A NOTE ON THE DEZINCIFICATION OF BRASS AND THE INHIBITING EFFECT OF ELEMENTAL ADDITIONS

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1. INTRODUCTION

The dezincification of brasses has been the subject of substantial conjecture and investigation over the past century and the technical press is littered with papers on the problem. Very broadly the technical literature can be subdivided into five main groups as follows:

(a) Observations of dezincification phenomena including mechanically induced dezincification and in-service experience in various solutions;

(b) Development of tests to assess the propensity of particular brasses to dezincify;

(c) Mechanistic theories and kinetics of dezincification;

(d) Inhibition of dezincification by alloying additions to the brass; and

(e) Inhibition of dezincification by chemical treatment of the brass.

This note is concerned only with the inhibition of dezincification by alloying additions, although some notice is taken of operating conditions such as water temperature and composition and the effect that alloying additions may have on other important properties of the brass, e.g., susceptibility to stress corrosion cracking.

A few notes on the effect of cold work on dezincification together with a short bibliography on dezincification tests are presented in the Appendix.

2. ALLOYING ADDITIONS

2.1 General

The intensity of dezincification of brass is very closely related to the structure of the alloy which is controlled by composition. As might be expected the resistance to dezincification increases with copper content of the brass, but the relationship is not linear. Major improvements in performance occur when the structure changes from all-beta to alpha+beta (duplex) and from duplex to all-alpha phase. Alloys containing less than 15% Zn rarely dezincify.

Some alloying additions have a large effect on the structure of brass, e.g., by altering the proportion of alpha, beta or gamma phase present. Many years ago Guillet and Portevin[1] established the concept of designating a "zinc equivalent value" for each commonly used alloying addition. Some zinc equivalents are listed in **Table 1.** However it is well to remember that these values were developed for *dilute* solutions of the alloying additions and it is not surprising that they sometimes generate inaccurate estimates. Consequently other values, based on experience of particular alloy systems, are sometimes used to provide a more realistic estimate of the likely structure that will be generated in practice. Thus, the value for aluminum is often reduced to 4, whereas that for lead probably approaches zero as the lead content exceeds about 0.5%. Brunhuber,[2] who made a study of Guillet and Portevin's work, dismissed the whole concept of zinc equivalents as being too unreliable for practical use.

However, whatever the factor used, it is quite clear that for some alloying additions an adjustment to the copper or zinc content in the brass is necessary to maintain or obtain the desired alpha, beta or gamma content in the structure of the new alloy.

Some investigators [3-5] have developed new dezincification resistant alloys that may also be hot worked and easily machined while having mechanical properties to suit their usage. Many of these alloys depend on having a duplex structure during some or all of the manufacturing stages, which subsequently can be converted to all-alpha (or nearly so) by heat treatment. Small amounts (around 5%) of beta-phase have little, if any, detrimental effect on the dezincification of otherwise all-alpha phase brasses *provided that the beta is finely divided and well dispersed throughout the alpha matrix.*

Weldon, [6] knowing that the all-alpha structure was more resistant to dezincification than duplex, deliberately generated an all-alpha surface layer on leaded duplex brass. These treated alloys were found to have a high degree of resistance to

dezincification, but at that time (1957) the process was considered to be too expensive and the technique was abandoned. However, the simplicity of the process, which is independent of the alloying additions, might now be well worth reexamination.

2.2 Arsenic, Antimony and Phosphorus

Very early on in the study of dezincification it was found that a small quantity of arsenic, antimony or phosphorus inhibited the preferential dissolution of zinc from the all-alpha brasses[7-9] and since then these elements have been added variously to those brasses for that purpose. The particular effectiveness of arsenic in 70-30 brass relative to a number of other elements as demonstrated by Bengough and May[7] is shown in **Table 2**. However, arsenic, antimony and phosphorus are ineffective in preventing the dezincification of the duplex (alpha-beta) and all-beta brasses, although some protection may be afforded to the alpha phase in the duplex alloys.[4] Furthermore, Sullivan[10] observed that an 0.25% arsenic addition to a 60-40 high purity brass more than tripled the dezincification rate. A similar arsenic addition to a 58.9Cu-38.37Zn-1.69Pb alloy also accelerated the dezincification rate, in this case by about 30%.

