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TYPICAL CASES OF THE DETERIORATION OF
MUNTZ METAL (60:40 BRASS) BY
SELECTIVE CORROSION

BY

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Bureau of Standards

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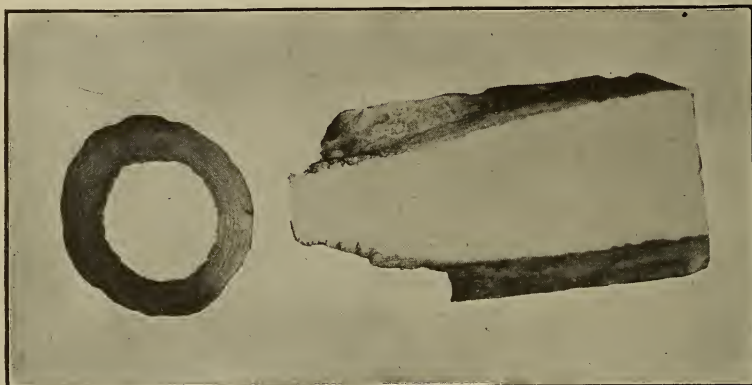
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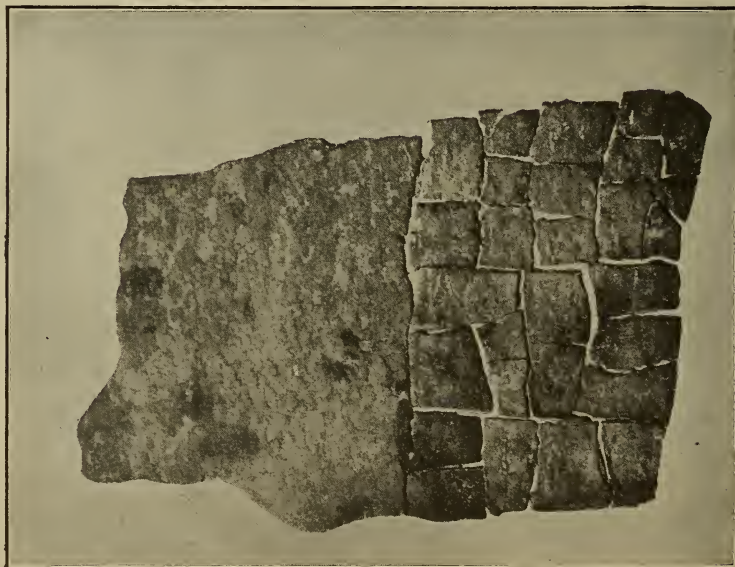
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a



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FIG. 1.—*Types of corroded Muntz metal*

- (a) Surface of a badly corroded Muntz metal bolt.
- (b) Cross and longitudinal sections of the corroded portion of bolt *a*, unetched ($\times 2$). The outer or attacked portion is copper-red; the center has the yellow color of uncorroded brass.
- (c) Boat sheathing after dezincification ($\times 1$). The portion at the right was broken into the fragments shown by the fingers alone.

TYPICAL CASES OF THE DETERIORATION OF MUNTZ METAL (60:40 BRASS) BY SELECTIVE CORROSION

By Henry S. Rawdon

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I. INTRODUCTION

Brass of the type 60 per cent copper and 40 per cent zinc, known under various trade names, primarily, however, as Muntz metal, has a variety of industrial uses, such as sheathing for boat bottoms; tubes for condensers; wrought forms, as bolts and rods; irregular extruded shapes, such as handrails for stairway balustrades, etc. One very common type of deterioration of metal of this composition, particularly when exposed to some electrolyte (e. g., sea water), is selective corrosion or "dezincification," the term "selective corrosion" being used to signify a corrosive attack of certain of the microstructural constituents of the alloy rather than a general uniform action upon the metal as a whole. Though this type of deterioration of brass has been known for years and numerous references on this subject have appeared in the technical

literature¹ the description of the various forms in which it may occur and of the changes produced in the metal by which it may be detected are very meager. The numerous samples illustrative of this type of metal failure submitted to this Bureau for examination, together with the inquiries received on this subject, suggested the utility of a description of typical cases of metal affected by this type of nonferrous corrosion as an aid in the detection and identification of similar cases of this type of deterioration of metals. A study of the various forms in which this type of corrosion may occur, together with the resulting structural changes within the metal, also aids in defining the conditions which are most favorable for such deterioration to occur.

II. CHARACTERISTIC APPEARANCE OF TYPICAL CASES

In general, by the attack, or process of dezincification, the clear yellow Muntz metal having an ultimate strength in tension of approximately 40 000 to 60 000 pounds per square inch, depending on the physical condition of the metal, is converted into a reddish-colored mass resembling poor copper, often so weak that it may be easily broken by the fingers alone or chipped and cut with a knife, though it still retains the initial shape and size. The red color of the attacked metal is intensified by rubbing the part with a cotton swab soaked in dilute ammonium hydroxide and then rinsing with water. The surface is freed from its film of oxide and the unattacked portions assume the original yellow color, the corroded spots become a brownish-red. Below are described five typical cases selected from material of this kind which was submitted to this Bureau for examination.

1. WROUGHT BOLTS

The Muntz-metal bolt illustrated in Figs. 1 and 2 was taken from the keel of a seagoing lifeboat after six years' service. The sample shown is illustrative of the condition of all the bolts used in this particular case to attach the keel to the keelson. To the casual observer the broken bolt appears to consist of a brass center with a heavy deposit of porous copper covering it. The location of that part of the bolt which was most severely attacked and its relation to the position within the keelson is of interest and is suggestive of one of the possible contributing causes to this type of corrosion. This is shown in Fig. 3.

¹ See, for instance, Second and Third Reports of the Corrosion Committee of the Institute of Metals, Jour. Inst. of Metals, 1913, X, and 1916, XV, respectively; J. O. Arnold, Engineer, 85, p. 363, 1898; and Milton and Larke, Proc. Inst. Civ. Engr., 154, p. 138, 1903.

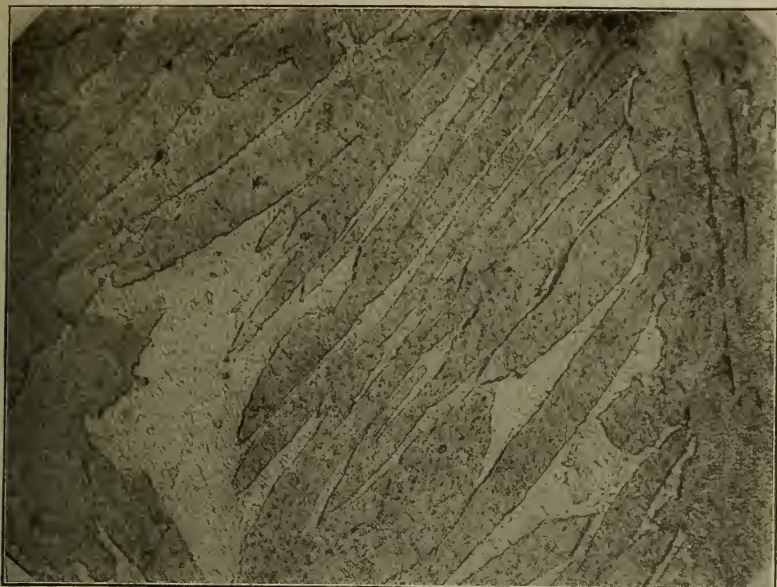
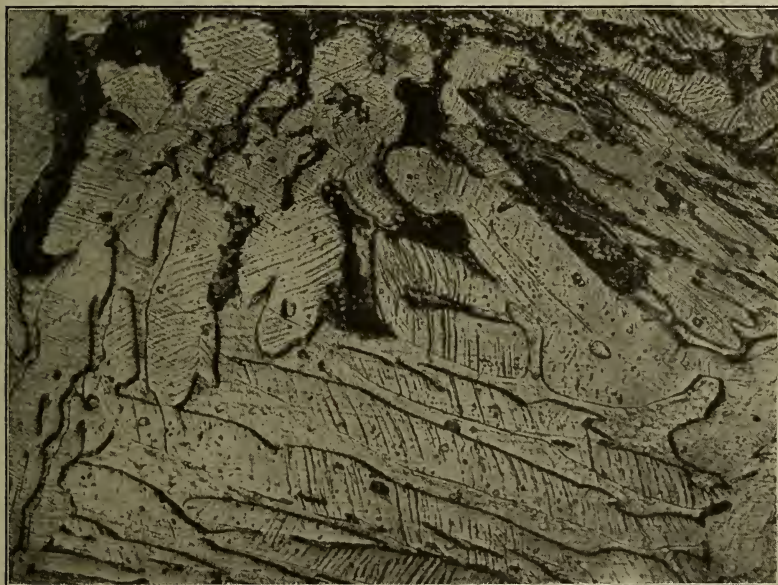
*a**b*

