DEZINCIFICATION OF BRASS AND ITS CONTROL-AN OVERVIEW

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ABSTRACT:

The increasing utilization of sea water as a medium for transportation, communication, energy generation, oil and mineral exploitation and as an industrial fluid has direct impact on problems associated with the maintenance of marine structures and machinery. Keeping this in mind, numerous investigations on the corrosion behaviour of various metals and their alloys in natural sea water, fresh water, and acid environments have been carried out. The present review deals with the physical and mechanical properties of brass, binary phase diagram of brass, potential pH diagram of brass, types of dezincification and mechanism of dezincification. In recent years, there has been an enormous growth of industries like chemical, electrochemical, etc., near coastal areas. Therefore, this review also looks at the effect of various pollutants on the dezincification process. Investigations on the control of dezincification of brass in various environments like acid, neutral and in the presence of pollutants are also discussed in detail. Finally, the effect of the addition of alloying elements on the reduction of the dezincification process are explained in detail.

1.0 INTRODUCTION

The copper-zinc alloys ranging in zinc content from 3% to 39%, commonly called brasses, are the most popular and versatile copper alloys, based on volume of use. They have reasonably high electrical and thermal conductivities with good strengths and they offer excellent forming and drawing characteristics. Brasses have good corrosion resistance in most natural environments such as air, water, soil, etc. /1/.

1.1 Physical and mechanical properties

The mechanical properties of brasses depend upon the chemical composition and the previous history of the alloy. The elongation and tensile strength of brasses increase with the increase in the zinc content. Fig. 1 shows the general trend of the changes. It has been noted that the elongation value rises rapidly in the α -range, showing a maximum at 30% zinc (approx). When the β -phase makes its appearance the ductility decreases. The tensile strength in the β -phase decreases with the increase in zinc content and with the appearance of the γ -phase the alloy becomes very brittle. In general therefore, the α -phase of a brass may be described as ductile, the β -phase as tough and the γ -phase as a brittle phase. Generally commercial brasses are restricted up to 40% zinc, because on further increase in zinc content β -phase forms and makes the alloy very brittle.

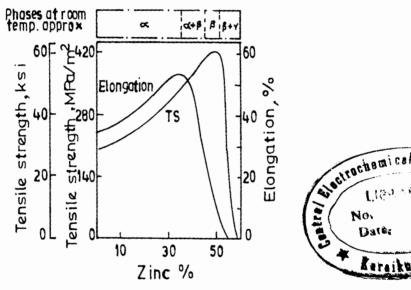


Fig. 1: Physical and mechanical properties of brass

1.2. Binary phase diagram

The atomic size of copper and zinc is 1.27A° and 1.37 A° with face centered cubic (FCC) structure and hexagonal close packed (HCP) structure respectively. They combine to form series of solid solutions and intermetallic compounds. The Cu-rich side of the binary phase diagram is shown in Fig. 2.

Three important phases occurring on the copper rich side of the phase diagram are α , β and γ .

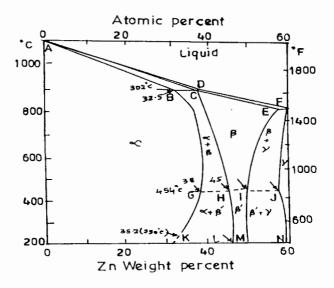


Fig. 2: Binary phase diagram of brass

The composition of alloys between A and B solidifies as the α -solid solution having maximum solubility of 39 (wt) % Zn at 454 °C. It has face centered cubic (FCC) structure having a short range order. In alloys of composition between B and C, the first crystal forms the α solid solution but at 902°C, an intermetallic β -phase is precipitated. It has a body centered cubic (BCC) structure and it extends from 46.6 to 50.6 (wt) % at room temperature. The β -phase itself undergoes allotropic transformation on cooling. On further increase in the zinc content another intermediate phase known as γ -phase is formed which has a complex body centered cubic (BCC) type of structure. It extends from 59.1 to 67.2 (wt) % Zn and this phase is very brittle. In brasses of intermediate composition either α or a mixture α + β or α + β + γ phases are present in the alloy. The properties of the alloy can be altered by changing the phase distribution.

1.3. Potential -pH diagram

The superposition of these experimental diagrams over the theoretical E-pH (Pourbaix diagrams) for the constituent metals of the alloy provides a

basis for predicting the tendency for dealloying as a function of potential and pH. For example, superimposed diagram for an α -brass in 0.1M sodium chloride is shown in Fig. 3. For initially copper-free chloride solutions, ranges of potential are indicated in which selective leaching of zinc predominates. The lightly shaded area indicates the domain in which selective removal of zinc is expected in solutions free of copper ions. The intermediate shaded area indicates the domain in which both copper and zinc dissolve. The dark shaded area indicates the region in which copper is expected to deposit /2/.

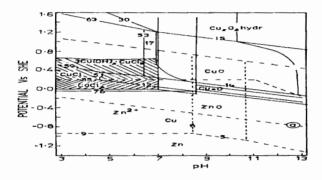


Fig. 3: Potential pH diagram of brass

1.4. Application

Brasses find use in many applications. They are mostly used for the engineering purposes where electrical and thermal conductivity, corrosion resistance, high ductility, pleasing colour, ease of working and the retention of tensile properties at extremely low temperatures or a combination of such attributes is required. Brasses are extensively utilised for the manufacture of valves, screens, tanks, heat exchangers, engine parts, propellers, etc., used in petroleum refineries, air-conditioning, refrigeration, chemical plants and marine engineering. Owing to their shining golden colour and ease of fabrication, brasses have also been used for making utensils, statues, artificial jewellery, grilles and other decorative items. By increasing the percentage of zinc in the alloy and giving suitable thermo-mechanical treatment, a large variety of Cu-Zn alloys having distinct properties and uses has been developed. Table-1 gives some of the physical and mechanical properties and applications of some important Cu-Zn alloys. /3/

