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on

Part I - Effects of Tin and Lead on Manganese Bronze
Part II - Dezincification of Manganese Bronze

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ABSTRACT

The effect of lead and other elements on manganese bronze has been studied in detail, especially in regard to the changes in mechanical properties and resistance to dezincification that may result from furnace charges of contaminated scrap metal. There appears to be little tendency for lead segregation in a well made manganese bronze. More lead may be permitted if the copper-zinc ratio and the tin content are carefully controlled.

Tin appears to be one of the best inhibitors of dezincification. Silver, phosphorus, arsenic, and lead are in general effective to a certain extent. Antimony not only decreases ductility seriously but also tends to increase the dezincification.

(b) The Zinc Equivalents

5. Work by Guillet has shown that the various minor elements such as iron, aluminum, manganese and tin may be considered equivalent to a certain amount of zinc in their effect on manganese bronze(4). Nickel is equivalent to a certain amount of copper. The table below gives zinc and copper equivalents according to Guillet.

Element	Equivalent
Copper (Cu)	1 x % Cu = Cu
Nickel (Ni)	1.1 x % Ni = Cu
Zinc (Zn)	1 x % Zn = Zn
Aluminum (Al)	6 x % Al = Zn
Iron (Fe)	0.9 x % Fe = Zn
Manganese (Mn)	0.5 x % Mn = Zn
Tin (Sn)	2 x % Sn = Zn

By adding the percentage of zinc and the sum of the zinc equivalents of Al, Fe, Mn and Sn (R x C) where R is the percentage of the given element and C is its zinc equivalent, the total equivalent zinc is obtained. Dividing the equivalent zinc by the sum of the equivalent zinc and equivalent copper, the apparent zinc content is obtained. The copper-zinc ratio is then computed as follows:

$$\frac{100 - \text{apparent } \% \text{ Zn}}{\text{Apparent } \% \text{ Zn}} = \text{Cu-Zn ratio}$$

(c) The Effects of Several Elements on Properties

6. Important as is the copper-zinc ratio in its influence on the mechanical properties of manganese bronze, there are many significant effects contributed by the individual elements. The intensity and direction of these effects depends to a considerable extent on the particular percentage of the alloying element. For instance, manganese greatly improves the ductility up to 2 percent, but beyond this percentage begins to embrittle the alloy. Iron likewise improves the ductility and has the advantage in not having a limitation on the percentage (at least reported in the literature). The effect of iron is probably allied to its grain refining action. Both the manganese and the iron within certain limits cause moderate increases in tensile strength. On the other hand, tin, which produces but slight increase in tensile strength and a corresponding decrease in ductility, is added primarily as an inhibitor of corrosion. In larger percentages the tin becomes harmful due to the formation of the brittle gamma phase. Although aluminum may have other functions, it is the major element for increasing the tensile strength of manganese bronze. The accompanying loss in elongation must

be counteracted by some of the other elements. The metallurgical basis for the production of manganese bronze thus depends on the proper proportioning of the above elements in order to have an alloy with optimum tensile strength, ductility and corrosion resistance.

(d) Manganese Bronze Castings

7. Some of the most important properties of manganese bronze are its foundry characteristics. It has the great advantage of not being susceptible to gas porosity. It generally presents a clean smooth looking appearance of the surface of the castings. One of the difficulties, however, is that its shrinkage is external rather than interdendritic as with tin bronzes and this makes necessary the use of large risers. Another difficulty is the narrow freezing range that may cause cold shuts if the metal is poured at too low temperature. The beneficial characteristics so far outweigh the disadvantages that manganese bronze has many important applications in castings such as marine propellers.

8. Several grades of cast manganese bronze distinguished by their tensile properties have been developed. The most common alloy covered by the Navy Department Specification 49B3e has a minimum 65,000 psi tensile strength and 20 percent elongation in 2 inches with the following composition:

	A Representative Alloy Percent
Copper	55-60
Tin	0.6
Lead	0.4 max.
Zinc	Balance
Iron	1.0
Aluminum	1.0
Manganese	0.5

(e) The Effect of Lead

9. Little has been published on the mechanical properties of sand cast manganese bronze, but some extensive researches on the chill cast and wrought alloy have been reported. Hensel(1) presented, in a correlated abstract, a condensed review of the principal factors in the production of castings. Ellis(2) found that lead in chill castings lowered the tensile strength rapidly at first and then less rapidly as the lead content exceeded one percent, while the elongation and reduction of area were reduced by the first addition of lead. Earlier investigators, Sperry(3), Guillet, and others in general found lead to be deleterious to the tensile properties of simple 70/30 and 60/40 brasses.