FIG. 2.—Microstructural changes induced in Muntz metal by dezincification

- (a) Unattacked Muntz metal (Fig. 1, b). The light-colored matrix is the zinc-rich or β constituent, in which are embedded the finger-like crystals of the α or constituent richer in copper.. ($\times 500$.)
- (b) Corroded Muntz metal. At the edge of the corroded portion (Fig. 1, b) the β constituent has been converted into a porous mass of copper (black in the figure) which still retains its former shape. ($\times 500$.)
- Etching in both cases, ammonium hydroxide and hydrogen peroxide.

It will be noted that the portion of the bolt which was most deeply corroded is that part which was subject to the greatest service stresses (transverse bending). Although apparently this material gave six years' service, it should be borne in mind in

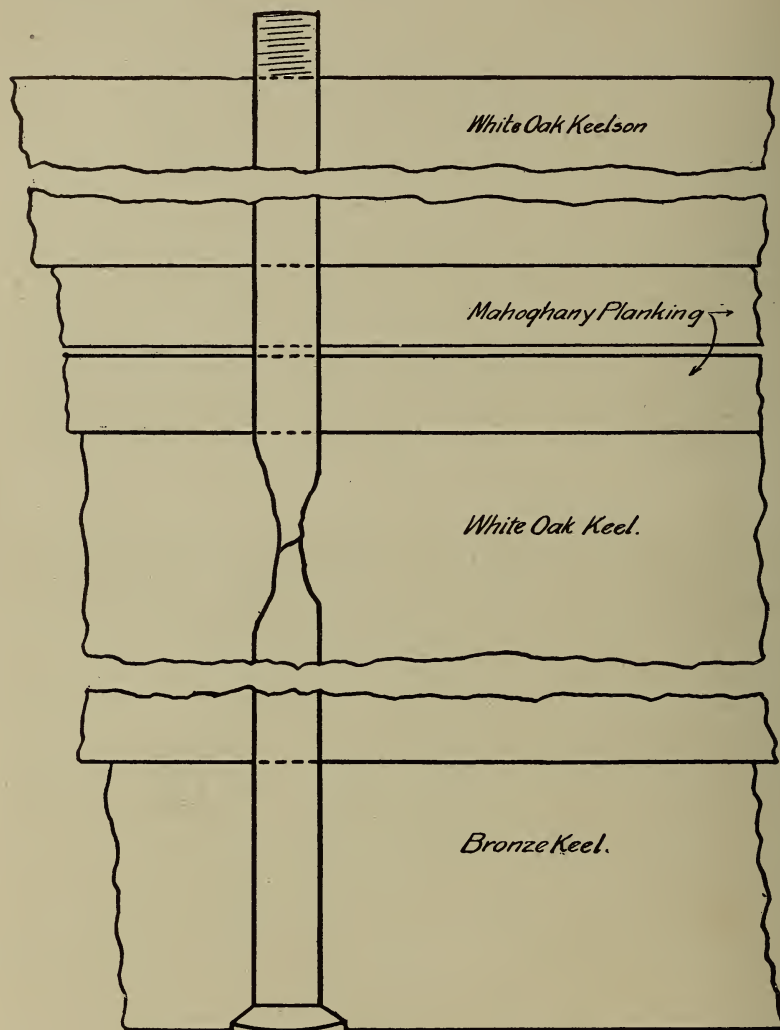
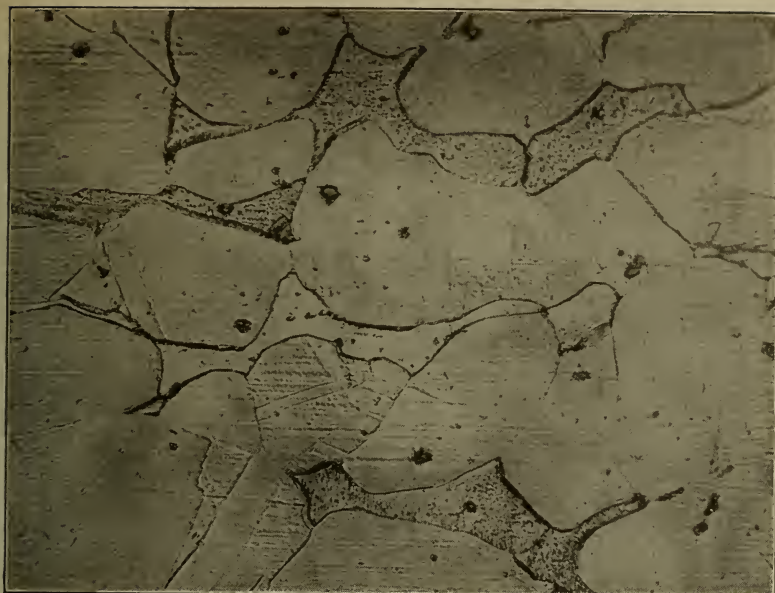


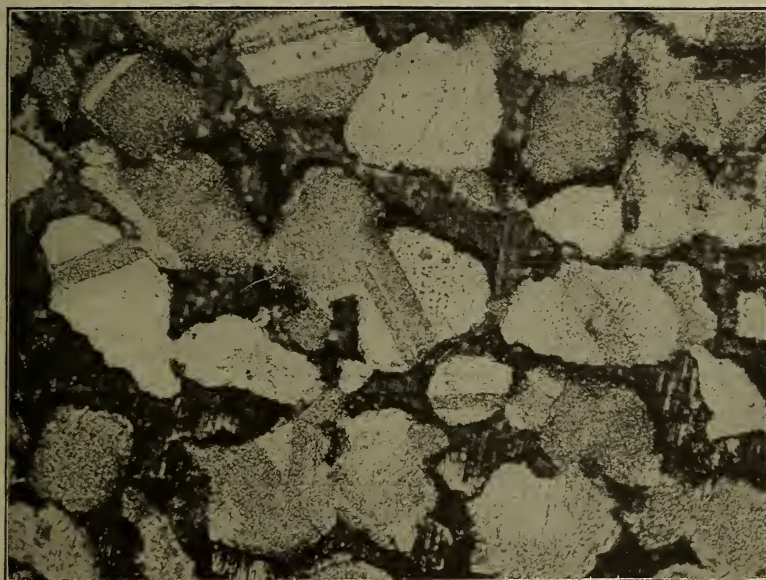
FIG. 3.—Arrangement of the Muntz metal bolts (type 1) in the keel of the boat

The part which was most severely corroded corresponds to the portion most highly stressed (i. e., transversely) in service.

comparing this case with the others described that the bolts were not constantly bathed in sea water for this period and that the periods of attack were intermittent, as illustrated by the concentric lines in Fig. 1*b*.



a



b

FIG. 4.—*Corroded Muntz metal sheathing*

- (a) Before attack; the light-colored β matrix fills in between the α crystals.
 (b) After 7 years' exposure to sea water (see Fig. 1, c) the β constituent has been entirely changed; the α , apparently not at all. The numerous twinned crystals in the α is indicative that the metal was annealed before use.