Table 1 Physical and mechanical properties and application of Cu- Zn alloys

tion Typical Applications		(q)	·		Coins, metals,	jewellery, tokens, fuse	caps, bullet jackets.	Etching bronze, grill	work, screen cloth,	marine hardware,	screws, rivets.	Weather stripping,	sockets fire	extinguishers.	condenser, plumbing	pipe.	Battery caps, musical	instruments, clock	dials, pump lines,	flexible hose.
Elongation	5mm	(2in % (b))	, 		45-4			50-3				55-3					53-3			
Properties		Yield	strength	(Mpa)	69-400			69-427				69-434					83-448			
Mechanical Properties		Tensile	Strength	(Mpa)	234-441			255-496	i			269-724					290-862			
Hard-	ness	(agh)	min)		38.73			42 78	<u>.</u>			56-71		-			\$7.75	:		
Annealing	Temn (°C)	(a) duna			425-800			425-800	200-574			175.775	C#1-C#				426.700	201-574		
Density		0000	2 -02 IE		98.8	0.00		000	0.00			37.0	٥./٠				6,70	9.0		
		Mn				l			<u> </u>				!					!		
		Pb	_	_		1		_	!			1	!		· · · · · ·		\perp	<u> </u>		
		Sn				!			!				1					i		
Composition %		Zn	-			<u>^</u>			2				15					20		
Omno	dino	C	3			95			8				82					08 		
A 11 ca.	Alloy					Gilding metal			Commercial	bronze			Red brass					Low brass		

Cartridge brass	70	30	1	1	1	8.53	425-750	55-93	303-896	76-448	66-3	Radiator cores and
												tanks, flash light shells,
												plumbing accessories,
												pins.
Yellow brass	65	35	1	1		8.47	425-700	55-91	317-883	97-427	65-3	Same as cartridge
												except hot used for
												ammunition.
Muntz metal	09	40	ł	-	1	8.39	425-600	55-75	372-570	145-379	21-10	Architectural panel
												sheets, large nuts and
												bolts, condenser plates,
												heat exchanger.
leaded	65	34.5	ţ	0.5		8.50	425-650	70-85	317-570	97-414	8-59	Bolts, hinger, mach
												backs, plumbing.
Medium leaded	65	34	}	0.1	ļ	8.47	425-640	20-87	324-607	103-414	2-09	Bolts, gears, nuts,
												rivets, dials,
												engravings, instrument
												plates.
cutting	61.5	35.5	ŀ	3.0	i	8.50	425-600	62-80	338-469	124-310	53-18	Automatic high speed,
					1							screw machine parts.
Admiralty	71	28	_	ł	!	8.53	425-600	06-98	331-379	124-152	65-60	Condenser, evaporator,
												heat exchanger,
												condenser tubing.
Naval brass	09	39.25	0.75			8.41	425-600	26-75	379-607	172-455	50-17	Aircraft, nuts, propeller
												shafts, welding rod,
												condenser plates,
-												marine hardware.

Table 1 continued

Cast red brass	1 brass	∞	5	5	2	8.80	8.80	1	09	25.5	117	30	Values, fl	langs, p	ipe
		S											fittings, plumbing	plumbi	ng
													goods, pump castings.	p castings	.,
Cast	yellow	58	40	_	_	ı	8.44 425-600	425-600	55	379	207	15	General puroose, high	irose, hi	gh
brass	brass												casting allcy having	llcy havi	ng
													moderate strength	trength	

2.0 DEZINCIFICATION OF BRASS

Dezincification is the most common form of dealloying. Copper-zinc alloys containing more than 15% zinc are susceptible to a dealloying process, called dezincification. Selective removal of zinc from the brass leaves behind the spongy mass of copper with poor mechanical strength.

2.1 Types of dezincification

a) Uniform layer type

In the uniform layer type, the active component of the alloy is leached out over a broad area of the surface. This is similar to general corrosion except that there is preferential dissolution of zinc from the surface leaving copper in the lattice. The surface appears to be just covered with a tarnish layer. The bulk of the alloy does not have enough strength.

b) Plug-type

This type of attack generally leads to more rapid failure than in the uniform layer type. This usually proceeds with greater speed and it is localised in nature. The plug type of attack penetrates deep into the metal, forming porous plugs of copper. The entire surface is not affected.

A study of kinetics and mechanism of brass dezincification process is quite important for corrosion research as it has several practical applications. Brass dissolution process mainly depends upon the nature of the composition /1,4/ and the corrosive medium such as acidic, alkaline and neutral solutions.

2.2 Mechanism of dezincification of brass

The kinetics and mechanism of dezincification of brass have been widely studied /5-10/.

a) Preferential dissolution of zinc

Bassett /11/, Polushkin et al. /12/ and Langenegger et al. /13/ have reported that dezincification occurs due to selective removal or preferential dissolution of zinc taking place at the brass surface in contact with a corrosive medium. Accelerated dezincification under both anodic stimulation and freely corroding conditions revealed that the separation of zinc must be

compensated by the diffusion of zinc atoms with the alloy lattice. It was believed that zinc is preferentially attacked at the active dezincification sites as this front moves progressively inwards. The exclusive extraction of zinc from the brass matrix is only possible theoretically. In practice, some copper unavoidably gets dissolved together with zinc. The dezincified phase, therefore, only represents the skeleton structure of the original brass matrix and is porous enough to allow the non-restricted outward diffusion of zinc ions.

b) Simultaneous dissolution of copper and zinc

A work by Evans /14/ indicated that zinc atoms cannot easily leave the alloy unless copper atoms accompany them. He explained that a slow dezincification of brass placed in NaCl solution takes place especially in the β -phase of α - β brass, or at the grain boundaries of insufficiently annealed α -brass, where relatively zinc rich areas exist. At such places zinc passes into solution leaving residual copper. These residual copper sites act as cathodes in the galvanic cell which is set up in the alloy. At the cathode, copper is deposited in amount equivalent to the copper entering the solution at the anode. Sugawara *et al.* /15/ studied the dezincification of brass by means of a potentiostat and an electron microscope analyser and reported that the mechanism of dezincification was mainly due to the redeposition of copper. The presence of both copper and zinc were identified during the electrodeposition of copper as reported by Horton /16/.

Popumin et al. /17/ used a combination of electrochemical and radiotracer techniques to study the dezincification of brass in HCl solution under the conditions of continuous addition of copper ions by means of anodic dissolution of auxiliary copper electrode. A relationship was established between the electrochemical characteristics of the alloy and the process of its dezincification as affected by the redeposition of copper from the solution.