Lombardi[11] conducted tests on an all-alpha 70-30 brass
and a duplex 60-40 brass both in the hard and annealed states and containing arsenic, antimony or phosphorus (each at three levels, viz.: 0%; 0.1%; and 0.2%), all samples being immersed in a 5% $CuCl_2$ solution. He showed that the annealed specimens performed better than the hard samples and that there was little or no further benefit to be gained by increasing the level of the inhibiting element above 0.1%. Antimony gave the best result; alloys containing arsenic or phosphorus gave variable results.

Nothing[12] also observed the inhibiting effects of arsenic, antimony and phosphorus on dezincification, but in addition he noted that each of these elements aggravated the tendency of the brass to fail by intercrystalline corrosion under conditions of static or fatigue stress (corrosion fatigue). This he thought was due to *grain boundary precipitation of low solubility phases.* Coarse grain sizes enhanced the effect. Consequently he recommended that the addition levels for arsenic and phosphorus should be limited to less than 0.04% and 0.015% respectively.

Ming and Ruon[13] examined the inhibiting effect of arsenic in 70-30 brass. They found that the dezincification and general corrosion rates dropped sharply with increasing arsenic content in the alloy up to 0.05%. At this level the corrosion rate was a minimum and the alloy corroded

uniformly, i.e., the copper and zinc dissolved at the same rate. They also conducted experiments on 70-30 brass plated with arsenic and came to the conclusion that arsenic at the metal-solution interface did not inhibit dezincification; the inhibiting effect was only produced by arsenic in the bulk of the brass. Langenegger and Robinson[14] also found that additions of As_2O_3 or Sb_2O_3 to the test solution (HCl-$CuCl_2$) did not retard the extent of the attack on 70-30 brass. Furthermore, an arsenical brass tested in similar solutions was severely pitted and neither arsenic nor antimony was deposited on the immersed brass samples.

Hollomon and Wulff,[8] by contrast, found that during corrosion of arsenical brass the arsenic entered the solution as a trivalent ion which could subsequently deposit upon the brass surface. The resulting arsenic-rich film increased the effective potential of the surface to practically that of copper, so preventing the deposition of copper. Barry[15] postulated that the beneficial effect of antimony and phosphorus may be explained analogously to that of arsenic, for films are formed during the corrosion of alpha brasses containing either of these elements.

Crampton and Burghoff,[16] commenting on Hollomon and Wulff's results, said that practical experience had shown that there was a tendency for intercrystalline corrosion attack in arsenical Admiralty brass in contact with seawater. Also they demonstrated that all brasses containing up to 0.014%As tended to dezincify and both arsenic and copper redeposit. Dezincification is inhibited in the alpha brasses by 0.024% As, and at this level only the arsenic redeposits. The minimum corrosion rate is obtained with an arsenic addition of 0.084%.

In further studies on 70-30 brass, Pryer and Giam[17] showed that arsenic additions are effective in preventing dealloying (dezincification) at potentials in excess of 0.02V. At these potentials the arsenic in the surface layers of the alloy is oxidised to arsenite or monohydrogen arsenate ions which can be *chemisorbed* from solution back on to the surface of the alloy (preferentially by the zinc) so preventing the solution of the zinc atoms.

A substantial body of work has been conducted on various complex brasses containing arsenic.[3-6,18-23]

In general, the all-alpha alloys exhibit resistance to dezincification regardless of the alloying additions; alloys containing small quantities of well dispersed beta phase completely enclosed by alpha or, in the case of tin-bearing brasses, a delta (tin-rich) phase also exhibit dezincification resistance. All of the other duplex alloys dezincify.

2.3 Other Elements 2.3.1 Aluminum

The excellent corrosion resistance of aluminum brasses, such as the 76Cu-22Zn-2Al alloy, was noted more than 60 years ago by May[24] and Bengough and May[7] who also reported that the aluminum addition inhibited the dezincification of 70-30 brass **(Table 2)**. Subsequently Kenworthy and O'Driscoll[25] suggested that aluminum has negligible effect in the all-alpha brasses and the duplex brasses containing aluminum are not dezincification resistant. Research conducted by Weldon[6] at the BNFMRA in the mid-1950s confirmed this latter

suggestion. Weldon found that simple additions of aluminum to duplex or all-beta brasses (containing 2%Pb) had no effect on the well known tendency of those alloys to dezincify (but see **Section 2.3.4** below).