Magnification in both cases, ($\times 500$). Etching, ammonium hydroxide, and hydrogen peroxide.

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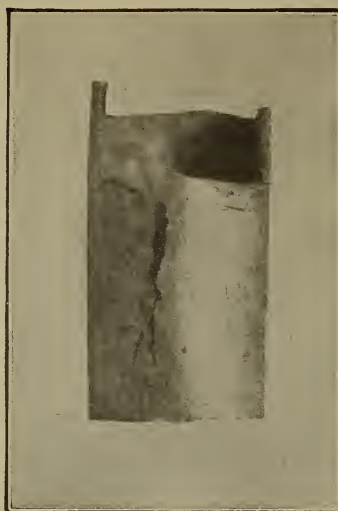
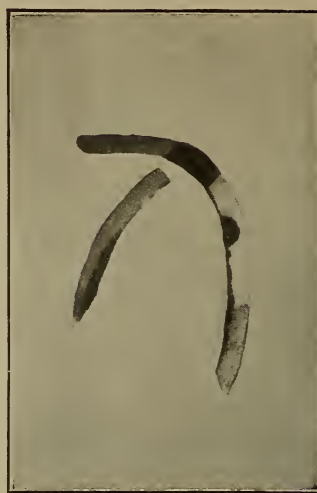
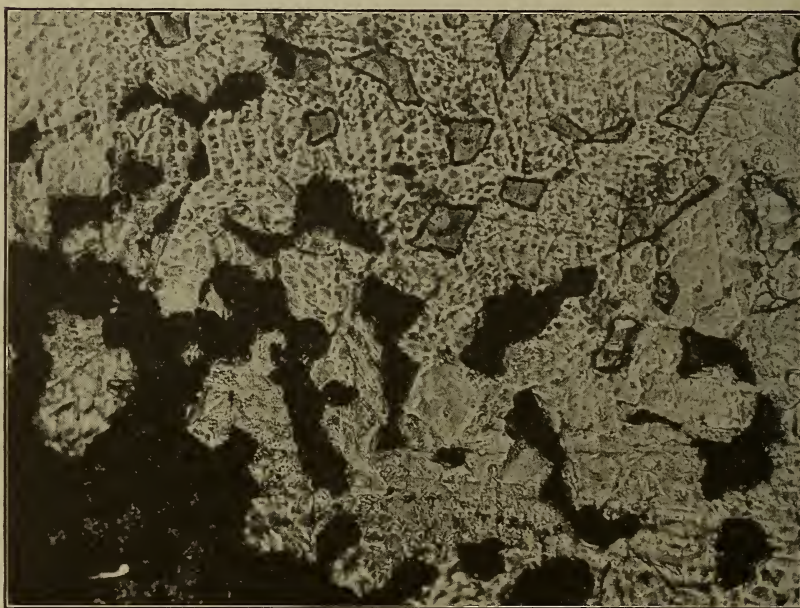
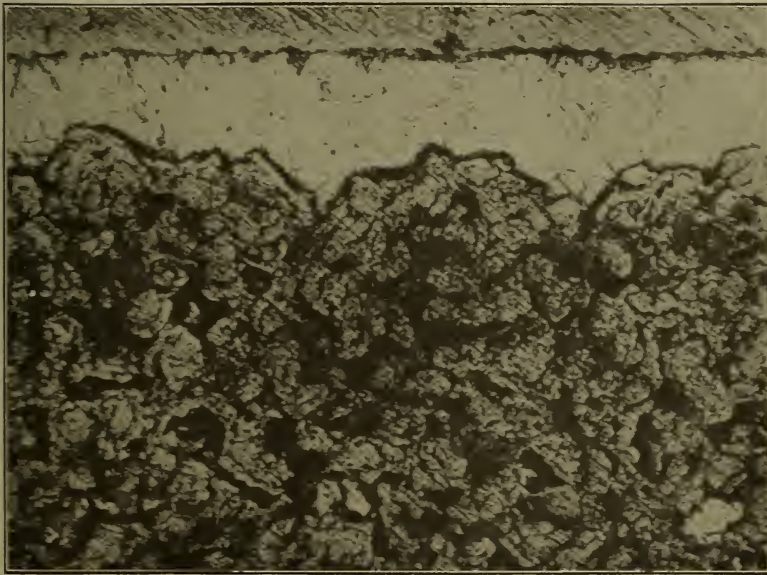
*a**b**c*

FIG. 5.—Corroded Muntz metal condenser tube

- (a) Appearance of the corroded tube. The darker portions are copper-red and very brittle. The metal here is easily cut with a knife. ($\times 1$.)
- (b) Cross sections of parts of *a*. In the dark portions the metal has been corroded throughout the entire cross section. ($\times 2$.) Etching, concentrated ammonium hydroxide, and hydrogen peroxide.
- (c) Microstructure of the metal of *a*. Both α and β constituents are attacked; a definite zone in which the β , only, is attacked separates the unchanged metal from the completely corroded portion. The α shows little or no evidence of annealing. ($\times 500$.) Etching, concentrated ammonium hydroxide and hydrogen peroxide.



a



b

FIG. 6.—*Corroded Muntz metal condenser tube*

- (a) Appearance of the corroded tube. No evidence of corrosion shows on the exterior, a thin unattacked layer of α completely masks the corroded portion below. This outer layer is easily stripped off as shown.
- (b) Material of *a* ($\times 250$). Etching, concentrated ammonium hydroxide, and ammonium persulphate. The outer thin layer of unattacked α is due to some zinc being volatilized from the surface during some stage in the manufacturing process.

2. SHEATHING

The sheathing shown in Figs. 1 and 4 was used for seven years upon an anchored lightship. The attack was local, certain isolated sheets only over the bottom of the boat were in the condition illustrated; others, though much thinner than when rolled, apparently were in the same structural condition as when placed in position.

3. CONDENSER TUBES

The condenser tubes are illustrative of a case in which this type of corrosion is very prevalent. Both the samples shown (Figs. 5 and 6) are from condensers using salt water. Type 3b (Table 1) is of particular interest in that it illustrates how this type of attack may be entirely hidden from view.

The outer layer of the tube shows no evidence of attack, and subsequent examination showed that this outer portion contained but one constituent—the α . During some phase of the manufacturing process, the tube was evidently heated strongly enough so that a sufficient amount of zinc was volatilized from the surface as to leave the composition here such that only the α constituent was present.

The corrosive attack which proceeded outward from the inner surface, which was in contact with the sea water, proceeded up to this outer α layer; the layer itself, however, remained unattacked and the tube appeared to be unchanged. This outer α layer can be easily stripped off from the corroded metal beneath, as shown in Fig. 6.

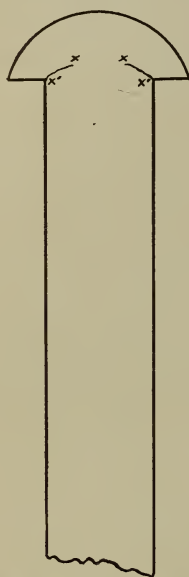


FIG. 7.—Diagram of the fracture of Muntz metal bolthead (type 4, Table 1)

4. CORROSION OF PARTS WHILE UNDER STRESS

Type 4 (Table 1) is particularly instructive in suggesting service conditions which may aid in this type of corrosion. Fig. 8 shows the face of the bolthead which was fractured as shown in Fig. 7. The head detached itself apparently spontaneously in service, suggesting in this respect the "season cracking" of brass. Dezincification of the surface metal in the outer marginal area, $x-x'$, occurred and penetrated to a depth of from 0.05 to 0.36 mm; the central area shows no corrosive attack, the fracture here having the appearance of a direct tension break. The most severe attack was near the apex of the right angle beneath the head. The easiest and most logical explanation is that the failure in this case is one of corrosion under stress.² The starting point perhaps may have