Warraky /18/ investigated the ratio of Cu and Zn by solution analysis under immersion. He suggested that a zinc content higher than that of the bulk alloy indicate that simultaneous dissolution of both Cu and Zn was followed by the redeposition of copper in the dezincification process.

c) Combination of the above two mechanism

Langenegger and Callaghan /19/ used the potential shift technique to determine the rate of dezincification of $\alpha+\beta$ brass in the chloride medium and reported that zinc preferentially got dissolved in the initial stages of

dezincification and redeposition of copper appeared to be a second step. Heidersbach and Verink /8/ have studied the mechanism of dezincification of single phase alpha and alpha + beta brasses using x-ray diffraction, electron microscope, metallographic, atomic absorption and electrochemical techniques, where the specimens were subjected to accelerated corrosion testing in non-oxidising 1N NaCl and 5N HCl solutions. They reported that both the above mechanisms could occur on the same specimen.

Natarajan *et al.* /20/ focused on dezincification of cartridge brass and reported that a selective removal mechanism might operate over a short distance from the electrolyte boundary which appears to shift progressively into the interior of the sample through the porous layer of copper and that the mechanism of dezincification was due to the redeposition of copper. Itoh and Hikage /21/ observed the dezincification rate of α and $\alpha+\beta$ brasses by thermogravimetry over the temperature range of 500-800°C in vacuum and discussed the results in the light of the structural changes occurring in the diffusion layer, and explained that dezincification reaction proceeded through three stages. In stage I, the weight loss was shown to obey the parabolic rate law as expected from an ordinary diffusion mechanism. In stage II, the dezincification rate was accelerated and in stage III, the weight loss was found to be nearly proportional to the square root of time. These three stages were characterized by the structural changes occurring during the dezincification process.

Pchelnikov *et al.* /22/ studied the kinetics and the mechanism of dezincification in alpha brass in NaCl by radiotracer and electrochemical techniques, and proposed a two stage mechanism of dezincification. After the short primary preferential dissolution which is controlled by the volume diffusion of zinc, and subsequent simultaneous dissolution of the alloy, a steady state secondary preferential dissolution due to the redeposition of copper started when a certain concentration of copper in the solution had been reached. At this stage, the process was limited by the non-steady state volume of zinc in the alloy. The increase in the corrosion rate of α - brass with time was due to the slow oxygen reduction on the alloy surface process, which became oxidized to cupric oxide by oxygen with these ions being more effective depolarisers than oxygen.

Pushpa Gupta *et al.* /23/ attempted to study the mechanism of dezincification in 70/30 brass in dilute H₂SO₄ by solution analysis as well as electrochemical techniques, and observed that in the initial stage, the rate of dissolution of zinc was greater than that of copper. They suggested that in the

apparently related to the growth of the chloride layers (paratacamite $Cu_2Cl(OH)_3/Cu_2O$) for Cu and simonkolleite $(ZnO/Zn_5(OH)_8\ Cl_2H_2O)$ and sodium zinc chlorohydroxy sulphate $(NaZn_4Cl(OH)_6SO_4.6H_2O)$ for zinc.

Chung et al. //34/ studied the initial stages of zinc atmospheric corrosion in the presence of chloride using ex situ electrochemical impedance spectroscopy (EIS) in a non-aqueous electrolyte (methanol), FTIR, XRD techniques and reported that the zinc hydroxy carbonate and zinc oxide were found responsible for the protectiveness of this surface layer against contaminated chlorides i.e., zincite, (ZnO), hydrozincite, [Zn₅(CO₃)₂(OH)₆] and showed it to be protective against a chloride environment. These corrosion products react with aggressive chloride ions from contaminated soluble NaCl to form insoluble simmkolleite providing protectiveness and reducing aggressive soluble chlorides.

Herman and Castillo /35/ studied short term atmospheric corrosion of various copper based alloys after two and four year exposure to natural environments (at New Haven, Connecticut, Brooklyn, New York and Daytona Beach, Florida) and reported significant changes in the % elongation of alloys Cu 70-30 Zn and Cu 56-25 Zn. Metallographic investigation revealed plug type dezincification of 70/30 brass at all locations and pitting coupled with plug type dezincification of Cu 56-25 Zn at the industrial and industrial marine sites respectively. They reported the lack of localized corrosion of this alloy in the marine environment strongly suggesting strongly that nickel, as an alloying element, was beneficial with reference to corrosion resistance of a Cu-Zn system in marine atmospheres.

3.2 Dezincification of brass in acidic environments

Saber *et al.* /36/ investigated the effect of various pretreatment procedures on the surface composition of 70/30 α -brass using X-ray diffraction (XRD) and Auger electron spectroscopy (AES) and reported that in general, wet cleaning caused dezincification, cleaning with acids (HNO₃, HCl, H₂SO₄) or acid brightener and electrochemical cleaning in H₃PO₄ caused surface dezincification.

Zembura *et al.* /37/ studied Cu-15Zn α -brass by rotating disc technique in argon, air or oxygen saturated 2M H_2SO_4 , in the temperature range 10-65°C. The dissolution rates of copper and zinc from Cu-15 Zn alloy were similar to that of copper corroding in similar conditions indicating that dezincification of α -brass did not occur.

Vora et al. /38/ reported that 63/37 brass in souring substances used as food additives containing organic acids was responsible for the corrosion of brass and observed that a film was formed over the surface of the brass specimen.

The dezincification mechanism of α -brass 70/30 in acidic solutions under various stress conditions was investigated by Badawy *et al.* /39/. The preferential dissolution rate of zinc was found to destroy the Cu(I) passive film and higher rates of corrosion were observed in the presence of stress.

Torchio *et al.* //40/ studied Al-brass in Cl⁻ ions in acidic sulphate solution; a Cl⁻ ion stimulating effect was observed either in environmental conditions in which competition between the precipitate of Cu₂O and CuCl could occur or in conditions in which Cu₂O was thermodynamically stable but the presence of a critical amount of Cl⁻ could induce an alteration of its defect structure. An inhibiting effect was observed at high Cl⁻ ion concentrations where CuCl was the prevailing stable phase.

Jennane *et al.* /41/ suggested a divacancy mechanism of brass dezincification by self diffusion parameters in β -brass (Zn65 in Cu-Zn alloy).

