Days in Bi-Pb-Sn at 800°C (Specimen 2)

a.

Micro 11,217

KOH-K₃Fe(CN)₆ Etch

b.

250X Micro 11,204

As-Polished

250X

These sections of molybdenum, made after the specimen had been heated in eutectic Bi-Pb-Sn alloy for 30 days at 800°C, exhibit no evidence of attack by the alloy. (The etchant used for micrograph "a" was an aqueous solution of 10% KOH mixed with a 10% solution of K₃Fe(CN)₆.) Similar micrographs of another molybdenum specimen in a parallel test likewise showed no evidence of reaction.

Figure 34. High-Sulfur Steel in Dynamic Test
a. Sketch of Heater Tube

Macro 16,234

1X

b. 1-1/3" Longitudinal Section of Failure Zone

Macro 4448

Approx. 4X

c. Tube Sections at Thermocouple Wells

Macro 4456

Approx. 2X

Failure and attack in free-machining steel tube after 1000-hour service with dynamic Bi-Pb-Sn alloy at 180 to 400°C.

Figure 35. High Sulfur Steel in Dynamic Test.

a.

1 mil

Micro 7099

As-Polished

1000X

b.

Micro 7098

2% Nital Etch

1000X

Same specimen as in Figure 34 but at higher magnification. Micrographs of section near failure zone show negligible depth of reaction zone (partly out of focus on the right of etched section) and only slight intergranular attack. Some decarburization may have occurred near the surface.

Figure 36. Type 347 Stainless Steel in Dynamic Test.

a. Longitudinal Section

b. Cross Section through Failure

10% Oxalic Acid Etch

Failure in heat affected zone near weld in Type 347 stainless steel tube after 1000-hour service with Bi-Pb-Sn alloy at about 300°C, and subsequent brief service with Bi-Pb alloy.

Figure 37. Type 347 Stainless Steel in Dynamic Test

a. Remote from Weld

1 mil

Micro 6864

As-Polished

1000X

b. Near Weld (Heat Affected Zone)

1 mil

Micro 6865

As-Polished

1000X

Same specimen as in Figure 36. but at higher magnification. A reaction zone is readily observable in a region affected by the heat of welding (Fig. 37b), but is scarcely observable in regions remote from the weld (Fig. 37a).

Figure 38. Stainless Steel in Bi-Pb-Sn, Semi-Oxidizing Test

Micro 6470

Light 10% Oxalic Acid Etch

500X

Section of 18-8 stainless steel plug after 7 days in contact with Bi-Pb-Sn alloy in a mild carbon steel container at 570°C. Although some oxide and air were present in the container, the plug may have prevented the entrance of additional air.

Figure 39. Stainless Steel in Bi-Pb-Sn, Oxidizing Test

a.

b.

Micro 6382-R

As-Polished

250X

Micro 6377-R

Etch: $\text{HNO}_3 + \text{HCl} + \text{Glycerol}$

250X

Austenitic stainless steel after 16 days in Bi-Pb-Sn in porcelain container at 500°C. Area near reaction zone is magnetic.

Figure 40. Eutectic Bi-Pb-Sn

Micro 6472

500X

Acetic-Nitric-Glycerol Etch

A typical specimen of Bi-Pb-Sn alloy of high purity. Compare this with the contaminated specimen of Fig. 41.

Figure 41. Contaminated Bi-Pb-Sn

Micro 6467

500X

Acetic-Nitric-Glycerol Etch

Some of the islands in this Bi-Pb-Sn probably are derived from the Cr-Ni steel with which the Bi-Pb-Sn was heated. These islands are characterized by a more yellowish hue.

FIG. 42 ORIENTATION OF SPECIMENS IN SLABS

Orientation of specimens with respect to the plate of high-chromium steel from which they were cut. The letters indicate the relationship to the grain texture of faces, angles and edges studied metallographically.