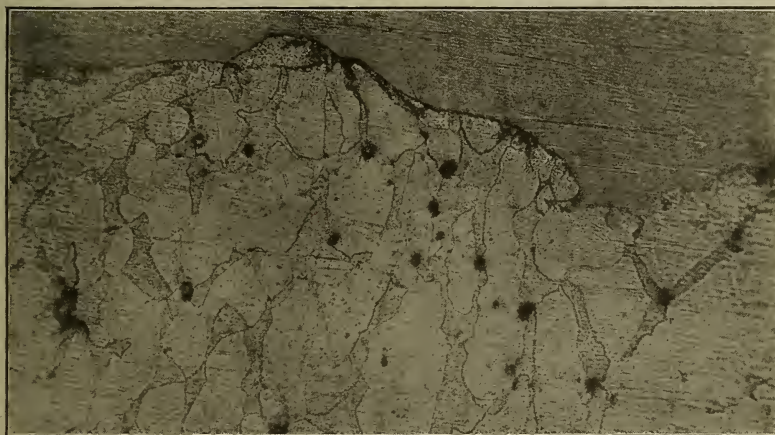
² For description of such cases of corrosion of brass under stress, see E. Jonson, Proc. Am. Soc. Test Mtls. p. 101, 1915; and P. D. Merica, B. S. Tech. Paper No. 83.



a



b



c

FIG. 8.—Muntz metal bolt corroded while under tensional stress

- (a) Face of the fractured head. The central portion *x-x*, has the appearance of a simple tension break; the marginal area *x-x'* which resembles a "detailed" fracture shows dezincification of the β . ($\times 1$)
- (b) Edge of the fracture of area *x-x*. This portion shows no change in structure. $\times 250$.
- (c) Edge of the fracture of area *x-x'*. The β constituent at the extreme edge has been dezincified. $\times 250$.
- Etching in both cases, ammonium hydroxide and ammonium persulphate.

been an initial flaw in the material, such as a forging crack. The β constituent appears to have become dezincified in the region of greatest stress—that is, in the sharp right angle—and to have preceded and accompanied the gradual or detail fracturing of this portion of the break until the central portion became so small that it broke in direct tension under the stress of the applied load the bolt carried.

Below are summarized the different types described, the service to which the material has been subjected, the macroscopic characteristics, the changes in the microstructure, as well as the chemical composition where available.

TABLE 1
Summary of Materials Described

Material	Service	Macroscopic appearance of corroded material	Microscopic structure	Chemical composition (in per cent)
1. Bolt of Muntz metal ^a	Attachment of bronze keel to oak keelson of seagoing lifeboat. Six years' intermittent service. All the bolts showed the same appearance.	In cross section it shows a yellow center and red outer layer and has the superficial appearance of a brass rod heavily copper coated; the coating is very brittle.	Both α and β constituents are attacked in the greater portion of the corroded part; on the inner margin only the β or zinc-rich matrix is replaced by "copper."	Initial: Cu, 59.7; Pb, 0.19; Sn, not detected; Zn (dif.), 40.11. Attacked portion: Cu, 93.4; Pb, 0.06; Sn, trace; Zn, and basic chlorides, etc. (dif.), 6.5.
2. Muntz metal sheathing, ^b	Used for seven years as sheathing upon an anchored lightship in latitude of New York (approx.).	Isolated sheets only were attacked, not the whole bottom. Sheets are somewhat thinner at first and are covered with basic deposits. Metal is brown and spongy and very brittle.	β constituent alone has been replaced throughout by porous "copper"; the α is unattacked.	Initial (according to specifications): Cu, 59 to 62; Zn, 41 to 38; Pb (max.), 0.60. Final: Cu, 75.79; Pb, 0.68; Sn, 0.36; Zn, 20.01; Fe, 0.16; S, 0.07; Cl, trace.
3a. Muntz metal tube, ^c	In a condenser using sea water six months.	Tube has a mottled appearance of yellow and red, red being most abundant on inner side. Tube is cracked along one side where the red had penetrated to the exterior.	Both α and β are attacked in completely corroded parts. In outer margins of corrosion spots only β is attacked.	Initial: Cu, 61.7; Pb, 0.2; Fe, trace; Sn, not detected; Zn (dif.), 38.1.
3b. Muntz metal tube, ^b	In a condenser using sea water; term of service unknown.	The exterior of the tube is bright yellow, and shows no corrosion. This yellow layer which is very thin can be striped off, and reveals the porous red metal beneath.	Both α and β constituents have been attacked on the side of the tube showing greatest corrosion. A clear yellow unattacked layer on the exterior consists of the α constituent only. The extent of the attack has been limited by this.	
4. Muntz metal bolthead, ^c	Term of service, two years. The bolt which was in tension was exposed to sea water. The head dropped off of its own accord.	The center of the fractured face has the appearance of a tension break; the outer margin, that of a detailed fracture.	The constituent has been attacked in the outer marginal area of the face of the fracture to an average depth of 0.05 to 0.36 mm.; neither α nor β have been changed in the central area.	Copper, 60.95; lead, 0.13; tin, 0.59; Fe, 0.00; Zn (dif.), 38.33.

^a See Figs 1 and 2 a and b.

^b See Figs. 1c and 4 a and b.

^c See Fig. 5 a, b, and c.

^d See Fig. 6 a and b.

^e See Fig. 7 and 8 a, b, and c.

III. MICROSTRUCTURAL FEATURES

1. UNCHANGED MUNTZ METAL

In order to understand clearly the method by which such pronounced changes in structure, composition, and properties are brought about, a knowledge of the microstructure of the alloy is

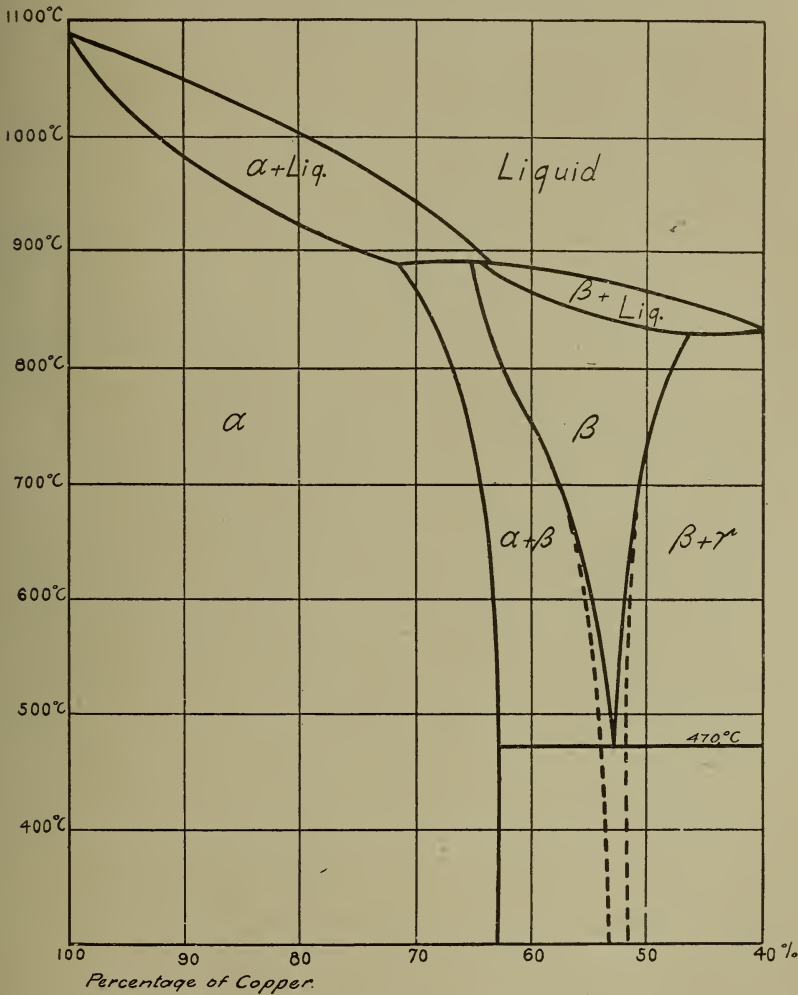


FIG. 9.—Structural diagram of the copper-zinc alloys

essential. The metal has a duplex structure, as is shown by Fig. 2a. As an example, consider the alloy of 60 per cent copper and 40 per cent zinc, the crystals or "grains" which, when heated sufficiently, are homogeneous throughout, on cooling break up into a complex of two constituents, as shown by the structural diagram (Fig. 9). This is brought about by a crystallization within and

throughout the previously homogeneous grain by which the crystallites or "fingers" of the new constituent form out of the substance of the mother matrix and remain embedded in it. The ground mass (Fig. 2a) is the zinc rich or β ³ constituent; the darker fingers embedded in this matrix, the α constituent, which in its saturated condition consists of very nearly 64 per cent copper and 36 per cent zinc. The percentage composition of the zinc-rich or β matrix will vary with the ultimate composition of the alloy in question, but it is always considerably richer in zinc than is the α phase.