The results of Kondrashin et. al.[26] seem to establish that aluminum additions to alpha brasses do not inhibit dezincification. On the other hand Oishi et. al.[27] observed that aluminum *retarded* dezincification in both duplex and all-alpha alloys and Beccaria et. al.[28] have since claimed that aluminum *retards* general corrosion as well as dezincification.

2.3.2 Tin

Desch and Whyte[29] included in their fundamental studies of brasses an examination of tin additions to both the all-beta and all-alpha alloys. Their results (**Table 3**), surprisingly, show that tin is beneficial in the beta but detrimental in the alpha brasses. However, they added a cautionary note in their paper to the effect that although the tin-bearing alpha alloy produced more corrosion products than any of the other 70-30 type brasses examined, it was evident that the dezincification rate of this alloy was diminishing near the end of the one-hour immersion test, whereas the reaction rates for all the other alloys remained at the same level for the whole test period. Because of this difference, Desch and Whyte predicted that in long-term immersion trials the tin-bearing alloy would outperform the simple binary alloy as well as the leaded alloys that were included in the short tests.

The results of later workers are, with few exceptions, in general agreement with this prediction. Bengough and May[7] list tin as inhibiting dezincification of alpha brasses (**Table 2**); and Pchelnikov and Marshakov[30] provide further evidence of the inhibiting effect of tin in 70-30 brass. These latter workers observed that during immersion of the tin-bearing 70-30 brass in aerated, weakly acidic, chloride solution, both the zinc and the tin suffered selective attack during the initial 10 minutes; but thereafter the zinc dissolved in proportion to the bulk composition of the alloy, and tin accumulated on the brass surface as a tenacious SnO_2 layer.

Weldon[6] observed that tin additions in the range 1.2% to 3.2% did not diminish the dezincification of either duplex or all-beta brasses containing up to 2.4%Pb. However, when he added aluminum to these tin-bearing alloys they exhibited a substantial resistance to dezincification, although such attack as occurred was inclined to be localized and deep. The optimum effect was achieved with a 1% addition each of tin and aluminum.

Beccaria et. al.[28] found that additions of tin with aluminum to 70-30 brass altered the properties of the passive film when the alloy was immersed in seawater and increased the alloy's resistance to both general corrosion and dezincification.

Work by Pai et. al.[31] has also demonstrated a beneficial effect of tin additions to 60-40 type brasses; the maximum benefit being realized with a 1%Sn addition which enhanced the dezincification resistance of the alloy in seawater. Tin also tends to inhibit dezincification of the duplex type high tensile brasses (representative composition: 59Cu-38.5Zn-1Fe-1Al-0.5Mn)[21].

Sukegawa and Watanabe[5], in experiments to develop a new brass alloy for valve stems, made tin additions to binary brasses containing more than 63%Cu. The structure of these alloys consisted predominantly of alpha phase with some gamma and, as expected, the proportion of gamma increased with tin content. It was quickly established that the presence of the gamma phase reduced the dezincification resistance of the alloys, plug type dezincification developing through the gamma. This they concluded was due to the relatively high tin and low copper levels in the gamma relative to the extra low tin and high copper levels in the alpha phase. After further experimentation they finally made an effectively all-alpha alloy by making a 0.5% (or more) nickel addition to the tin bearing alloys. These quaternary alloys were dezincification resistant and equivalent to arsenical alpha alloys in performance. The alloy has since been used successfully for valve stems in places where duplex brasses were subject to dezincification. Oishi et. al.[27] later confirmed this finding.

2.3.3 Silicon.

Weldon[6] added 0.33%Si to a 58.4Cu-2.4Pb-Zn alloy. The resulting brass had a duplex structure which he found was very susceptible to dezincification. He also found that two arsenical (0.04%As) brasses containing 3.1Si-68.2Cu-2.3Pb-Zn and 3.0Si-76.2Cu-2.0Pb-Zn, respectively, were susceptible to dezincification, both alloys displaying "a silicon-rich precipitate in an alpha matrix." It is not clear whether this silicon-rich phase was an intermetallic or what is now known as a silicon-rich beta phase isomorphic with zinc-rich beta.