3.3 Dezincification of brass in neutral environments

Morales et al. /42/ observed passivation and localized corrosion of $\alpha,\,\beta$ and $\alpha+\beta$ brass in borate - boric acid buffer solution (pH9) in 0.5M NaCl solution by electrochemical techniques and x-ray diffraction studies. They observed the potential values to be slightly more negative than the breakdown potential of copper and markedly positive with respect to the presence of a complex ZnO. xH₂O / Cu₂O - CuO layer which was less positive towards Cl ions attack than the Cu₂O-CuO layer formed on Cu. The pitting resistance increased from $\alpha+\beta$ and β -brasses to α - brass, the latter approaching the Cu behaviour. The increase in resistance of brass to pitting corrosion with respect to zinc is due to the formation of a Cu-rich layer at the alloy/oxide layer interface which was immune to corrosion at negative potential where the pitting corrosion of zinc took place in N₂O containing solutions.

Kharafi and Badawy investigated /43/ the corrosion and passivation behaviour of brass alloys α , $\alpha + \beta$, (Cu 24 Zn, Cu 30 Zn, Cu 39 Zn) in aqueous solutions at different pH (2.0, 7.0, 12.0) by polarisation, EIS, XRD and SEM techniques and reported that it was dependent upon the stability of the passive Cu(I) compound. The presence of O_2 or oxidizers in acidic

solutions beside the selective leaching of the alloy enhanced the disproportionation of the Cu(II) compound, leading to passive film breakdown and appearance of copper on the alloy surface. Copper patches initiated active galvanic couples and flawed regions, which increased the rate of corrosion of the alloy.

Panagopoulos *et al.* /44/ studied the hydrogen induced cracking and blistering in α - brass (70/30) and reported that the hydrogen charging of α - brass could result in the formation of intergranular and transgranular cracks and hydrogen blisters. The current density increased from 15 to 25 mAcm⁻² resulting in more severe cracks and from 35 to 85 mAcm⁻², increasing the number of blisters.

Pitting attacks on admiralty brass in brackish water by electrochemical and x-ray diffraction measurements were reported by Zia et al. /45/.

Arvia et al. /46/ studied the α - and β -brass in aqueous borate/boric acid buffer (pH 9) in NaCl in the temperature range 5°- 45°C. They observed pitting corrosion when the breakdown potential (E_b) was exceeded. At constant temperature, the value of E_b shifted negatively as either NaCl or the zinc content in the alloy was increased. For β -brass the value of E_b decreased slightly with temperature. For α -brass, from 5°-25°C, the value of E_b was close to that reported for copper, whereas for $T > 25^{\circ}C$ it approached those values measured for β -brass. The dealloying measurements indicate that zinc surface enrichment of α -brass was responsible for the decrease in pitting corrosion resistance at temperatures greater than 45°C.

Newman and Shahrabi /47/ have indicated how dezincification of α-brass occurs in crevices. Oxygen reduction on relatively bare parts of the brass surface supported diffusion controlled copper dissolution (as CuCl₂) under deposits or corrosion products that acted as diffusion barriers. The solution on the corroding surface was equilibrated with copper in the alloy, and dezincification started. Diffusion controlled partial anodic current density of copper was much less than that achievable by zinc. The latter varied with the chloride concentration, temperature, alloy zinc concentration, and cold work. Especially, the presence of alloyed arsenic inhibited zinc dissolution, probably by reducing the surface self diffusion co-efficient of copper. The dezincification only occurred when there was CuCl₂ in the solution, and this might be interpreted as evidence for a Cu⁺ exchange or dissolution redeposition mechanism, but no evidence exists for this occurring in a bulk sense.

Grezegorzewicz and Kuznicka /48/ carried out failure analysis studies on brass tubes of a heat exchanger and indicated that the water flow rate through the heat exchanger was reportedly close to the turbulent flow rate.

Aaltonen and co-workers /49/ studied the industrial brass, Cu20Zn, Cu37Zn and CoZnAlFe alloy subjected to electrochemical oxidation in tap water resulting in the selective dissolution of zinc by low temperature internal friction. For dezincified brass in the temperature range of 230 - 300K a complex two component peak was observed. This peak was considered to be caused by dissolution of excessive vacancy interaction and is of a non relaxation nature. This conclusion was based on the position annihilation data obtained with dezincified brasses.

Badawy and Kharafi /50/ investigated the α -brass (70%Cu) and leaded brass (58%Cu) in Kuwaiti tap water by electrochemical polarisation, EIS and morphology techniques. The effect of anions such as phosphate, chloride etc. and oxygen was also investigated. The rate of corrosion was found to increase in oxygen rich water. This was attributed to enhanced disproportionation reactions which destroyed the surface passivity of the alloy.

Redd and Breslin /51/ studied Cu 37 Zn brass alloy in borate buffer (at pH 9.2 and 13.0) in 0.025 M NaCl solutions by potentio-dynamic polarisation, cyclic voltametry and complex impedance spectroscopy under the influence of UV illumination. A significant decrease in the breakdown potential on increase in the passive current density and lower charge transfer resistance values was observed on illumination of brass in pH 9.2 solutions. A much lower photo activation effect was observed at pH 13 solution. These findings may be explained in terms of the photo decomposition of ZnO, which existed in the complex passive layer formed on CuZn alloy.

Sahoo /52/ studied the corrosion of yellow brass SeBiLOYIII alloy in near aqueous environments by spectroscopy. The spectrum of dezincification tests ranging from very aggressive to natural simultation showed that grain refined SeBiLoyIII alloy and grain refined C85800 containing $\sim 36\%$ zinc were prone to dezincification particularly at any center-line porosity in permanent mold castings.

Studies on 70/30 α -brass were attempted by Badawy *et al.* /53/ in naturally aerated, oxygen saturated and oxygen free acidic, neutral and basic solutions at a constant pH using polarisation and surface analysis techniques. The electrochemical behaviour of α -brass was dependent on the pH of the ambient electrolyte. The alloy passivity was due to the formation of a Cu(I)

compound (mainly Cu_2O) which was relatively stable in neutral and basic solutions. The corrosion rate of the alloy increased in oxygen-rich acidic solutions due to the oxidation of the Cu(I) passive film to the soluble Cu(II). The presence of oxidizers such as dichromate $(Cr_2O_7^{2^2})$ ions enhanced the oxidation reactions in the acidic solutions, leading to a high corrosion rate. The preferential dissolution of zinc was found to destroy the Cu(I) passive film, especially in the acidic solutions leading to higher rates of corrosion.