In passing, it should be remarked that the color of the two constituents may be varied considerably by the etching medium used. However, with slight etching by means of alkaline reagents, the β always appears yellow at first; deeper etching or other conditions—e. g., slight oxidation of the surface—may cause it to appear darker than the α . In no case, however, was the β found to appear red as is stated by some observers⁴ of this alloy.

2. MICROSTRUCTURE AFTER DETERIORATION

There is to be observed a very sharp line of demarcation between the attacked and unattacked portions. The change in composition and properties is not a gradual one, but is very abrupt and complete. After corrosion the attacked portion of the metal consists of a porous mass, apparently of copper, still showing indistinctly its initial structural arrangement. Often well-defined laminations parallel to the corroded surface are seen, corresponding undoubtedly to the intermittent periods of service to which the metal was put (Fig. 1b). The interstices of the porous "copper" are filled with basic chloride deposits—the products of corrosion. These are very abundant in the inner layer adjacent to the unattacked metal and under the microscope appear blue-gray in contrast to the red of the copper.

At the boundary surface between the changed and the unchanged portions is plainly seen the method of attack. Figs. 2b and 5c show this. The β or zinc-rich matrix is the constituent which is first acted upon, and appears to be replaced by one higher in copper; in reality it is not a "replacement." The preferential attack of the β phase is to be attributed to its higher zinc content, which renders it more electropositive than is the α constitu-

³ This assumption disregards the question whether this constituent is β' , a polymorphic modification, or an intimate mixture of two other phases, α and γ . (See *Jour. Inst. Metals*, 1912, VII, p. 70, and 1912, VIII, p. 51.)

⁴ Shepherd, *Jour. Phys. Chem.*, 1904, VIII, p. 421; and Gulliver, *Metallic Alloys*, p. 269.

ent which is richer in copper. When an electrolyte is present and electrolysis occurs either by means of the application of an external emf, by contact with some metal which is less electropositive than either constituent of the alloy or by reason of the electrochemical difference between the α and β phases, the β is always attacked first; its zinc largely passes into the solution leaving behind the porous copper masses occupying the spaces initially filled with the β matrix. This type of corrosion may be then regarded as an electrolytic "leaching out" of the zinc. The α constituent is later often attacked, so that the copper content of the whole mass may be raised as high as is indicated in Table 1.

A definite, though narrow, intermediate zone in which the β is completely attacked always precedes and separates the layer in which the attack upon the α begins from the unchanged material. It is to be expected from theoretical considerations that the rate of corrosion of pure β or of pure α brass is much less than that of the α - β metal. Desch and Whyte⁵ have shown that such is the case.

The extent to which the α constituent is affected determines largely the properties of the corroded metal. In the case of the Muntz-metal sheathing described, the α remained unattacked even after seven years of exposure to sea water. The sheet, when cleaned, still retains much of its yellow color and is not nearly so brittle as some of the other samples. The metal after the attack consists essentially of a skeleton of α , the pores and interstices of which are filled by the pulverulent copper which resulted from the corroded β crystals. In the bolts described (type 1), the attack, though similar, is very different in regard to the rate at which the corrosion of the α phase follows that of the β . The attack of this constituent follows almost immediately that of the β grains, the intermediate layer in which only the β is attacked averaging only 0.25 mm in depth. The same is true of the condenser tube (type 3a); the deterioration of the α follows very quickly that of the β .

3. BEHAVIOR OF α BRASS UNDER SIMILAR CONDITIONS

The behavior of α brass—that is, brass in which the copper is high enough so that the β constituent is entirely absent—when placed in comparable conditions is of interest. Fig. 10b illustrates how this behavior differs from that of metal containing both phases. The material here shown is from brass bolts which

⁵ Jour. Inst. of Metals, 1914, XI, p. 235; *ibid.*, 1915, XIII, p. 80.

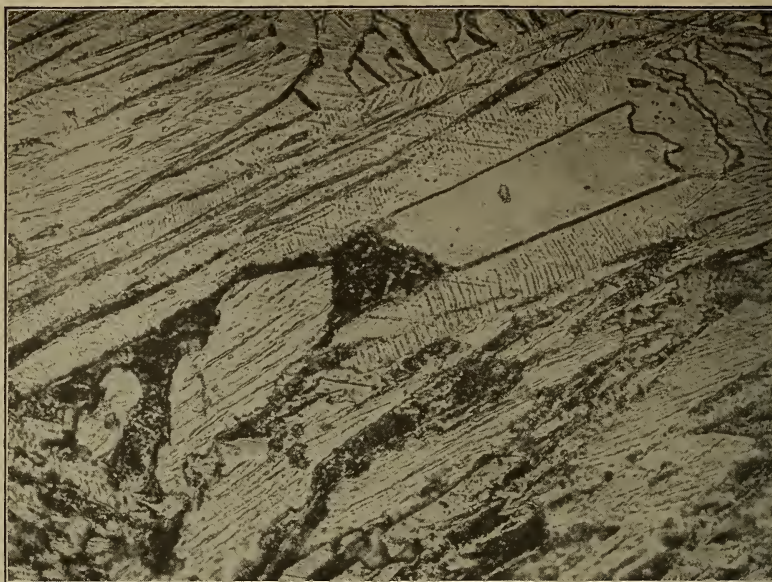
*a**b*

FIG. 10.—Method of dezincification

- (a) Method of attack within the β crystals. The attack here as shown by the large central β grain is not a gradual one but abrupt and complete. ($\times 500$.) Etching, ammonium hydroxide and hydrogen peroxide.
- (b) Corrosive attack of α brass. The material (bolts) was used in a "water" rheostat. The attack induced by the external emf is very complete and shows a slightly greater rate of attack at the crystal boundaries. ($\times 500$.) Etching, ammonium hydroxide and hydrogen peroxide.

were used in the construction of a "water rheostat." The macroscopic appearance is very similar to that of attacked Muntz metal. Fig. 10*b* shows, however, that the method of attack is very different. The normal (i. e., unchanged) metal consists of the polyhedral crystals of the α solution of zinc in copper with the numerous twins characteristic of annealing after strain. In any section the line separating the corroded portion from the unchanged center is very smooth and even. A few sharp bends in this line are to be noticed. These peaks are found to correspond to crystal boundaries, thus indicating a slightly faster rate of attack on the crystal surfaces, which is to be expected from theoretical considerations. Aside from these variations the whole "line of attack" is very even and shows no such preferential action as when both constituents are present.

4. PROGRESS OF ATTACK WITHIN THE β CRYSTALS

In Fig. 10*a* is shown the method of attack within the individual β crystals of Muntz metal. The advance within each β crystal is very uniform and similar to that within any crystal of α when but one phase is present. The line separating the unchanged β from the porous "copper" which results from the attack is very distinct; the change is not a gradual one even here, but is abrupt and complete.

