

THE DEZINCIFICATION OF BRASSES IN MARINE ENVIRONMENTS

A SURVEY OF EXISTING KNOWLEDGE

by

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Synopsis

A brief survey of existing knowledge on dezincification has been made with special reference to Admiralty experience. The mechanism of the process is discussed and the various factors influencing dezincification are described, including the structure and composition of the alloy and the environment.

Introduction

Dezincification is the term applied to the selective corrosion of zinc from copper zinc alloys, a form of deterioration which is easily recognisable by the copper coloured appearance of the corroded metal. It is often described as either "plug" or "layer" dezincification, but this division is largely arbitrary and merely indicates the appearance of the progress of attack and whether it is localised or general. Dezincification is not usually accompanied by any significant changes in the dimensions of the part undergoing attack, but the metal so attacked has no physical strength and has a structure of spongy copper. Consequently, components attacked in this way become weakened by reduction in effective cross section and eventually mechanical failure may occur.

Many metallurgical reports on service failures by dezincification in brass have been issued by the Central Metallurgical Laboratory and Admiralty Corrosion Committee. Many more instances have been examined but not fully reported, as the incidence of failure by dezincification has been very large and the various features concerning it have frequently been commented on in the past. Nevertheless, it seems possible that the factors affecting dezincification are not sufficiently widely recognised and the present brief survey has been written in the hope of giving wider publicity to the present knowledge of the subject.

MECHANISM OF DEZINCIFICATION

It is not proposed in the present paper to discuss in detail the various theories that have been put forward to explain the mechanism of dezincification. The main point to note is that they centre around two main issues, namely, whether the copper produced is 'residual' or whether it is 're-deposited'. The former presupposes the selective corrosion of the zinc from the alloy, leaving the copper behind; the latter assumes the solution of both copper and zinc at the same time, followed by re-deposition of the copper. There is considerable evidence in support of both theories. Thus, Milton and Larke,¹ Bassett,² Polushkin and Shuldener,³ and Bialosky,⁴ consider that the copper is 'residual' while Bengough and May,⁵ Hollomon and Wulff,⁶ Abrams,⁷ and Storey,⁸ are of the opinion that it is 're-deposited'.

The truth is probably more nearly approached by Stillwell and Turnipseed⁸ and by Finks¹⁰ who conclude that both types are possible and that the precise



FIG. 1.—H.T. BRASS MOTOR BOAT PROPELLER SHAFT

mechanism of the process depends on environmental circumstances, but that the most usual form involves re-deposition of copper.

Whichever theory is involved there is no doubt that dezincification is an electro-chemical process and as such it is controlled by the precise nature of the anodic and cathodic reactions. The rate of attack is largely governed by the cathodic reaction ; this may proceed either by the discharge and subsequent deposition of copper ions, or by ionization of oxygen. The fact that dezincification may proceed in the apparent absence of oxygen and that dimensional changes are not encountered, may be explained by assuming the former theory. Thus, it frequently occurs that, after the initial action has commenced and a surface layer of copper has formed, the alloy underneath dissolves as a whole and the copper is re-deposited on the underside of the layer formed. The zinc ions diffuse away through the spongy copper into the bulk of the electrolyte. Such a process can thus act inwards without any apparent physical changes on the outside.

The anodic reaction sometimes involves the solution of both copper and zinc together from the brass, as previously mentioned. To maintain progress of attack this anodic action must be counter-balanced by an equivalent cathodic one ; it is clear however, that cathodic deposition of copper can only account for a portion of the total anode current and the remainder must be maintained by oxygen ionisation.

The initiation of the anodic process is an important step in setting up dezincification and it has been attributed to many mechanisms. There seems little doubt however, that it is more liable to occur in the more zinc-rich phases, i.e. in the beta phase of an alpha-beta brass. It has also been shown as early as 1902¹ that galvanic action is possible between the zinc-rich beta phase which acts as an anode, and the cathodic alpha phase in an alpha-beta brass. Further details of the influence of structure are discussed later.