10. To determine the influence of lead on mechanical properties, a very accurate control of all variable elements must be maintained so that the basic structure of the alloys from one heat to another will not be changed and that the only variable will be lead.

EXPERIMENTAL PROCEDURE

(a) The Influence of Tin and Lead on the Mechanical Properties

11. To determine the effect of lead on the mechanical properties of manganese bronze, an alloy of the following nominal composition was selected because it was representative of the most common commercial alloy:

59.0 percent copper
38.5 percent zinc
1.0 percent iron
1.0 percent aluminum
0.5 percent manganese

All of these elements were constant except zinc and copper which, depending on the amount of tin, were varied to obtain the desired copper-zinc ratio. Lead, when present, was not considered in computing the copper-zinc ratio, since it is insoluble in copper alloys. This meant that the reported percentages had to be revised to compensate for the fact that lead was not to be included in the computation of the copper-zinc ratio. It became apparent early in the investigation that tin, as well as the copper-zinc ratio and lead content, was an important factor in the control of mechanical properties.

12. The alloys were made from the best grades of virgin metals, ingots, and selected scrap. The charges were melted in a graphite crucible in an induction furnace under a charcoal cover. The iron and aluminum were added as a 50-50 master alloy which melts at approximately 1150°C (2100°F). The manganese was added in the form of a manganese-copper alloy, and tin and zinc were added in the order named as virgin metals. A few heats were melted in a gas-fired furnace under slightly oxidizing conditions. Melting in different types of furnaces appeared to have no appreciable effect on the properties of manganese bronze.

13. All melts were deoxidized with one ounce of 15 percent phosphor-copper per hundred pounds of metal before pouring at 980 ± 10°C (1796 ± 18°F) into bottom-fed "separately cast bar" tensile molds prepared in accordance with N.D. specification 49-B-3e. The molds, which were made of No. 00 Albany sand containing about 6 percent moisture, were air dried at least 24 hours before using. The "separately cast bar" castings provided sufficient metal for standard 0.505

inch tensile bars, standard Izod impact specimens, chemical samples, micrographic specimens, and sea water corrosion test plates.

14. The study of the effect of lead on manganese bronze was divided into four general groups on the basis of tin content: (1) tin content above 1 percent; (2) tin content between 0.4 percent and 0.6 percent; (3) tin content 0.3 percent; and (4) tin free. The reason for dividing the work into these groups was to study the effect of lead and tin singly and in combination on the properties of manganese bronze.

(b) Pouring Temperature

15. Heat 194 was cast into five "separately cast bar" molds at intervals of 25°C (45°F) beginning at 1025°C (1877°F) and ending at 930°C (1706°F) to determine the influence of pouring temperature on the mechanical properties and density of manganese bronze. In all instances, pouring temperatures were observed by means of an immersion type platinum vs platinum 10 percent rhodium thermocouple which was calibrated at the necessary temperatures against a standard couple.

(c) Lead Segregation

16. Manganese bronze alloys, containing nominally 1.0 percent lead, melted in a gas fired furnace under oxidizing conditions and deoxidized with phosphorus-copper following standardized procedures, were poured into bottom-fed horn-gated molds which produced solid cylinders, 2, 4, and 8 inches in diameter for the lead distribution study. The cylindrical castings were cut longitudinally through the diameter, and chemical and micrographic samples were selected from the inside surface (Plates 1 and 2) to determine the magnitude of the lead segregation.

DISCUSSION OF RESULTS

(a) The Effect of Tin and Lead on Mechanical Properties

17. When all data had been compiled, it was found that using the copper-zinc ratio as a basis, definite trends could be established concerning the effect of lead on manganese bronze, if the tolerance on the other minor elements (Fe, Al, Ni, Sn and Mn) was closely controlled.

18. The effect of from zero to two percent lead on the tensile strength, elongation, and impact strength is shown in Plates 3, 4, and 5. The data used for the preparation of these plates are given in Tables I, II, and III. A careful study of these curves indicates that several factors control the amount of lead that can be permitted without lowering the present specifications. The impact strength may vary from a

high to a low value depending upon the amount of lead present in the alloy. The greatest drop in impact strength occurs between 0 and 0.5 percent lead. When the amount of lead exceeds 0.5 percent, the impact strength is lowered but little.