3.4 Dezincification of brass by pollutants

Lee and Shih /54/ were able to report on the effect of halide ions in aqueous environments using 67/33 α -brass by electrochemical, slow strain rate tension (SSRT) and scanning electron microscope techniques. Electropolarisation analysis confirmed that a passive Cu₂O film could be formed on α -brass in 0.1M NaF solutions. This passive film could however break down. Film rupture and slip dealloying dissolution may be involved in intergranular stress corrosion cracking (IG SCC) of 67/33 α -brass in F solution. In 0.1M Cl⁻, Br⁻ and l⁻ solutions no SCC susceptibility was observed which could be due to the formation of soluble cuprous complexes controlling the dealloying process through precipitation of metal ion salts on the surface of α -brass.

Pore formation during dezincification at different temperatures has been reported by Kuperman and Troiani /55/.

Rylkina and Kuznetsov /56/ studied copper, zinc and brass (L63:64, 36 at % Cu) in neutral media (borate buffers with pH 7.4) with activators of inorganic acid salts of sodium Nax ($x^* = F^*$, Cl⁻, Br⁻l⁻, SO₄²⁻, NO₂⁻, NO₃⁻ and ClO₄⁻). Brass L63 was less stable to pit formation as compared with copper in the borate buffer containing Cl⁻ anions. The stability was higher in the presence of l⁻ ions. The pit formation potential was independent of the nature of anion - activators.

Shams Eldin *et al.* /57/ reported galvanic corrosion of Cu, Zn and brass in 0.1M KCl, KNO₃ and Na₂SO₄ solution by galvanic corrosion test and potential scanning.

Torchio /58/ observed stress corrosion cracking of admiralty brass condenser tube in sulphate solution. The cracking was intergranular in strongly acidic solutions and transgranular in a wide range of moderately acidic solutions.

According to Newman and Burstein /59/, the Cl⁻ anions which complex directly might well cause blunting of incipient cracks in pure metals but could cause SCC in alloys owing to additional features such as de-alloying coarse slip and grain boundary chemical heterogenity in 0.1M KCl, KNO₃ and Na₂SO₄ solution as shown by galvanic corrosion test and potential scanning. It was concluded that both techniques took place between pairs involving copper and any of the three brass alloys, or between pairs of the Cu-Zn alloys.

Findings of Yun Zou *et al.* /60/ showed corrosion of α -brass in Na₂SO₄, NaCl, H₂SO₄ and CuCl₂ solutions by chromo-amperometry and positron annihilation methods and indicated that the transient currents were caused by the sole dissolution of zinc from α -brass at the constant potential much more negative than the potential of onset of dissolution of copper in brass in the solution. They reported that the current time relations followed the Cottrell Law in the initial period of dissolution of alloy, and there was no effect of stirring solution on the transient current. Thus the selective dissolution of zinc from brass was controlled by a solid state diffusion process. The positron life time spectra have been measured for α , β , ν , and ϵ - brass specimens before and after dezincifying in 1% CuCl₂ solution. The variation of the mean positron life time (Δ m) and 2/b value of corroded specimens suggested that the solid state diffusion of zinc atoms occurs via (di) vacancies created on the alloy surface during corrosion of brass.

Malki and Legris /61/ studied the corrosion of yellow brass (Cu - 37 Zn) in sodium nitrite by slow strain rate loading tests. There existed a critical stress below which no embrittlement occurred. Such a threshold need not be necessarily associated to the cracking of the oxide film that could instead, be related to the nature of the chemical bonding in the oxide film and at both metal/fim/electrolyte interfaces.

Giordano *et al.* /62/ studied α -brass (Cu 35 Zn, Cu 30 Zn, Cu 20 Zn, Cu 10 Zn) in cupric nitrate by polarisation, SCC and SEM techniques. The effect of Cu²⁺ concentration on the stress corrosion crack propagation rate (CPR) was measured. A linear relationship between the logarithm of the CPR and the logarithm of the Cu²⁺ concentration was found in all the alloys studied. The slope of this relationship was very close to that reported for the cuprous ion exchange current density and the cupric ion concentration. $\delta \log i_o$ (Cu⁺ \rightarrow Cu) / $\delta \log [Cu^{2+}]$. All the cracks were transgranular in nature and the crack propagation mechanism could be explained through the surface mobility mechanism. CPR was accelerated by increasing the Cu²⁺ ion content

in the solution. The relationship between the CPR and the Cu²⁺ ion concentration followed the predictions of the surface mobility SCC mechanism.

Dehri and Erbil /63/ went on to study the corrosion of 63/37 brass in neutral aqueous solution containing SO₄²⁻, NH₄⁺ and Cl⁻ ions by semi ellipse model in EIS and reported that the ammonia ion was corrosive to brass and the charge transfer resistance R_t values decreased with an increase in ammonia concentration in the electrolyte. The formation of [Zn (NH₃)₄]²⁺ complex ion was easier than the formation of Zn (OH)₂ in a medium containing OH⁻ and NH₃ since NH₃ was a stronger ligand than OH⁻ and also Zn(OH)₂ dissolved more readily in aqueous solutions that contained NH₃. They also suggested that when the (NH₄)₂ SO₄ concentration increased in the solution; this equilibrium was displaced towards the right hand side and the NH₃ concentration increased. The chloride ions were not effective in the corrosion of brass. This was due to the rate of corrosion being controlled by diffusion of Cl⁻ to the surface of the electrode through a porous layer of CuCl film.

Tromans /64/ studied the corrosion of α -brass in NH₃ solution using polarisation studies. Potential - pH diagrams for the Cu-NH₃-H₂O and Zn-NH₃ - H₂O systems have been constructed for 15M NH₃ solutions commonly used for studying SCC of α -brass. The anodic polarisation tests indicated that formation of the zinc tetramine complex in ammonia might involve transient zincate ions.