FIG. 43 DIAGRAM SHOWING MILD-STEEL BOMB CONTAINING SPECIMEN TUBES AND Bi-Pb BATH. THEY ARE ARRANGED IN TILTING FURNACE SO THAT Bi-Pb BATH CAN BE DRAINED FROM BOMB AT TEST TEMPERATURE WHEN HEATING IS COMPLETED, AND SO THAT Bi-Pb-Sn WITHIN THE SPECIMEN TUBES CAN BE DECANTED FROM THE SPECIMENS.

Figure 44. Type 430 Stainless Steel after 30 Days in Bi-Pb-Sn at 600°C

a. Hydrogen-Treated Bi-Pb-Sn

Micro 10,110-R

250X

1HNO₃: 2HCl: 2 Glycerol Etch

b. No Treatment of Bi-Pb-Sn

Micro 10,109-R

250X

1HNO₃: 2HCl: 2 Glycerol Etch

The facing edges of "a" and "b" both represent surfaces transverse to the grain.

The intergranular penetration appears to be deepest on the transverse face of the specimen that was in contact with the Bi-Pb-Sn alloy that had been pretreated with hydrogen. The build-up of reaction product (which would not readily wipe off when warmed above 100°C) appears to be greater on the longitudinal faces than on the transverse faces, but not to have been affected by pretreating the Bi-Pb-Sn with hydrogen. Z and A in the corners of the respective sections indicate their orientation with respect to the diagram of Fig. 42.

Figure 45. Type 430 Stainless Steel Heated 30 Days in Argon.

a. Heated at 800°C

Micro 10,107-R

b. Heated at 600°C

250X Micro 10,108-R

250X

1 HNO₃: 2HCl: 2 Glycerol Etch

These blank specimens were heated in argon, instead of in Bi-Pb-Sn alloy, but otherwise under the same conditions and at the same time as the test specimens for the respective temperatures. Micrographs of similar specimens before heating have not been reproduced as there was no apparent difference in surface or structure before or after heating. These micrographs are useful as standards in comparing the effects of treatment with Bi-Pb-Sn alloy. The sections represent orientations "C" and "Z", respectively, of Fig. 42.

Figure 46. Type 430 Stainless Steel after 30 Days in 800°C Bi-Pb-Sn

a. Longitudinal Surface

Untreated Bi-Pb-Sn

Micro 10,115

1HNO₃: 2HCl: 2 Glycerol Etch

250X

b. Transverse Surface

Hydrogen-Treated Bi-Pb-Sn

Micro 10,116

1HNO₃: 2HCl: 2 Glycerol Etch

250X

Edges V and B (see Fig. 42). The extent of the attack by Bi-Pb-Sn indicates that orientation and pre-treatment with hydrogen are minor factors at 800°C. Decarburization accompanies envelopment of the surface grains.

Figure 47. Type 430 Stainless Steel after 30 Days in 800°C Bi-Pb-Sn

a. Edge of Reaction Zone on Transverse Face. Untreated Bi-Pb-Sn

5 mils

Micro 10,113

As-Polished

100X

b. Edge of Reaction Zone on Transverse Face. Hydrogen-Treated Bi-Pb-Sn

Micro 10,114

As-Polished

100X

Corresponding faces of specimens: "a" heated in untreated Bi-Pb-Sn alloy, "b" heated in hydrogen-treated Bi-Pb-Sn alloy. The reaction zones are 30 mils and 25 mils, respectively. The faces are U and G of Fig. 42.