19. The horizontal lines drawn in all graphs in Plates 3 and 4 represent the minimum tensile strength and elongation requirements, respectively. It may be observed that when the other variable elements such as manganese, iron and aluminum are constant in addition to lead, the copper-zinc ratio and tin content have an important influence on the mechanical properties. For example, an alloy of which the copper-zinc ratio is 1:26 - 1:28 containing 1.5 percent lead may meet the mechanical requirements if between 0.4 and 0.6 percent tin is present. However, if no tin is present, the same alloy may contain a maximum of only 1 percent lead. If the copper-zinc ratio is 1.30 to 1.34 the alloys may contain a maximum of 1 percent lead if between 0.4 and 0.6 percent tin is present, and no lead if no tin is present. When the copper-zinc ratio is 1.20 to 1.25 no lead can be tolerated if 1 percent tin is present, and 0.7 percent lead if less than 0.6 tin is present. Therefore, the amount of lead which may be permitted without changing the specifications depends upon the copper-zinc ratio and the tin content if the manganese, aluminum, and iron are constant. When the latter elements are varied, some deviations in mechanical properties are to be expected. In this investigation, the optimum condition which will permit a high lead content seems to exist in alloys of which copper-zinc ratios are from 1.26 - 1.28 and tin content 0.4 to 0.6 percent. These requirements are not too stringent for large scale production.

(b) Pouring Temperatures

20. Variations in the pouring temperature of manganese bronze between 950°C (1740°F) and 1025°C (1880°F) have no influence on the mechanical properties (Table IV). The melt poured at 930°C (1706°F) was poured at too low a temperature as shown by the decrease in tensile strength and elongation.

(c) Lead Segregation

21. The lead content at certain points in the 2, 4, and 8 inch diameter cylinders was determined and the percent lead for each location is given in the encircled numbers in Plate 1. Photomicrographs of unetched specimens taken from the same positions as the chemical specimens are shown in Plate 2. No appreciable segregation of lead is evident in either case. This is what might be expected since the freezing range of manganese bronze is very narrow. Thus since solidification takes place directionally and almost instantaneously, the lead which is mechanically suspended does not have the opportunity to segregate that it has in the wide freezing range alloys, such as leaded tin bronze.

SUMMARY AND CONCLUSIONS

22. When manganese bronze containing one percent lead is thoroughly mixed before pouring, no serious segregation of the lead will occur during solidification. Since no other data are available, this statement is limited to cylinders 8 inches in diameter by 5 inches long or smaller.

23. The limit to which lead can be added to manganese bronze assuming that aluminun, iron, and manganese are constant, depends upon the copper-zinc ratio and the percentage of tin.

RECOMMENDATIONS FOR PART I

24. Although Guillet's zinc equivalents are apparently reliable, they should be studied more extensively in order to determine the ranges of composition over which they are most accurate.

25. Investigate the casting of simple shapes.

26. Continue the work on manganese bronze made from leaded yellow brass scrap.

27. Improve the mechanical properties of the alloy containing 81 percent copper, 3 percent tin, 7 percent lead, and 9 percent zinc by additions of nickel, iron and aluminum.

SUPPLEMENT TO PART I

28. Two typical foundry projects on the salvaging of scrap metal were undertaken in order to test some of the conclusions that had been reached in the investigation, such as the effect of the copper-zinc ratio on the mechanical properties.

29. The first problem was to convert yellow brass scrap of approximately the correct proportions of copper and zinc into manganese bronze by the addition of the necessary aluminum, iron and manganese. The iron and aluminum were added as a master alloy 50 percent iron-aluminum and the manganese was added as 50 percent manganese-copper alloy. The tensile strength of the alloy made in this manner, #B37-1 (Table IV), failed to meet the requirements of the Navy specifications, but the elongation passed by a narrow margin. It was believed that the low tensile strength could be attributed to the unfavorable copper-zinc ratio, and the rather low elongation to the high percentage tin. Consequently, a suitable composition of tin-free scrap was added in order to lower the copper-zinc ratio and dilute the tin. Heat B37-2 was improved sufficiently by the lower copper-zinc ratio to pass the Navy specification on manganese bronze. The additional benefit of improved elongation was the result in Part 1 of the decreased percentage of tin.