Lu and his co-workers /65/ observed that corrosion induced tensile stress during the dezincification of the alloy Cu 38 Zn brass in 1 mol/L $NH_4OH + 5$ g/L $CuCl_2$ solution and further noted that an additional tensile stress would be generated at the metal / dezincification layer interface during original corrosion of brass. The steady value of the additive tensile stress was 24.4 MPa (about 1/5 of the yeild strength).

Natesan *et al.* /66/ reported that the monel exhibited superior corrosion resistance due to the formation of a compact film and the other alloys such as admiralty brass, Al-brass, 90/10 Cu-Ni and 70/30 Cu-Ni alloy initially corroded and subsequently formed corrosion product film to protect the metals in synthetic sea water.

Xie et al. /67/ studied copper alloys (HSn 70-1 + As and B 30) in H_2O containing S^{2-} ions by electrochemical and surface analysis and observed dezincification.

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Kermani and Scully /68/ investigated the stress corrosion of α -brass in ammonical solution containing Cl and Br ions by constant strain rate technique. The increasing Cl ion or Br ion caused a decrease in crack velocity due to black tarnish film.

3.5 Dezincification in the presence of microorganisms

The microbiologically influenced corrosion (MIC) of copper and its alloys is not very well understood. This is probably due to the general belief that copper is toxic to microorganisms, which is not, however, the case for all microorganisms. As an example, bacteria of the genus Thiobacillus may tolerate copper concentrations up to 2%. Early histories of MIC on copper and its alloys have been reported from piping systems and heat exchangers where heat transfer problems have been observed with growing biofilms, wherein the corrosion has been found to increase after the death of the microorganisms within the biofilm. This is believed to be due to the production of ammonia and carbon dioxide upon the death of cells that may result in pitting corrosion and/or stress corrosion cracking (SCC) for copper and its alloys. The production of hydrogen sulfide by SRB is also believed to be a cause for pitting corrosion and SCC on copper and copper alloys. In this case, the corrosion is due the formation of a thick non adherent layer of chalwite (Cu₂S)or covellite (CuS). Pitting corrosion may occur where the coppersulfide film has been removed, with the cathodic reaction taking place on the intact copper sulfide film /69/.

Microbiologically induced pitting corrosion has also been observed in copper pipes used for potable water system /70/. This has been observed in both warm and cold water systems. Generally a biofilm is observed under a black deposit of copper (II) oxide. However, it has been suggested that the role of biofilm could be predominantly conversion of copper (I) oxide to copper (II) oxide /71/.

Subramanian *et al.* /72/ studied 70/30 brass and copper in sea water by culture media using SEM, optical metallurgical microscope and XPS measurements and observed that biofilmed coupons of brass experienced less corrosion in culture media than that of commercial copper. In AP1 based mixed culture media the bio filmed coupons of Cu and brass experienced corrosion due to the hostile H_2S - O_2 environment created by aerobes and SRB. The nature of the sulfide film and susceptibility to pitting corrosion were confirmed by surface analysis.

4.0 CONTROL OF DEZINCIFICATION OF BRASS

In order to minimize the corrosion and dezincification, various preventive measures have been developed. Most of them are based on the isolation of the metal from harmful environments. This is achieved either by the use of a foreign coating or by the formation of corrosion resistant passive film on the surface of the metal. Alternatively, the corrosion environment may be modified either by removal of harmful constituents or by addition of a substance which may be termed "inhibitor" causing a decrease in the corrosion rate.

4.1 Effect of inhibitors and behaviour of brass in various environments

a) Acid Media

Gupta et al. /73/ studied pyridine derivatives such as 2-picoline, 3-picoline, 4-picoline and pyridine as inhibitors for 70/30 brass in dilute sulphuric acid by potentiostatic solution analysis and weight loss techniques. All these were found to be of mixed type except 3-picoline which was anodic. All prevented both Cu and Zn dissolution, but the effect of inhibitors decreased after 48 hrs. Aniline derivatives /74/ such as aniline, ortho, para nitroaniline, ortho, para chloroaniline, dibenzylamine, N-butylamine and triethylamine were used as inhibitors for 70/30 brass in 1% H₂SO₄ and reported that all exhibited poor efficiency. Among these, aniline, p-nitroaniline, triethylamine and N-butylamine were found to be effective for decreasing the dezincification rate. Aniline was a good inhibitor for zinc while the derivatives of aniline (except p-nitroaniline) containing electron withdrawing groups i.e., Cl and NO₂ were more effective for copper than zinc and the compounds containing electron denoting groups were more effective for zinc than for copper.

The work of Gupta *et al.* /75/ indicated that mixed inhibitors like malachite green, congo red, crystal violet, alizarin and methyl orange along with BTA were used for minimizing the corrosion and dezincification rate of 63/37 brass in 1% H₂SO₄.

Studies by Pushpa Gupta *et al.* /23/ on 2-MBT, BTA and benzimidazole for the corrosion of 70/30 brass in 1% H₂SO₄ indicated that the inhibition was due to the formation of a protective complex film mainly with copper ions on the surface.

Bag et al. /76/ examined the effect of benzimidazole and its derivatives such as 2-amino and 2-hydroxy benzimidazole on 70/30 brass in HNO₃. Thermodynamic parameters (ΔE , ΔG , ΔH , ΔS) for adsorption revealed that the inhibition occurred by blocking of the reaction sites on the surface of brass via chemisorption of the additives following the Langmuir isotherm. The efficiency could be explained on the basis of a change in the electron density around the imino nitrogen (>NH) of the pyrazole arising arising from the electron donor substituents.

Jinturkar et al. /77/ studied the corrosion of copper, zinc and their alloys in H₂SO₄ solution with oxygen and ferric ions using BTA as an inhibitor and reported that the zinc dissolved preferentially in the initial stages followed by simultaneous dissolution of Cu and Zn and BTAH formed a protective layer on the surface, thereby inhibiting corrosion.

Hussain and Singh /78/ reported that the dimethyl acrylamide was a cathodic inhibitor with efficiencies upto 90%. It decreased with an increase in temperature and concentration.