ENVIRONMENTAL FACTORS

One of the important environmental factors which influences dezincification is the oxygen content of the surrounding medium, a restricted supply favouring attack.⁵ Hence, dezincification is more prevalent in stagnant than in quickly moving waters. Mainly for this reason, high tensile brass securing bolts passing through wooden hulls suffer severely. Similarly, deposits of all kinds as well as scale formation assist dezincification by restricting oxygen supply.

As an example we may consider the effect of adding 2% of aluminium to a straight 70/30 alpha brass. The zinc equivalent of the aluminium content would be $2 \times 6 = 12$, making the total apparent zinc content $12 + 30 = 42$. Reduced to a percentage basis, the effective zinc content is therefore $\frac{100}{112} \times 42 = 38.5\%$ of zinc. It will therefore be seen that the effect of including 2% aluminium to 70/30 brass is to convert the structure from the all alpha to the alpha plus beta range.

The relevant Admiralty specifications for the more usual type of brasses used in Naval service, i.e. Admiralty brass, aluminium brass, Naval brass and high tensile brass, are shown below in Table II. The physical properties of these alloys are given in Table III.

TABLE II—CHEMICAL COMPOSITION OF COMMONLY USED BRASSES

Elements	Constituents (Per Cent.)			
	Admiralty Brass (alpha)	Aluminium Brass (alpha)	Naval Brass (alpha-beta)	High Tensile Brass (alpha-beta)
Copper	70	76—78	61	56—58
Tin	1.0	—	1.0	0.7—1.2
Aluminium	(Total impurities >0.3)	1.8—2.3	(Total impurities >0.6)	>0.3
Arsenic		0.01—0.05		—
Lead		>0.03		>0.05
Manganese		(Total impurities >0.3)		>0.3
Iron	—	impurities >0.3)		0.8—1.2
Silicon	—			>0.05
Zinc	Remainder	Remainder	Remainder	Remainder
E. in C. Specn. Clause	391	368	391	413

TABLE III—PHYSICAL PROPERTIES OF COMMONLY USED BRASSES

Physical Properties	Admiralty Brass (alpha)	Aluminium Brass (alpha)	Naval Brass (alpha-beta)	High Tensile Brass (alpha-beta)
Ultimate tensile strength (Tons/sq. in.) ...	15—20	20—25	25—30	32—38
Elongation % ...	60—70	70—80	20—30	10—15

From the corrosion point of view, the essential difference between alpha and alpha-beta brasses is that the former are single phase solutions of zinc in copper whereas the latter are two-phase alloys. Since all electro-chemical cells (and corrosion cells are no exception), are based upon a degree of heterogeneity, it is thermodynamically impossible to obtain electrical energy and in consequence corrosion, from a completely homogeneous system. Hence a dual phase alpha-beta alloy is more susceptible to corrosion than a single phase alpha brass,^{16, 17} by nature of the possible electrochemical interaction between the individual phases. The nature of attack is likely to be more uniform in an alpha-beta brass, whereas corrosion when it does occur in an alpha brass tends to be localised. This is evidenced by the fact that aluminium brass

(76/22/2), a single phase alpha brass, is subject only to "plug" or localised type of dezincification.

That alpha-beta brasses are very susceptible to dezincification has been known for some time. One of the first instances¹¹ recorded by the Admiralty of the corrosion of alpha-beta brass was about 1875, when some bolts in the propeller of a large wooden vessel were reported to be extensively dezincified. It is quoted that the bolts had deteriorated in tensile strength from 24 tons/sq. in. to 2 tons/sq. in. In 1902, as a result of the increasing number of instances of the corrosion of alpha-beta brasses of the Muntz metal (i.e. 60/40) type in Admiralty service, it was decided that 1% of tin should be added to retard attack. Further recommendations stipulated that special patent bronzes were to be used for propellers, whilst 70/30 alloys were specified for condenser tubes. An extensive (unpublished) bibliography prepared by the British Non-Ferrous Metals Research Association, quotes some 76 papers published between 1861 and 1942 on the subject of the corrosion and dezincification of 60/40 alpha-beta brasses. It is interesting to note that of the many cases of dezincification investigated at the Central Metallurgical Laboratory, with few exceptions these have all concerned alpha-beta brasses.