The above is true, however, of β which is in an annealed state. Metal which was quenched (the sample used was quenched in water from approximately 675° C) shows an attack of the β very different from that ordinarily observed. The β crystals in this case are attacked most readily along certain planes, often along two sets of intersecting planes within the same crystal (Fig. 11 *a* and *b*). The attack then proceeds from these planes of attack until the whole crystal has been converted into the same condition as occurs more directly in the annealed material.

IV. CONDITIONS INFLUENCING DEZINCIFICATION

1. STRUCTURAL COMPOSITION

Although α brass is subject to dezincification, the attack is not nearly so rapid as when both α and β constituents are present.⁶ Several of the samples of Muntz-metal sheathing, which were heat treated (see below) previous to subjecting them to conditions favorable for corrosion, were heated strongly enough so that zinc

⁶ Second Report of Corrosion Committee, Jour. Inst. Metals; 1913.

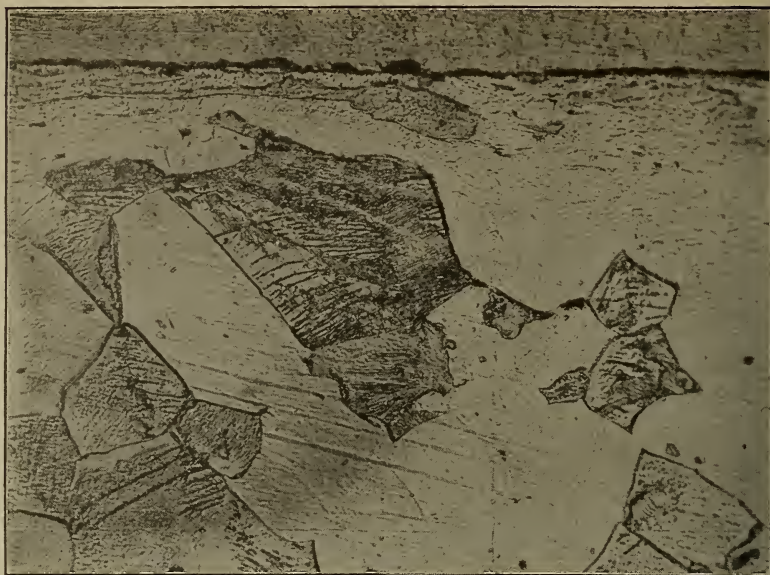
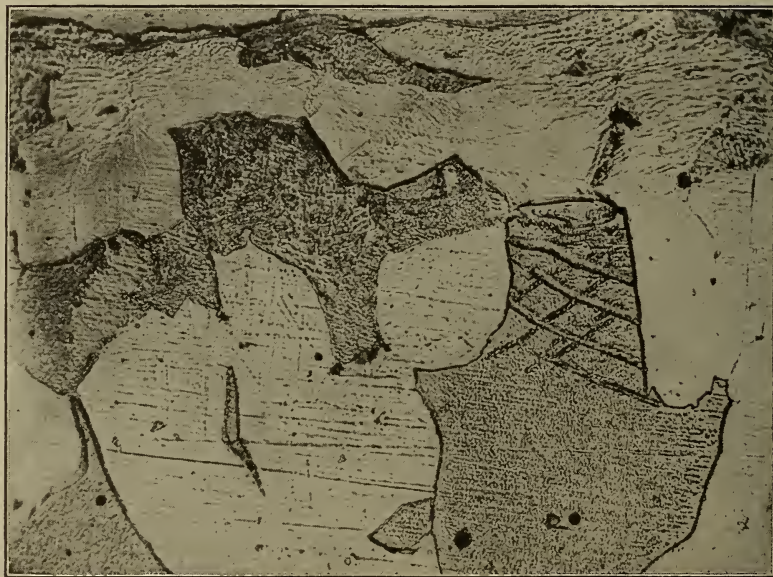
*a**b*

FIG. 11.—*Method of dezincification*

The material was quenched after heating to 675°C . The β crystals are attacked most readily along certain planes arranged approximately in parallel sets in any individual crystal and resembling twinning planes. The material was thin sheathing and the attack was at right angles to the surface photographed. ($\times 500$.) Etching, concentrated ammonium hydroxide and ammonium persulphate.

was volatilized from portions of the surface, leaving a layer of α . This layer was in every case free from dezincification during the course of the experiment and served as a protective covering for the α - β alloy beneath. One of the samples of condenser tubing described illustrates the comparative freedom of α from attack. That the attack of the α does not follow that of the β at the same rate in all corroded samples is very evident from the types described. In the case of the corroded sheathing, the α is intact and apparently little changed even after seven years' exposure to sea water, while in others a few months' exposure disintegrates both constituents; the attack of the α very closely follows that of the β in such cases.

2. CONTACT WITH ELECTRONEGATIVE SUBSTANCES

If a sample of Muntz metal is in intimate contact, while immersed in an electrolyte (e. g., solution of sodium chloride), with a strongly electronegative metal (i. e., more electronegative than the α or β constituents), dezincification of those portions of the brass which is in immediate contact with the other metal will readily occur. As part of the study of the material of type 1, samples of the unchanged metal of the center were placed in contact with copper, others with steel, in a 5 per cent solution of sodium chloride. This electrolyte was chosen since this type of corrosion usually occurs in sea water. The copper readily induces dezincification, evidences of the attack showing after 12 hours' exposure, but only at or very near the point of intimate contact (Fig. 12*a* and *b*.) The attack is not general over the entire surface of the brass sample. No dezincification of the brass occurred in the case of the brass-iron couple. Although intimate contact with the proper substances will induce and accelerate the corrosive attack of brass, in none of the types previously described can this condition be assigned as the principal cause of the attack.

3. ACCELERATING EFFECT OF THE PRODUCTS OF CORROSION

The accelerating effect of deposits of basic zinc chloride formed on the surface of the corroded specimen by the corrosion of the brass, upon the further attack of the metal has been known for some time and has been previously described.⁷ The exact way in which this acceleration occurs, however, is not clear, as yet. The basic zinc-chloride deposits have been described by some as

⁷ C. H. Desch, Physical and Mechanical Factors in Corrosion, Jour. Faraday Soc.: 1915. (See, also, footnote 1.)