Otienoalego et al. /79/ used polarisation and surface enhanced Raman scattering techniques for 60/40 brass in aqueous H₂SO₄ with 1-[N, N-bis-(hydroxy ethyl) amino-methyl] - benzotriazole (BTLY) as inhibitors. The overall inhibition for Cu and Zn dissolution increased with concentration to a maximum of 63% efficiency. The BTLY was ineffective in preventing dezincification as revealed by solution analysis but polarisation studies showed that BTLY acted initially in suppressing both the cathodic and anodic reactions.

Gad Allah *et al.* /80/ reported that some amino pyrazole derivatives can show 91% efficiency (cathodic type) for the system 67/33 brass in hydrochloric acid.

Mayanna and Sethy /81/ attempted to study the effect of BTA on the dissolution of copper single crystal planes in dilute H₂SO₄ and they reported that the dissolution rates were controlled by surface reaction and Cu-BTA film appeared on the surface.

Ross and Berry /82/ used BTA as an inhibitor for the corrosion of Cu in H_2SO_4 and reported that the lower concentrations BTA were more satisfactory than the higher ones.

N-ethyl thiourea, N, N-diethyl thiourea, N, N-dibutyl thiourea and M-chloro phenyl thiourea were studied by Patel *et al.* /83/ for controlling the corrosion of 63/37 brass in 0.5N HNO₃. These inhibitors were found to be effective at higher concentrations.

On the same lines, Desai *et al.* /84-86/ studied the effect of thiourea, allyl thiourea and phenyl thiourea on the corrosion of 63/37, 70/30 and 60/40 brasses in HNO₃ solution and found that in the case of 63/37 brass, thiourea and allyl thiourea were effective as cathodic inhibitors while phenyl thiourea was a mixed inhibitor.

Dinnappa and Mayanna /87/ from their works reported that allyl thiourea, methyl thiourea, dimethyl phenyl thiourea and diphenyl thiourea act as good inhibitors for the corrosion of 60/40 brass in HNO₃ solution. Works of Patel et al. /88/ also indicate that phenyl thiourea, diphenyl thiourea and 1, 3 - di-0-toly thiourea act as good inhibitors for the corrosion of 63/37 brass in acetic acid. Substituted thiourea was studied by Saha et al. /89/ as an inhibitor for reducing the corrosion of 70/30 brass in acetic acid.

Desai et al. /90/ studied the corrosion of cold rolled 63/37 brass in 2, 3 and 4N HNO₃ solutions at 30°C in the presence of O-, m-, and p-derivatives of aminophenol and phenylene.

Patel et al. /91/ have reported that p-thiocresol exhibited very good inhibition effect against the corrosion of 63/37 brass in acetic acid, poor effect in HNO₃ and least effect in alkaline solution.

Dambal and Ramachar /92/ studied the inhibitive action of formaldehyde and urea towards the corrosion of 63/37 brass in HNO₃ and reported that the inhibition efficiency improved with the concentration of inhibitor and immersion period. Desai *et al.* /93/ considered the amino benzoic acid to be a good inhibitor towards the corrosion of 60/60 brass in HNO₃ solution. The effect of chloro-, dichloro-, trichloro-, bromo-, and iodo acetic acids on the corrosion of 60/40 brass in dilute HNO₃ acid was studied by Dinnappa and Mayanna /94/.

Different concentrations of thioglycolic acid, dithioglycolic acid and thio benzoic acid have been studied as inhibitors to minimize the corrosion of 63/37 brass in acetic acid solutions by Patel *et al.* /95/.

b) Neutral Media

Shih et al. /96/ studied the inhibitive action of urea, indole, thiourea, 1,2,4 triazole and 1,2,3-benzotriazole towards the corrosion of 70/30 brass in 3.5% NaCl solution containing HgCl₂ and reported that BTA was a good inhibitor among others.

Hussain and Singh /78/ used n, n-dimethyl formamide (DMF) as an inhibitor for the corrosion of 63/37 α -brass in aqueous solution and reported that the electrochemical behaviour of the brass was cathodically controlled,

and that the brass was anodically more active in the water rich than in the DMF rich region, but no clear passivity was found.

Karpagavalli and Rajeswari /97,98/ investigated BTA and Triton x-100 and a combination of both as inhibitors towards the corrosion of brass in NaCl and sea water and reported that the BTA and triton x-100 had a synergistic effect and the mechanism obeyed the Langmuir adsorption isotherm.

The findings of Zhang et al. /99/ on BTA derivatives such as 2-amino benzothiazole, 2-amino 7-methoxy benzothiazole, 2-MBT acting as inhibitors towards the corrosion of 65/35 brass in 3% NaCl solutions indicate that these inhibitors were more effective in preventing dezincification. The structure parameters of these compounds were calculated by PPP-SCF quantum chemistry method. It was shown that the formation of π coordinate bond by a filled d-orbital of metal atom and an empty π^* of inhibitor had an association with their inhibition efficiency.

Faroogi et al. /100/ and Quarishi et al. /101/ used triazole derivatives such as aminomethyl mercaptotriazole, amino ethyl mercapto triazole and aminopropyl mercapto triazole as inhibitors for the corrosion of brass in 3% NaCl solution. Their experimental results indicated that the reaction was under diffusion control. The solution analysis showed preferential dissolution of zinc in the absence of inhibitors. However, the dissolution of zinc decreased as the concentration of inhibitors increased.

Oung et al.. /102/ investigated the corrosion of 67/33 α-brass in fluoride solution and its inhibition with BTA using SSRT, polarisation, SEM, EDS and XRD techniques. They found that the rupture of Cu₂O films at OCP was followed by a slip dealloying dissolution phenomenon. They explained the mechanism by the formation of copper matrix vacancies when F ions enter the oxide and replace some of the O² ions there, and thus enhance the dealloying dissolution of zinc. Addition of BTA was able to inhibit IGSCC and electrochemical dissolution of brass.

Shih and Tzou /103/ also reported that the addition of BTA could prevent SCC of 70/30 brass in aqueous solution containing fluoride ions.

Ashour and Ateya /104/ studied di-sodium hydrogen phosphate (DSHP) as an inhibitor for the corrosion of α -brass in 0.1M sodium nitrite solution. They noticed the formation of zinc phosphate film on the surface of alloys, which inhibited dezincification and subsequently the SCC of the brass.

4.2 Addition of alloying element to brass

Egamy et al. /105/ studied the corrosion of leaded brass in acidic chloride and sulphate solutions by EIS and polarisation measurements. Increasing Pb content in the alloy increased its corrosion resistance.