Staley and Davies[32] have since observed that as-cast silicon brasses, although not immune to dezincification, were nearly as good as the CZ132 heat treated arsenical brasses; their resistance to attack increased with increasing silicon content (up to 3.7%, the highest level tested). These silicon-bearing alloys contained about 5% of each of the zinc-rich and the silicon-rich beta phases in an alpha matrix, for all the silicon levels examined. This was achieved by adjusting the copper content to maintain the same zinc equivalent from alloy to alloy (using the Guillet coefficients described in **Section 2.1** above). Unfortunately, the silicon-rich beta phase decomposes at temperatures in excess of about 100C to give alpha+gamma phases, which severely weakens the alloy. Further work is required to establish whether the silicon-rich beta can be stabilized, e.g., by another alloying addition, so that the material can be used safely at elevated temperatures.

The results of work by Oishi et. al.[27] tend to indicate that a small addition (0.5%) of silicon retards dezincification in duplex (60-40) brass. However, in alloys having silicon-rich

particles in an alpha matrix such as may be produced by adding 0.5%Si to a 70-30 brass, dezincification follows preferential attack of the silicon-rich particles.

2.3.4 Iron, Manganese, Nickel and Cobalt

In fundamental studies on brasses, Desch and Whyte[29] discovered that the presence of iron accelerated the dezincification of beta brass. They studied four beta brasses containing about 53%Cu and 46%Zn (**Table 3)** and all suffered dezincification; but the iron bearing alloy produced around 38% more corrosion product than the simple binary alloy. Subsequently, Bengough and May[7] observed that iron also accelerated dezincification in 70-30 brass (**Table 2)**. They also found that manganese similarly accelerated dezincification in that alloy, although at a lower rate than iron.

Other investigators[26, 27, 33] have also observed the detrimental effect of manganese. Bailey,[33] in studies on intercrystalline cracking (ICC) in sand-cast complex beta brasses, found that additions of iron with manganese or iron with nickel suppressed ICC but at the expense of lessening those alloys' resistance to dezincification. Under load, in NaCl solutions, transcrystalline fracture occurred in the regions weakened by dezincification. In experiments conducted by Oishi et. al.,[27] dezincification was accelerated by an 0.5% addition of either iron or manganese to a duplex (60-40) or an all-alpha (70-30) brass, or a combination of 0.5% of each of these elements to the duplex brass. A similarly bad result was obtained from a 60-40 brass to which had been added 0.5% iron with 0.5% nickel.

Brasses containing 60% or more copper and in excess of 4% nickel have long been known to be completely resistant to dezincification[34]. Bengough and May[7] and Kondrashin et. al.[26] found that smaller additions of nickel, e.g., 0.5% to 1%, also tended to inhibit the dezincification of all-alpha brasses. The results of Sukegawa and Watanabe,[5] described in

Section 2.3.2 above, and Oishi et. al.,[27] confirm a slight beneficial effect of 0.5% nickel in all-alpha 70-30 brass, but little benefit of a similar addition in 60-40 duplex brass.

Bailey[33] found that an addition of either 1.4% cobalt by itself, or 0.8% cobalt with 1.4% nickel, improved the resistance of as-cast beta brass alloys to ICC but at the same time accelerated dezincification with consequential weakening and subsequent fracture of the alloys.

2.3.5 Tungsten

Bengough and May[7] found that a 0.5% addition of tungsten improved the dezincification resistance of 70-30 brass.

2.3.6 Lead

Colegate[35] claimed that leaded brasses show no improvement over non-leaded alloys of otherwise similar composition insofar as susceptibility to dezincification is concerned. However, the results obtained by Bengough and May[7] and Desch and Whyte[29] clearly indicate that lead additions to alpha brasses tend to inhibit dezincification (**Tables 2** and **3**). In contrast, Sullivan's results[10] show equally clearly that lead accelerates dezincification of duplex brasses; a 59.8Cu-38.4Zn-1.7Pb brass was much more heavily dezincified than a lead-free 60-40 brass. Kenworthy and O'Driscoll,[25] on the basis of observations made on the in-service performance of leaded brass fittings, also suggested that lead accelerated dezincification.