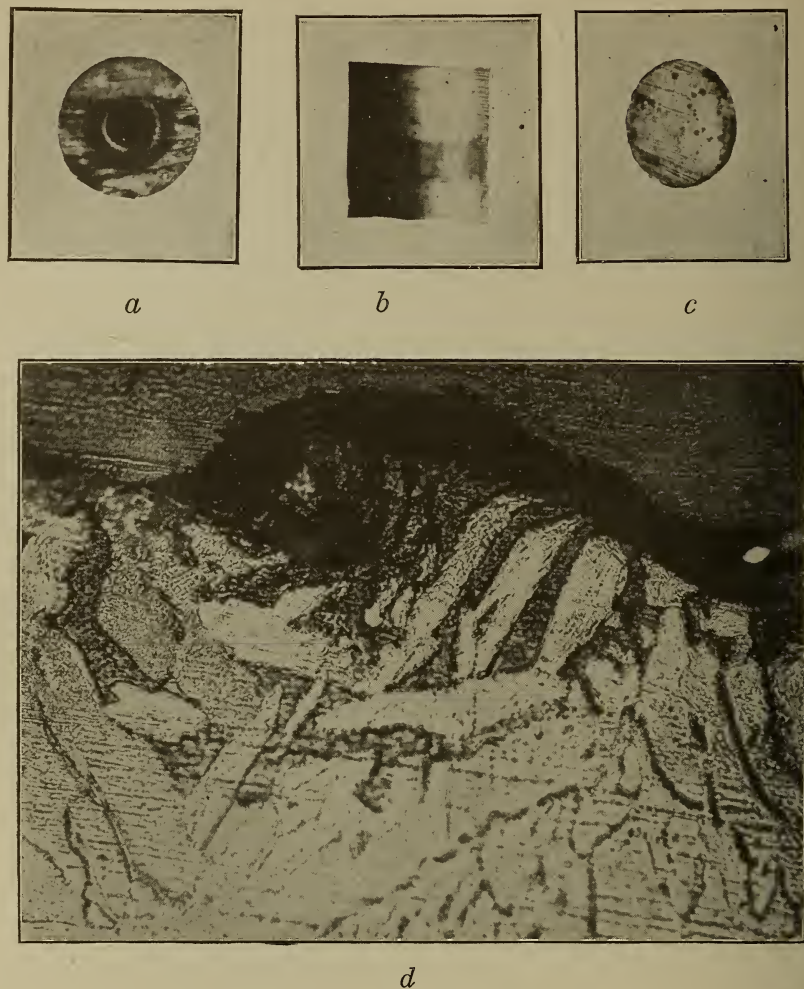


FIG. 12.—*Illustration of various conditions affecting dezincification*

- (a-b) Samples of Muntz metal which were in contact with copper while immersed in sodium chloride solution. In *a* the wire was inserted in the central hole; in *b* it was wrapped around the sample. The attack is immediately adjacent to the copper wire. ($\times 2$).
- (c) Muntz metal sample which has been immersed in 5 per cent sodium chloride solution. The dark spots are corroded areas which formed beneath adhering deposits of basic zinc chloride. ($\times 2$) unetched.
- (d) Cross section of one of the spots shown in *c*. ($\times 500$.) Etching, ammonium hydroxide and hydrogen peroxide. The dark band is the basic zinc chloride deposit which accelerated the attack of the metal beneath. A copper layer, shown in the upper two corners, was deposited in the sample to protect the edge of the specimen during the polishing.

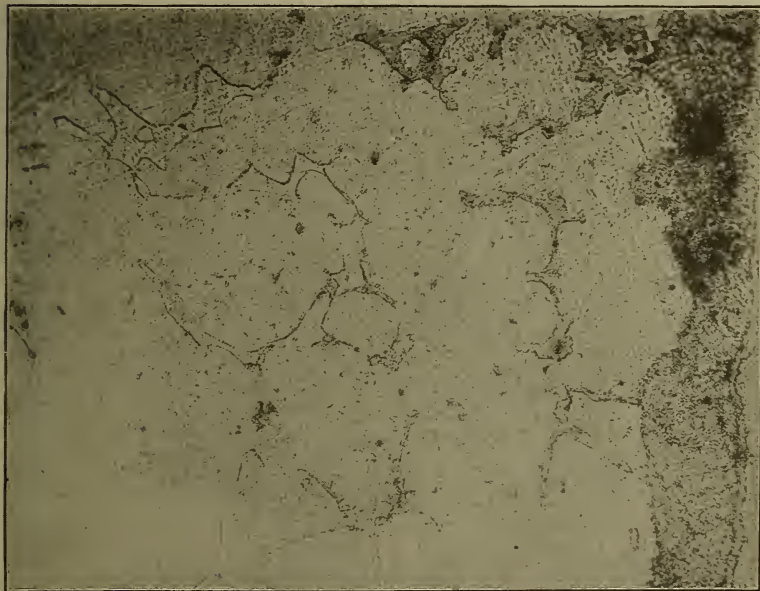
*a**b*

FIG. 13.—Illustrations of different conditions affecting dezincification

- (a) Base of V-groove in stress-corrosion specimen (No. 11, Table 2). The sample was nickel-plated and then copper-plated to protect the edge during polishing. The β has been dezincified at the extreme base of the notch. ($\times 250$.)
- (b) Sample of Muntz metal dezincified by heating in molten zinc chloride. Both α and β are completely attacked in the surface layer, an intermediate layer in which the β only, has been dezincified separates this portion from the uncorroded part. ($\times 250$.) Etching for both *a* and *b*, concentrated ammonium hydroxide and ammonium persulphate.

acting "catalytically," by others as being strongly electronegative toward both the α and β constituents and thus inducing dezincification in the same way that copper does. Heavy deposits of basic zinc chloride and carbonate were observed on the inside of the condenser tubes and on the outer or exposed surface of the sheathing. In type 1 (wrought bolts used for attachment of a boat keel), though no pronounced deposit on the outside was found, the "copper" coating was observed to be impregnated with a similar substance. The deterioration of the metal directly adjacent to the deposits is in nearly every case entirely complete; that is, both α and β are attacked. The degree to which the metal is attacked decreases with the distance from these deposits. In the examples described below (secs. 4 and 5), closely adhering hard, smooth specks of white basic zinc chloride were often found on the surface of the specimen when allowed to stand in the sodium-chloride solution. The metal immediately beneath such deposits was invariably in the red corroded condition. Fig. 12 *c* and *d* illustrate the appearance of such corroded samples.

4. EFFECT OF HEAT TREATMENT

It has been suggested that the differences shown by different lots of Muntz metal in their resistance to this type of corrosion is to be attributed to unavoidable variations in the heat treatment such samples have received,⁸ and that thorough annealing of the alloy at 650° to 800° C will prevent the preferential attack of the β , or zinc-rich, constituent. A series of samples of new sheet Muntz metal of the following composition were annealed for periods varying from 30 minutes to 4 hours; one series at approximately 370° C (360–373° C), the second at approximately 640° C (625–655° C):

	Per cent
Copper.....	61.35
Lead.....	.46
Tin.....	.16
Iron.....	.20
Zinc (difference).....	37.83

These two annealing temperatures were chosen so as to illustrate the possible effect of heating below or above the transformation which occurs in the β constituent at 470° C. The samples were then immersed in 5 per cent solutions of sodium chloride for a period of 70 days, each sample being suspended

⁸ Second Report of Corrosion Committee, discussion by Sir Gerard Muntz, Jour. Inst. Metals, X, 1913, p. 101.

by silk thread, proper care being taken to avoid contact with each other or with the glass sides of the container. No effort was made to regulate the temperature of the solution; it varied between 12°C and 20°C . At the close of this period a microscopic examination of cross sections of the samples showed that each one had been attacked to a slight degree. This attack, which is confined to the β constituent, was not general over the entire surface but was confined to small local centers. Each sample showed closely adhering white specks of basic zinc chloride; the metal under such speck showed a dezincification of the β constituent to an average maximum depth of 0.39 mm (0.0156 inch). The depth to which this attack of the β constituent had penetrated varied from 0.31 mm (0.0124 inch) to 0.05 mm (0.0020 inch), but apparently bears no relation to the previous heat treatment of the sample but rather to the character of the surface, a slightly roughened or pitted surface forming a much better support for holding the zinc-chloride deposits, which form from the slight general attack of the metal when first immersed, than a smoother one does. The samples heated for two and four hours at the higher temperature, 640°C , had lost some of the zinc by volatilization, so that much of the surface layer consisted of but the α constituent. No attack of such portions was observed.

Samples of the same material used above were quenched in water after heating to a temperature of 690°C . At this temperature both constituents, α and β , still persist (Fig. 9). The attack in this case was more rapid, the β having been attacked to a depth of 0.125 mm (0.005 inch) after 13 days' immersion in 5 per cent sodium-chloride solution.

The obvious conclusion to be drawn is that thorough annealing of the metal is not sufficient to entirely inhibit the selective corrosion of the material. The accelerating influence of the adhering deposits of the basic zinc chloride, however, appears to be a necessary condition for such an attack of the annealed metal.