30. The second investigation was carried out at the New York Navy Yard in order to salvage a large quantity of manganese bronze ingot which had been purchased on Navy Contract #NXS 2757. This manganese bronze failed to meet the mechanical properties in Navy Specification 49B3e although the chemical composition was within the limits of this specification. The ingot was melted under a charcoal cover in a slightly oxidizing atmosphere in a gas fired furnace. The metal was poured at 980°C (1796°F) into bottom fed "separately cast bar" molds. Three heats (B20, B22, B29, Table IV) were made to show the effects of the following treatments:

(1) Flaring followed by replacement of the zinc lost in this superheating process.
(2) Deoxidation with phosphor copper.
(3) Holding 10 minutes at 1000°C (1932°F) before pouring.
(3a) Flaring 10 minutes at 1100°C (2012°F) after holding.

31. The metal was then poured into "separately cast bar" molds. Treatments 3 and 3a were successive treatments of the same charge. Test molds were cast from the untreated bronze, treatment 3 and 3a. The results in Table IV indicate that the low elongation which had been the cause for the failure to meet the specifications was improved sufficiently only in heat #B-29-3. The removal of some of the zinc by the volatilization in the flaring improved the ductility by increasing the copper-zinc ratio.

32. In addition to the above studies a quantity of scrap was procured from the Naval Gun Factory and remelted at the Naval Research Laboratory. It was melted under a charcoal cover in a gas fired furnace and poured into a separately cast bar mold. The low elongation as shown in Table IV might be explained by the copper-zinc ratio.

PART II

Dezincification of Manganese Bronze

STATEMENT OF PROBLEM

33. The presence of foreign elements introduced from the scrap in cast manganese bronzes has a marked effect on their tendency to fail by dezincification when exposed to certain corrosive media such as chloride, sulfate and nitrate solutions. This tendency for corrosion by the selective loss of zinc in the high zinc brasses is inhibited by the addition of tin and some other elements. In the 70-30 brasses, the additions are usually in such small amounts that the results are favorable to corrosion resistance and not harmful to the physical properties. The addition of tin to manganese bronze, while being essential to the corrosion resistance, may, on the other hand, be detrimental to the ductility.

34. The purpose of the present investigation is to evaluate the effectiveness in manganese bronze of the small amounts of inhibitors to dezincification that have already been proved beneficial for 70-30 brass.

KNOWN FACTS AND THEORETICAL CONSIDERATIONS

(a) The Nature of Dezincification

35. In the last forty years, there have been nearly forty papers dealing with some form of dezincification. Largely because of the work of the Corrosion Research Committee of the British Institute of Metals, the process of dezincification is now understood to be due to the solution of the brass as a whole followed by the redeposition of spongy embrittled copper from the solution (9)(10)(11). Abrams(8) in this country later confirmed the above explanation advanced by Bengough and his associates. Both sources are in agreement that dezincification is favored especially by low concentrations of chlorides or other salts and acids, low concentration of dissolved oxygen, elevated temperature, and low velocity or stagnation of the corroding solution (3). Bengough included the presence of iron and manganese as prime factors in the promotion of dezincification.

(b) Previous Work on 70-30 Brass

36. In previous investigations, the study of the influence of composition on dezincification have been almost entirely restricted by the 70-30 or alpha brass composition. Bengough and associates investigated the effects of a large number of elements on this type of brass (11). They found that 1 percent tin, over 0.01 percent arsenic, 0.5 to 1 percent nickel, 0.5 percent tungsten, 0.5 to 0.75 percent aluminum all

tended to diminish dezincification while manganese and iron increased the corrosive attack. The research of Lynes (14) in the United States on 70-30 brass proved that small additions (0103 percent) of not only arsenic but also antimony and phosphorus were effective in suppressing dezincification.

(c) The Dezincification of Manganese Bronze

37. No work was found in the literature on the effects of these various elements on the dezincification of manganese bronze. Since manganese bronze is so different in composition, microstructure and properties, we cannot be sure that the manganese and iron would not destroy the supposedly favorable effect of the aluminum. The effects of arsenic, antimony, and phosphorus are also open to question. The closest composition to manganese bronze that has been reported in the literature on dezincification was the 60-40 brass containing 0.5 percent of arsenic investigated by Masing(15). He found that the arsenic in the 60-40 brass did not inhibit dezincification.

NARRATIVE OF ORIGINAL WORK DONE AT THE NAVAL RESEARCH LABORATORY

38. The effects of tin, silver, phosphorus, arsenic, lead and antimony on the dezincification and mechanical properties of manganese bronze were investigated by means of an accelerated test which consisted of tensile tests on specimens which had been suspended for various lengths of time in a 3 N HCl solution at 50°C.