2.3.7 Bismuth

Price and Bailey[36] made a detailed study of all-alpha and duplex brasses with deliberate additions of bismuth. They expected that the bismuth would behave in the same way as phosphorus, arsenic and antimony in inhibiting dezincification. This expectation was founded on the crystallography of the Group VB elements and the similarity of bismuth to arsenic and antimony. Much to their surprise they found that bismuth did not inhibit dezincification, but rather it seemed to accelerate the attack. However, close examination now, i.e., 50 years on, of the tabulated results raises a doubt as to the validity of their conclusion. In particular, the compositions of the alloys examined show that the beta phase content of the bismuth-bearing brasses would have been substantially greater than in the binary reference alloy (**Table 4**) and this would have been so whether the zinc equivalence of bismuth was 0, 1, or any other positive number (**Table 4**). Simple inspection of the results then reveals a strong relationship between the tensile properties of the exposed samples and the calculated beta content, and the alloys may be listed in a sensible order of resistance to dezincification, independent of bismuth content.

More recently, a few dezincification tests have been performed on two extruded, drawn and beat treated bismuth-bearing brasses,[37] with nominal compositions of 61.5Cu-2Bi-Zn and 62Cu-lBi-0.12As-Zn. The results of these tests showed that the alloys were dezincified to about the same extent as the equivalent 2% or 1% leaded brasses, respectively. In particular, the arsenical alloy behaved in an exactly similar manner to the CZ132 type arsenical leaded dezincification resistant alloys. These results, although not conclusive, certainly add weight to the idea that bismuth additions have a neutral effect on the dezincification resistance of duplex and nearly all-alpha brasses. Further investigation of bismuth bearing alloys would appear to be required.

2.3.8 Rare Earth Elements

Sullivan[10] investigated the effect of additions of yttrium and

other rare earth elements, these latter added as Mischmetal on 60-40 (duplex) brasses. His results showed

that these additions marginally increased dezincification rate. However, similar additions made to arsenical 60-40 brass had a beneficial effect and the level of dezincification was reduced; a 0.1% Mischmetal addition gave the best result.

Verma et. al.,[38] in experiments on aluminum bronze, found that small (0.05%) additions of lanthanum, cerium or neodymium improved the general corrosion resistance of the alloy in dilute sulphuric acid solutions. Similar results were obtained by Singh et. al.[39] who tested the alloy in dilute nitric acid solutions.

Weldon[6] added 0.5% Mischmetal to a 63.5Cu-2.5Pb-Zn brass. The resulting alloy, however, contained only 0.04% rare earth elements, the bulk of the addition presumably being lost through oxidation during melting and pouring. *In the hot worked state,* e.g. hot stamped, the alloy behaved as a simple duplex brass and was very susceptible to dezincification; whereas *in the annealed state,* the alloy showed considerable dezincification resistance and was far superior to ordinary duplex brasses.

2.3.9 Gold and Silver

Kondrashin et. al.,[26] in studying the effect of elemental additions on the electrochemical behavior of copper and brasses, observed that gold was an effective inhibitor of anodic dissolution as well as cathodic precipitation of Cu^+ ions from the solution, and thus, it inhibits dezincification. Silver is likewise reported to inhibit dezincification.[40]

3. DISCUSSION

The inhibition of dezincification of alpha brasses by arsenic, antimony and phosphorus is well known and not in question. Unfortunately, antimony and phosphorus and, to a lesser extent, arsenic also have embrittling effects in copper base alloys, although sometimes these effects may be limited by strictly controlling the level of addition.

There is some evidence that each of these elements may lessen, but not prevent, dezincification in the duplex brasses, although Sullivan's results[10] suggest that arsenic under some conditions may accelerate the phenomenon.

Other elements which tend to inhibit dezincification in specific brasses include gold, silver, aluminum, tin, nickel, silicon and tungsten.

Elements that accelerate dezincification include iron (the worst so far encountered in the literature), manganese and cobalt

Under some conditions, the rare earth elements inhibit dezincification, whereas under other regimes, they

appear to accelerate the attack. Likewise, the position of lead and bismuth is not clear. Some investigators claim that lead is beneficial while others say it is detrimental. Bismuth is claimed throughout the literature to accelerate dezincification. but all of these claims appear to be based on one investigator's interpretation of his own results which, on close inspection may be incorrect. More recent but unpublished results tend to show that bismuth has no effect on dezincification.