5. TEMPERATURE

Practical cases of the effect of temperature upon this type of corrosion have been brought to the attention of this Bureau. One striking example is that of the corrosion of the tubes of a condenser using sea water. The outlet pipe, in which the water was always considerably warmer than the incoming stream, corroded badly enough to require replacement several times

while the inlet pipe was still intact and in service. The effect of temperature upon corrosion of similar material has also been studied by Bengough.⁹

6. STRESSES

The appearance of two of the types described (1 and 4) suggest the possible accelerating influence of the stresses to which these

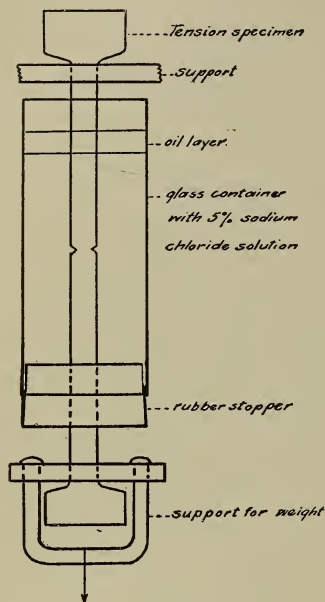


FIG. 14.—Arrangement for applying tensional stress while specimen was immersed in sodium chloride solution

The specimen is one-eighth inch in diameter at the base of the groove.

samples were subjected as one of the causes contributing to corrosion of this type. To illustrate this, a series of specimens were subjected to tensional stress while immersed in a 5 per cent solution of sodium chloride. The specimens were turned down to a diameter of approximately one-fourth inch, a very narrow V notch was then cut so that the diameter at the point of the notch was reduced to one-eighth inch. The purpose of the experiments was to see whether along the line of maximum stress—that is, the base of the V groove—the metal corroded more uniformly and readily than elsewhere on the same specimen. The samples were removed periodically from the solution and examined to make certain that no deposits of basic chloride had formed within the groove which might thus accelerate the attack at that point.

Fig. 14 shows the method of the set-up.

The material used was of the α - β type of structure and of the following composition:

	Per cent
Copper.....	62.26
Tin.....	.18
Lead.....	.00
Iron.....	.00
Zinc (difference).....	35.56

The samples were used both in the cast condition and after annealing at approximately 520° C. A determination of the mechan-

⁹ Second Report of Corrosion Committee, Jour. Inst. Metals; 1913.

ical properties of the material as cast and as annealed gave the following results:

Sample	Cast	Annealed
Ultimate strength, pounds per square inch.....	37 800	27 200
Proportional limit, pounds per square inch.....	5 000	7 500
Reduction of area, per cent.....	34.2	35.7
Elongation, (2"), per cent.....	39.5	25.0
Fracture.....	(a)	(b)

a Irregular; lemon-colored spots.

b Flaw at center.

Table 2 gives the results obtained after immersion for varying periods in 5 per cent sodium-chloride solution, the sample being under tension, which was maintained constant for the specimen throughout the period. The temperature was that of the room, which varied between 10 and 18° C (approximate).

TABLE 2
Corrosion of Muntz Metal While Stressed in Tension

Specimen	Stress	Period	Physical state of material	Results ^a
	lbs./in. ²	Days		
3a ^b	6 400	60	As cast.....	No dezincification at base of V groove.
3b ^b	16 000	17	do.....	β is attacked in base of groove to a depth of 0.25 mm.
4.....	6 400	59	do.....	No dezincification in groove.
5.....	9 600	10	Annealed; 50 minutes at 515° C and cooled in air.	No dezincification in groove. A network of very fine hairlike intercrystalline cracks opened up in the metal. The metal immediately adjacent to the cracks was dezincified, both α and β being attacked.
6.....	12 800	35	do.....	The β has not been attacked in the groove.
10.....	9 600	60	do.....	β was attacked in base of groove to a depth of 0.25 mm. The α was slightly attacked.
11.....	12 800	40	As cast.....	Dezincification of the β to a depth of 0.16 mm at the base of the groove occurred (Fig. 13a).
12.....	9 600	58	Quenched from 685° C in cold water.	No dezincification was observed in the groove.

^a The slight dezincification induced by the rubber stoppers or by small adhering specks of basic zinc chloride on the cylindrical surface of the specimen is not included here. Fig. 13a illustrates this attack.

^b 3a and 3b are the same specimen; after 60 days the load was increased to 16 000 pounds; that is, above the proportional limit.

The tension tests made on samples of the material used as well as the fine cracks noted in some of the samples (some were discarded entirely for this reason) show that the material was not very uniform. The results of the tension tests are to be regarded as approximate only for the material

Though the results are not to be regarded as conclusive, they are strongly suggestive that brass of the α - β type highly stressed is more prone to selective corrosion than when not so, particularly when the stress is highly localized; for example, at the base of a fine hair crack or a narrow groove. Of the eight samples used, the four which showed dezincification were all stressed above the proportional limit. Both specimens 3a and 4, which were stressed below the proportional limit, failed to show any trace of attack even after 60 days' exposure. It should be noted, however, that all which were stressed above the proportional limit were not alike in developing dezincification. Specimen No. 12 (9600 pounds load), which was quenched, is not strictly comparable with the others in that the mechanical properties are not necessarily the same as those in the cast condition. Also, this sample lacked the decided duplex structure shown by the others; this may be due to a slight difference of chemical composition. No adequate reason can be assigned for the failure of specimen No. 6, which was loaded above the proportional limit to develop dezincification. The change induced in the surface layer by the machining which the specimens received may be suggested as one of the possible contributing causes. The surface flow of the constituent in some cases is sufficient to entirely cover the β and thus protect it from the attack of the electrolyte. The results of the stress-corrosion tests, while not entirely conclusive, are in keeping with the general appearance and service behavior of some of the types described (1 and 4, Table 1).

Metal which has been quenched from a relatively high temperature may be readily shown to be internally stressed, due to the different rates of cooling of the outer layers relative to the interior, the differential rate of expansion of the different constituents, if more than one is present, etc. The peculiar manner in which the crystals of Muntz metal are corroded when the specimen has been quenched (Sec. III-4, above) suggests that this difference as compared with the manner of attack in the annealed metal may be induced by the stressed condition of such crystals resulting from the extremely rapid rate of cooling.

7. ACTION OF "FLUX" ON MUNTZ METAL

Muntz metal which has been cleaned by the use of zinc chloride, ammonium chloride, etc., often used as a "flux" for cleaning metal surfaces, by heating the metal and rubbing with a swab saturated

with a solution of the substance used often assumes a red color. That this reddening of the surface is a particular case of dezincification is shown by microscopic examination of cross sections of the metal taken through such reddened areas. Fig. 13*b* shows the result of heating a sample of Muntz metal in molten zinc chloride; in the surface layer both α and β are attacked, a thin intermediate layer in which only the β is attacked precedes the attack upon the α . The suggestion is offered that metal which has been so cleaned and, consequently, which shows dezincification to a slight extent may be, perhaps, more readily attacked in service, particularly if the metal contains any slight surface cracks and depressions which might serve to hold the chloride and thus act as centers for later corrosion in service.

V. SUMMARY

1. The deterioration of Muntz metal by selective corrosion is illustrated by four types, including tubing, sheets, and forgings. The metal becomes red in color, very weak, and brittle by this type of corrosion, which takes place when the piece is exposed to some electrolyte.

2. The metal has a duplex structure, one of the constituents, β , being very much higher in zinc than the other, α . In all cases, the selective corrosion consists of a preferential attack of the zinc-rich constituent and the formation of a porous "copper" mass which fills the network of holes previously occupied by the β . This attack may or may not be followed by that of the second constituent.

3. The rate at which the α phase is attacked is variable. The attack of this constituent may follow almost immediately that of the β or may be indefinitely delayed.

4. A state of dezincification may result in α brass under certain conditions, although the method of attack as revealed by the microstructure is different.

5. The line of demarcation between attacked and unattacked portions is very sharply defined. The action is not a gradual one, but the change is an abrupt and complete one even within the individual β crystals.

6. One of the most important conditions favorable to this type of corrosion, which occurs commonly while the metal is immersed in sea water, is the accelerating effect of the closely adhering deposits of basic zinc chloride resulting from the attack of the metal. Other influences which may accelerate the rate of attack

are contact with substances more electronegative than either the α or β constituents, an increase of temperature, and the effect of stresses to which the material may be subjected while in service.

7. Thorough annealing of Muntz metal does not entirely prevent the selective corrosion of the β constituent.

WASHINGTON, June 4, 1917.