Figure 48. Type 430 Stainless Steel after 30 Days in Bi-Pb-Sn at 800°C

a. Long. Section Untreated Bi-Pb-Sn

Micro 10,200

50X

b. Trans. Section H₂-Treated Bi-Pn-Sn

Micro 10,201

50X

Corners W and D of Figure 42, respectively. The reaction zones on the right of each specimen were formed on corresponding faces. As with the specimens of Fig. 47, the depth of reaction zone formed with hydrogen-treated Bi-Pn-Sn alloy is approximately 25 mils as compared to 30 mils for the zone formed with untreated Bi-Pb-Sn. The reaction zone at the top of section "a", although on a transverse face, is of the same depth as the lateral zone, which is on a face parallel to the grain. Orientation therefore seems unimportant at 800°C. Hydrogen treatment of the Bi-Pb-Sn may have a slight influence.

Figure 49. Attack by Bi-Pb-Sn Containing No Added Oxygen

a. Diagonally opposite corners of Type 430 steel as-polished after 800°C Bi-Pb-Sn treatment for 30 days.

Micro 11,196

250X

2 mils

Micro 11,195

250X

b. Same specimen, etched

5 mils

Micro 11,211

Oxalic, aqueous, electrolytic etch

100X

This specimen, which was heated in Bi-Pb-Sn containing no added oxygen, had a 10 to 15 mil reaction zone, greater than for oxygen-protected specimens. (See Figs. 51 and 52.)

Figure 50. Attack by Bi-Pb-Sn without Added Oxygen on Type 430 Stainless Steel at 800°C for 30 days.

Opposite corners of specimen at different magnifications. The extensive erosion of one corner, shown in Micro 11,193, is a freak effect not observed on the similarly treated specimen of Fig. 49. The depth of attack elsewhere was 6 to 20 mils.

Figure 51. Attack by Bi-Pb-Sn Containing Trace Addition of PbO

a. Diagonally opposite corners of Type 430 steel etched after 800°C Bi-Pb-Sn treatment.

Six to 10 mil reaction zone in Type 430 stainless steel specimen after 30 days at 800°C in 39 g. of Bi-Pb-Sn alloy containing 0.0001 g. of PbO. (Compare with Figs. 49 and 51.)

Figure 52. Attack by Bi-Pb-Sn containing Large Addition of PbO on
Type 430 Stainless Steel at 800°C for 30 Days.

a. Diagonally
opposite corners.
Etched

Micro
11,208 100X

Micro 11,209 Oxalic-electrolytic Etch 100X

b. Below: Diagonally opposite corners as-polished.

Micro 11,192
Left: Micro 11,191

250X

The 1 to 7 mil reaction zone on this specimen is less than was observed on similar specimens pre-treated with less oxygen. (See Figs. 49 and 50.)

Figure 53. Iron-Chromium
Crystals

Macro 10,096

2-1/4X

Sample of crystals obtained on filtering Bi-Pb-Sn that had been in contact with Type 430 stainless steel at 800°C. Nitric acid was used to clean the crystals. These crystals, which are highly magnetic, had the following w/o composition: 15.1-Cr, 82.6-Fe, 1.5-Sn, 0.01-Pb, and less than 0.01-Bi.

Figure 54. Standard Specimen Heated in Argon

Micro 11,212

100X

Type 430 stainless steel specimen heated with argon at 800°C for comparison with specimens heated with Bi-Pb-Sn and added oxygen.

Figure 55. Type 446 Stainless Steel after 30 Days in 800°C Bi-Pb-Sn.

a. As Polished (446 SS I)

Micro 11,198

250X

b. Oxalic-Electrolytic Etch

Micro 11,213

100X

c. As Polished (446 SS II)

Micro 11,200

250X

d. Diagonally Opposite c. Etched

Micro 11,215

100X

The upper face of specimen 446 SS I (Figures 55a and 55b) was so close to a companion specimen which was also present in the Bi-Pb-Sn during the heating, that it was not so badly attacked as the adjacent faces. Figures 55c and 55d, showing opposite corners of a different specimen, shows nearly equal attack on two adjacent faces. Although the depth of the reaction zone is somewhat less than found on Type 430 steel, the amount that has gone into solution is more. This can be determined by comparing weight losses or, qualitatively, the space between enveloped grains.