Liu et al. /106,107/ reported the corrosion of α -brass and $\alpha + \beta$ brass with the addition of element As and Sn in sea water and indicated that the corrosion with intergrannular and dezincification characteristic occurred in brass with addition of As. The addition of Sn element inhibited dezincification of brass due to easier enrichment at grain boundaries.

The corrosion, corrosive wear and erosion resistance of boron modified Cu-base alloys have all been well investigated by Jiang and Wang /108/.

Jiang et al. /109/ and Wang et al. /110/ studied the corrosion of Al-brass with the addition of boron and arsenic elements and reported that the addition of boron and arsenic atoms moved into the divacancy and blocked the way of dezincification so that dezincification could not take place.

Kim and Kwon /111/ investigated the corrosion of leaded and unleaded brass in potable water and reported that the addition of bismuth increased the corrosion resistance of unleaded brass. The leaded brass had only a slight tendency to dezincification whereas the bismuth containing unleaded brass exhibited more susceptibility.

Shalaby et al. /112/ evaluated the addition of 5 ppm Mn or 4 ppm Cl to sea water for the corrosion of Al-brass. The polarisation resistance decreased in the presence of Mn with an increase in film thickness. The film became porous and became easily detached at a high flow rate. The film formed in the presence of Cl was smooth and well adherent.

The findings that dezincification of brass can be fully inhibited by the pair of As-B and the synergistic effect of As-B weree documented by Li *et al.* /113/.

4.3 Prevention of dezincification of brass in the presence of pollutants

Gupta et al. /114/ studied the action of urea derivatives such as thiourea, N-phenyl thiourea and diphenyl thiourea as inhibitors towards the corrosion of 63/37 brass in 1N ammonia solution. They reported that all the three inhibitors were able to reduce both copper and zinc dissolution and obeyed the Langumir isotherms.

Bag et al. /115/ and Gupta et al. /116/ reported the inhibitory effect of azoles compounds, 2-amino benzimidazole as an inhibitor for the corrosion of 70/30 brass in ammonia solution. An increase of surface coverage and decrease of free energy of adsorption with temperature indicated that 2-ABZ inhibited corrosion by blocking the reaction centres on the surface of brass. Benzimidazole was found to give complete protection against corrosion as well as dezincification of brass.

Gupta *et al.* /117/ also noted the effect of mercaptans as inhibitors towards the corrosion of 60/40, 63/37 and 70/30 brasses in 13.4 N NH₄OH solution using potentiostatic studies. They reported that the 2-mercapto mercaptan and 2-mercapto ethanol were effective in minimizing the dezincification in brasses and were of mixed type.

Ashour *et al.* /118/ reported the action of benzotriazole (BTAH) as an inhibitor for the corrosion of 70/30 brass in 0.58 M NaCl solution containing sulfide ions and indicated that the decrease of the inhibiting efficiency of BTAH and the momentary increase of the dissolution rate of α -brass was due to the decomposition of the protective Cu(l) BTA film and formation of Cu₂S, leading to loss of its inhibition efficiency.

5.0 SUMMARY

The copper-zinc alloys ranging in zinc content from 3% to 39%, commonly called brasses, are the most popular and versatile copper alloys. They have reasonably high electrical and thermal conductivities with good strength. The mechanical properties of brass depend upon the chemical composition of the alloy. Elongation tensile strength increases with increase in the zinc content.

Dezincification is the most common form of dealloying. Selective removal of zinc from the brass leaves behind the spongy mass of copper with no mechanical strength. Normally two types of dezincification process will occur: one is uniform type and the other one is plug type.

The mechanism of dezincification was explained by three methods.

1. Preferential dissolution of zinc, 2. Simultaneous dissolution of both zinc and copper, followed by redeposition of copper. 3. In chloride environments, a combination of the above two mechanisms occurrs.

In the atmospheric corrosion of copper and its alloys, it is reported that the formation of green patina Cu (11) oxide and one or more copper salts takes place. In chloride environments, zincite, Zno and hydrazincite are formed.

In general, wet cleaning caused dezincification cleaning with acids like HNO₃ HCl, H₂SO₄or acid brightener and electrochemical cleaning in H₃PO₄ carried surface dezincification. The preferential dissolution rate of zinc was found to destroy the Cu (II) passive film and higher rates of corrosion were observed in the presence of stress conditions. The effect was strong when zinc dissolution was limited by the solid phase diffusion of zinc in the alloy.

The electrochemical behaviour of α - brass was dependent on the pH of the ambient electrolyte. The alloy passivity is due to the formation of Cu (l) compound (mainly Cu₂O), which was relatively stable in neutral and basic solutions.

The effect of pollutants on dezincification reveals that Cu_2O film could be formed on α - brass in 0.1 M NaF solutions. This passive film could however break down. Film rupture and slip deallloying dissolution may be involved in intergranular stress corrosion cracking.

In 0.1M Cl, Br, and l solutions no SCC susceptibility was observed. The stability was higher in the presence of l ions. It was observed in the dezincification process in the presence of microorganisms that biofilmed coupons of brass experienced less corrosion in culture media than that of commercial copper. The nature of sulfide film and susceptibility to pitting corrosion were confirmed by surface analysis.

In order to control the dezincification process, mostly based on the isolation of material from harmful environments, the following actions could be taken: In HCl environments, 2,3,4- picoline and pyridine can be used as inhibitors of 70/30 brass. Aniline derivatives effectively control the dezincification process of 70/30 brass in H_2SO_4 environments. Moreover 2-MBT, BTA and benzimidazole can be utilized for corrosion of 70/30 brass in 1% H_2SO_4 solutions.

Urea and thiourea derivatives work at higher concentrations in 0.5M H_2SO_4 solutions for 63/37 brass. Dimethyl formamide was used as an inhibitor for 63/37 α -brass. BTA derivatives were used in 3% NaCl solutions for 65/35 brass and DHSP is used as an inhibitor for α - brass in 0.1M sodium nitrite solutions.

Apart from this, the additions of alloying elements such as As, Sn, boron, Mn and bismuth can also control dezincification. Thiourea derivatives can effectively control the dezincification process in the presence of pollutants like ammonia and sulfide.

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