A number of arsenical complex brasses have been developed which are dezincification resistant by virtue of the arsenic and an almost 100% alpha structure after heat treatment. These alloys have not been considered here. However, the literature is very clear about complex alloys; it is difficult to establish the effect of individual elements on general corrosion and dezincification rates for there may be synergistic effects for certain combinations of elements.

The literature is also very clear about the nature of dezincification; the phenomenon is very much dependent upon the nature of the surface film and the chemical reactions occurring in that film. Any attempt to develop new dezincification resistant alloys must address the question of whether the alloying additions are able to inhibit anodic dissolution as well as prevent cathodic precipitation of Cu^+ ions from solution. To this end, the test technique of Kondrashin et. al [26] is recommended.

There is a notable absence of information about oxygen either in solid solution or present as oxide particles in the alloy matrix. Weldon's Mischmetal addition to a brass melt[6] presumably acted as an oxygen getter in the same way as, for example, phosphorus, lithium, calcium and magnesium. Staley and Davies[37] observed similar losses when making additions of Mischmetal and other elements to simple binary brasses which could only be avoided by deoxidizing the melt with, for example, phosphorus before making the alloying addition. These observations indicate that some brasses may contain substantial amounts of oxygen and pose the question as to whether the beneficial effect of Mischmetal was due to its deoxidising effect. If so, the same question should be asked about some of the other "beneficial" elements.

In **Section 2.2** above, mention was made that arsenic and phosphorus additions to inhibit dezincification may affect grain size, and Nothing[12] recommended that the phosphorus level should be controlled to less than 0.015%. This limit was no doubt due to Miekk-Oja[41] who had found that "variations in phosphorus and iron content as small as 0.000 to 0.010% cause considerable differences in the final grain size in annealed 70-30 brass." Miekk-Oja showed that, in the absence of phosphorus, grain size depended on annealing temperature and iron content (up to 0.024%, the highest level examined) and the final grain size was uniform and slow to generate so making it possible to produce 70-30 brass in numerous tempers, each corresponding to a different grain size. At iron levels of 0.007% or more, small amounts of phosphorus (0.002-0.019%) *strongly inhibit* grain *growth* at temperatures up to 670 C. When the iron content is less than 0.005%, small amounts of phosphorus *accelerate grain growth* at high temperatures thus making control of final grain size very difficult. Miekk-

Oja suggested that these effects were due to the presence or absence of high concentrations (but not precipitates) of phosphorus and/or

iron at or near the grain boundaries. As corrosion tests were not performed on these 70-30 brasses, it is not known whether such small quantities of the contaminants would have caused premature dezincification.

Other investigators have examined the effect of small additions of grain refiners to specific types of brass, e.g. Fox[42] has demonstrated a beneficial effect of boron and chromium additions on the stress corrosion cracking resistance of yellow casting brasses, while Perryman and Goodwin[43] showed that small additions of zirconium or titanium tended to inhibit intercrystalline cracking in beta brasses. Likewise, Ahmed[44] observed the beneficial effect of chromium and silicon additions on the corrosion resistance of cast aluminum bronzes. It is not clear from these results whether the beneficial effect of the additions was due to grain refining, grain boundary strengthening or some other feature. It has been claimed that matrices composed of large grains are more susceptible to attack than those made up of uniformly fine grains;[12, 45, 46] whereas other investigators[47, 48] have shown, equally well, that grain size has no effect on the dezincification characteristics of duplex, 70-30 or aluminum brasses. However, whether or not grain size has an effect, there is no doubt that grain boundaries are preferentially attacked (although not necessarily dezincified) under some operating regimes.[15, 16, 34, 49] Thus alloying additions, which may affect grain boundaries in any way

whatsoever, might be expected to have some effect, beneficial or otherwise, on dezincification.

4. RECOMMENDATIONS

Further work is clearly required on bismuth-bearing brasses, not least because of the current interest in these materials. The work should include studies of those materials with and without additions of phosphorus, indium and tin and should extend over a wide range of copper contents, e.g., through the duplex to well within the all-alpha ranges.

There is a need to reexamine the silicon brasses to establish more precisely the effect of silicon, over a wide range of compositions (both silicon and copper), on their resistance to dezincification. The work should also include a study on ways and means of stabilizing the silicon-rich beta phase at elevated temperatures. Addition elements that might be usefully included in that program are aluminum, germanium, tin, and nickel.