EXPERIMENTAL PROCEDURE

(a) Melting Technique

39. The special elements, tin, silver, phosphorus (phosphor copper), arsenic, lead, and antimony, were added to forty pound heats. All heats were deoxidized with phosphor copper except those heats which were for comparison with bronzes low in phosphorus. One percent of the zinc content was added separately to compensate for zinc losses. Each forty pound heat was cast into a standard manganese bronze tensile mold which provided enough metal for ten 0.313 inch diameter tensile specimens, two standard Izod specimens, one sea water corrosion plate, and a sample for chemical analysis. The pouring temperature was approximately 980° in all cases. All of the volatile elements like arsenic and antimony were wrapped in copper foil and plunged below the surface of the melt just before pouring.

(b) The Dezincification Test

40. The tensile strength of the 0.313 inch diameter tensile bars exposed to 3N hydrochloric acid at 50°C was taken as the accelerated test for dezincification. The

threads of the test bars were coated with apiezon wax to protect them from corrosion. The wax was closely adherent and did not flow or soften at 50°C. After the test it was removed by melting in a bunsen flame. The test bars were suspended vertically in the solution in an 800 cc beaker and an air line was introduced in the center (Plate 6). A separate beaker was used for each composition in order to avoid the possibility of contamination by soluble constituents. The beakers were put in a constant temperature furnace. At one week intervals the solutions were renewed and two test bars taken from each beaker. The elongation was not taken in the tensile test because the outer dezincified layer pulled apart from the undezincified core.

DISCUSSION OF RESULTS

(a) The Nature of the Corrosive Attack

41. Considerable attention was given to the uniformity of the dezincification. Representative tensile bars of the "as cast" manganese bronze of the arsenic, antimony, phosphorus and tin series were sectioned transversely, polished, and etched with ferric chloride. Microscopic observations revealed that the corrosive attack was uniform in every instance. By the term "uniform" it is meant that the lines of demarcation shown in Plate 8 between dezincified and undezincified portions of the cast test specimens were clear cut. There were no local penetrations of the corrodent along grain boundaries beyond the line of demarcation. The dezincification in the corroded zone occurred first in the beta constituent and to a certain extent in the alpha constituent. This is proven by the following chemical analysis of dezincified material and by the fact that there was 40 percent of alpha in the "as cast" material:

	Undezincified Core %	Dezincified Zone %
Cu	59.01	94.8
Zn	38.39	5.02
Sn	0.61	0.03
Al	0.99	0.04
Fe	0.58	0.07
Mn	0.42	0.04

With 40 percent of alpha there would be nearly 15 percent of zinc left if the alpha islands had not been attached.

42. In Plate 8 it will be noted that some of the residual alpha is in dendritic form in the completely dezincified samples B19 and B26. Several cross-sections have non-symetrical dezincification because the tensile bars fell over into a horizontal position.

(b) The Effects of Added Elements

43. The somewhat beneficial effects of arsenic and phosphorus are shown in the three week specimens of B21 and B27. Antimony in an increased percentage is harmful as shown by B26. The best resistance to dezincification is evident in B31 which contains 0.49 percent tin.

44. Numerical values of dezincification resistance of the same group of alloys are represented by the curves of tensile strength in Plate 7.

45. The complete tensile test data are shown in Table V. It is seen that silver is the only element in this group besides tin that gives comparable resistance to dezincification. The presence of small percentages of lead, up to 0.73 percent, in general appeared to decrease slightly the corrosive attack. In the tin-lead series the average tensile strength of B30-3 and B30-4 containing 0.29 percent tin fell below the composition with 0.5 percent tin.

CONCLUSIONS TO PART II

46. According to the accelerated tests, tin is one of the best inhibitors of dezincification of manganese bronze. Other elements which might be equally good in sufficiently large amounts either are too costly, or are detrimental to the mechanical properties. Silver, phosphorus, arsenic, and lead are a few of these elements that provide a certain amount of resistance to dezincification but which do not appear feasible to use. Antimony not only tends to increase the dezincification but also reduces the ductility of manganese bronze.

RECOMMENDATIONS FOR PART II

47. In order to determine the minimum amounts of tin and silver that will provide reasonable protection to dezincification, two heats containing 0.05 and 0.10 percent tin, and two containing 0.05 and 0.10 percent silver respectively, have been prepared.

48. Long time tests should be made for correlation with a few selected compositions.