INFLUENCE OF MINOR CONSTITUENTS

As already shown, the addition of certain elements to brasses, to give improved physical properties, may cause modifications in their structure, which in turn affect dezincification susceptibility; but besides influencing structure the presence of certain elements either as deliberate additions or as impurities, may, *per se*, have a profound effect upon the tendency towards dezincification. The effect of individual elements is discussed below.

Aluminium

Aluminium increases strength and improves the corrosion resistance of alpha brasses²⁰ and excellent results have been obtained in sea water from the so called aluminium brass (76/22/2). Its effect on dezincification however, is probably negligible.

Antimony

Several workers^{23 24 25 27} have reported that additions of antimony have strong inhibitive properties, though there is some doubt as to the amount required and the tests have, in general, been confined to alpha brasses.

Arsenic

Arsenic has been shown^{5 6 10} to be a powerful dezincification inhibitor in 70/30 brasses, and is specifically added for this purpose; 0.02 — 0.04% is sufficient to resist attack by sea water. On the other hand, arsenic has only a small effect on the resistance of the two-phase brasses.^{18 19}

Bismuth

The presence of bismuth in 60/40 alpha-beta brass has been shown by Price and Bailey²⁶ to accelerate dezincification.

Iron

The presence of iron^{1 13 14} is stated to increase dezincification susceptibility.

Lead

The influence of lead, which is added to brasses to improve their machinability appears indefinite. It has been stated¹² on the one hand that leaded brasses show no improvement over unleaded ones so far as dezincification is concerned,



FIG. 2.—SECTION OF FLAME WELDED JOINT IN A COPPER FIRE MAIN

whilst other workers^{14 15} quote that the addition of lead is a definite improvement. It is of interest to note that amongst some of the recent dezincification failures of H.T. brass examined at the Central Metallurgical Laboratory, high lead content has been a noteworthy feature, although no serious inferences should be drawn from these relatively isolated results.

Manganese

This is one of the constituents which is stated²¹ to stimulate dezincification.

Nickel

Nickel appears to have little effect in either direction.

Phosphorus

Tests^{24 25} carried out, chiefly on Admiralty brass, show that small additions of phosphorus (0.03 — 0.05%) reduce dezincification susceptibility; its effectiveness in this respect is claimed to be as great as that of arsenic.

Tin

Tin is added to brasses chiefly as a corrosion inhibitor. The addition of 1% to straight 60/40 brasses to give Naval brass has long been practised and the presence of the tin considerably increases the resistance of the alloy to dezincification.¹⁸ Tin added to 70/30 brasses has a similar effect, as was shown by Bengough and May¹⁵ in 1924, but is not nearly as effective as arsenic in this type of alloy.

CONCLUSIONS

1. The dezincification of brasses in sea water is accelerated by the following :—
 - (a) Low oxygen supply (as for example in stagnant conditions or under scale and deposits).
 - (b) High temperature.
 - (c) Contact with a more cathodic metal.

2. Duplex alpha plus beta brasses are more prone to failure by dezincification than single phase alpha brasses, although the latter are not immune except possibly if the zinc content is less than 15%.

3. Various alloying elements of brass affect dezincification in the following ways :—

- (a) Arsenic and tin tend to inhibit dezincification (and similar claims have been made for antimony and phosphorus).
- (b) Iron, manganese and bismuth are thought to be harmful.
- (c) Nickel and aluminium are probably without effect.
- (d) The action of lead is uncertain.

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