There is circumstantial evidence that deoxidizing the brass before casting has a beneficial effect on dezincification, and there is scope for a project to examine this issue in depth. Deoxidizers that might be included in the program are phosphorus, lithium, calcium, magnesium and the rare earth elements. The effectiveness of these elements in inhibiting dezincification could also be assessed at the same time in fully deoxidized brass melts. The additions should be made at impurity as well as minor alloying levels.

A program should be undertaken on grain refiners and grain boundary strengtheners. The alloying additions and grain refiners that might usefully be investigated could include titanium, zirconium, chromium, molybdenum, tungsten and boron.

TABLE 1. GUILLET ZINC COEFFICIENTS[1]

Element	Si	Al	Sn	Mg	Pb	Fe	Mn	Ni
Zinc Equivalent	10	6	2	2	1	0.9	0.5	-1.3

TABLE 2. DEZINCIFICATION OF 70-30 BRASS[7]

Dezincification	Element[E]	Effectiveness
Decreased	Arsenic Nickel Aluminum Tungsten Lead	Best
Increase	Manganese Iron	Worst

[E] 0.5 wt % additions

TABLE 3. EFFECT OF ALLOY COMPOSITION ON CORROSION PRODUCT MASS GENERATED DURING IMMERSION IN A 5% NaCl SOLUTION[29]

Alloy Condition	Composition, wt %					Wt of Corrosion Product[w]
	Cu	Zn	Sn	Fe	Pb	
Slow cool	52.95	47.05	--	--	--	58.52
Quench from 750C	52.95	47.05	--	--	--	69.97
Slow cool	53.58	45.26	1.16	--	--	38.32
Slow cool	53.24	45.71	--	1.05	--	80.86
Not annealed	69.88	30.12	--	--	--	21.80
Annealed	69.88	30.12	--	--	--	20.75
Annealed	69.88	29.03	1.08	--	--	23.23
Annealed	70.15	28.85	--	--	1.00	19.67
Annealed	69.99	28.11	--	--	1.99	14.47

[w] mg. after 60 minutes immersion.

TABLE 4. EFFECT OF BISMUTH AND BETA-PHASE CONTENT ON THE DEZINCIFICATION OF 60-40 TYPE BRASSES[36]

Composition, %			Estimated Beta Content,[x] %		Elong., %	Dezinc.
Cu	Zn	Bi	A	B		
61.83	38.17	Nil	16	16	38.5	Best
60.00	39.00	1.00	28	34	31.5	2
60.26	39.66	0.08	31	31	25.5	3
60.00	39.75	0.25	32.5	34	11.0	Worst

[x] Beta phase content estimated from Zn Equivalent values assuming
  Case A: Bi = 0; and Case B: Bi = 1

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APPENDIX

Al. Mechanically Induced Dezincification

In 1934, Stager[45] demonstrated that cold working all-alpha (63-37) or duplex (60-40) brasses decreased their general resistance to corrosion and, under some conditions, to dezincification. Stager also suggested that grain size affected the corrosion characteristics of the alloys under certain operating regimes, large grains tending to corrode more rapidly than fine grains.

Many other workers have noted this effect on these and other brasses and some examples are as follows:

(i) Lombardi[11] found that the performance of 70-30 and 60-40 type brasses in the as-cold-worked state was much worse than in the fully-annealed condition even in the presence of inhibitors.

(ii) Namboodhiri et. al.[50] showed that 50% plastic deformation (by cold rolling) affected general corrosion and dezincification. Thus cold work increased the dezincification rate in both 70-30 and 63-37 brass (the general corrosion rate also increased in this latter alloy), whereas in 60-40 brass both corrosion and dezincification rates were *retarded.*

(iii) Pathasarathi and Polan[51] in experiments on three binary alpha brasses (Cu-15.3%Zn; 19.7%Zn; and 30.8% Zn, respectively) and a ternary nickel silver (Cu-28%Zn-12.2%Ni) observed that dealloying could be induced by deformation and each of these alloys was dezincified under stress. In this condition the crack initiation sites, e.g., grain or twin boundaries and dislocation pile-ups intersecting the surface, are likely to be local areas of high dissolution, and stress corrosion cracking was initiated after dezincification had commenced at these sites. They also noted that the level of dealloying (dezincification and possibly denickelification in the nickel silver alloy) increased with loading rate but appeared to be independent of the final load.

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