

Influence of arsenic, antimony and phosphorous on the microstructure and corrosion behavior of brasses

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Abstract The effect of minor additions of As, Sb and P on phase distribution and corrosion behavior has been studied in brasses. The alloys investigated were 60Cu–39Zn–1Pb, 48.95Cu–45Zn–5Pb–1Sn–0.05As, 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P. Immersion tests in 1% CuCl₂ solution indicated that the addition of As improved corrosion resistance while the combined addition of As + Sb and As + Sb + P was not beneficial. The hardness increased significantly with the addition of As, Sb and P. Microstructural observations indicated an increase in β phase fraction in the As, Sb and P containing alloys. X-ray diffraction studies confirmed the formation of intermetallic compounds in As, Sb and P containing alloys. Based on the microstructural observations, the intermetallic compounds appear to be primarily precipitated in the β phase with As + Sb and As + Sb + P additions. The lower corrosion resistance of the alloys 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P has been related to increase in β phase volume fraction and precipitation of intermetallic compounds in the β phase.

Introduction

The corrosion behavior of brass alloys has been extensively studied with reference to preferential dissolution of zinc

[1], stress corrosion cracking [2–4], passivation and pitting corrosion [5–7]. Dezincification or preferential dissolution of zinc is a common corrosion concern in brasses [8–10]. Brass alloys can be protected against dezincification by addition of small quantities of tin, arsenic, antimony and phosphorous [11, 12]. The studies on inhibition mechanism of Sn-containing brasses suggested that the corrosion resistance was exhibited due to the formation of Sn-enriched corrosion product film [13]. The role of arsenic in lowering dezincification of brass alloys has often been related to effects on the surface film [14, 15]. Bowers [16] reported that the inhibitive effect of As was restricted to α -brass and even traces of iron or manganese results in the formation of brittle intermetallic compounds with arsenic. This caused a deterioration of mechanical properties as well as a reduction in the efficiency of As addition. Torchio [17] suggested that As and P mutually influence the stress corrosion cracking behavior of Al brass and maximum cracking susceptibility was observed when relatively high percentages of these elements are present. Mazza and Torchio [18] concluded that higher or joint addition of As and P induces increasing susceptibility to localized corrosion in aluminum brasses. Zucchi et al. [19] studied the influence of P, As and Sb on the susceptibility to stress corrosion cracking of α - β brasses and concluded that the brasses containing more β phase were highly susceptible to stress corrosion cracking than the brasses containing less β phase. They also proposed that Sb drastically increased stress corrosion cracking susceptibility of the brasses while As showed a beneficial effect. The inhibiting effect of these elements (P, As and Sb) on susceptibility to stress corrosion cracking in brasses containing more β phase was limited.

In the present study, the correlation between microstructural changes and corrosion behavior in brasses

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alloyed with minor additions of As, Sb and P has been investigated.

Experimental method

The composition of the brass alloy used for reference purpose was 60Cu–39Zn–1Pb. This is commercially used for casting decorative objects. An alloy development program to develop corrosion resistant brasses was initiated in collaboration with one of the largest manufacturers of these brass decorative objects in India, D.S. Gupta & Sons, Moradabad. Since the brass objects with the composition of 60Cu–39Zn–1Pb were susceptible to dezincification, 2% Sn was added to improve the dezincification resistance. The Pb content was also increased to 5% to improve machinability. Although the alloy 48Cu–45Zn–5Pb–2Sn exhibited improved corrosion resistance, it was decided to reduce the Sn content in this alloy because Sn is a relatively costly addition. The amount of Sn was lowered to 1% and minor amounts of As, Sb and P were added to obtain the brass compositions of 48.95Cu–45Zn–5Pb–1Sn–0.05As, 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P. The samples were supplied in the form of flat strips of thickness 0.2 cm with rough surface finish.

Immersion tests were performed in 1% CuCl₂ solution. The solution was prepared using Analar grade chemicals and distilled water. The dimensions of the specimens used in the immersion studies were 1 × 1 × 0.2 cm. The brass samples were cleaned with acetone, washed with distilled water and dried before immersion. The specimen was immersed in 100 mL of 1% CuCl₂ solution for 72 h at room temperature. A Mitutoyo screw gauge with precision of ±0.01 mm was used to determine the thickness of the brass samples. The thickness was measured at 10 different locations for each sample, before and after immersion. The mean and standard deviation of thickness reduction were calculated. The experiments were repeated and the results were reproducible.

The micro-hardness of the brass alloys was measured by using a Leitz micro-hardness tester, applying a load of 100 g. Scanning electron microscopy (SEM) observations were performed using a FEI Quanta 200 microscope. Metallographic samples were prepared by hot mounting the samples in epoxy resin. The hot mounted samples were polished till 1000 grit emery paper and finally cloth polished using 1 μ alumina powder. The samples were degreased using acetone and etched in 5% aqueous ferric chloride solution to reveal microstructural features. The volume fractions of α and β phases were determined by quantitative metallography using Image-Pro Plus software (version 4.1.0.0). X-ray diffraction (XRD) patterns were

recorded in a Rich-Siefert 2002 X-Ray diffractometer using Cu K_α radiation at a scan rate of 3°/min. The XRD data was analyzed using Diffrac^{PLUS} software (Bruker Advanced X-ray Solutions, Germany) and JCPDF database.

Results and discussion

Immersion tests

The thickness reductions evaluated after 72 h of immersion in 1% CuCl₂ solution are presented in Table 1. The thickness reduction can be used as a measure of corrosion resistance, with a higher reduction implying lower corrosion resistance. A lower thickness reduction of 0.037 ± 0.03 mm was observed for the alloy 48.95Cu–45Zn–5Pb–1Sn–0.05As as compared to 60Cu–39Zn–1Pb (0.212 ± 0.12 mm). The alloys 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P exhibited improved corrosion resistance than 60Cu–39Zn–1Pb, as indicated by the lower thickness reductions (Table 1). However, the corrosion resistance of these alloys was relatively lower compared to the alloy with only As addition, 48.95Cu–45Zn–5Pb–1Sn–0.05As. In order to understand the effect of minor additions of As, Sb and P on the corrosion behavior of Sn-containing brasses, the microstructures of the alloys were examined.

Microhardness

The microhardness of the samples are presented in Table 1. The hardness increased with increasing presence of As, Sb and P. The combined addition of As, Sb and P provided the highest hardness, significantly higher than that of the reference alloy. The addition of As, Sb and P also rendered the alloys brittle. This was not determined by mechanical testing but rather understood while cutting the samples for immersion studies. The brittleness increased with increasing hardness of the alloys.

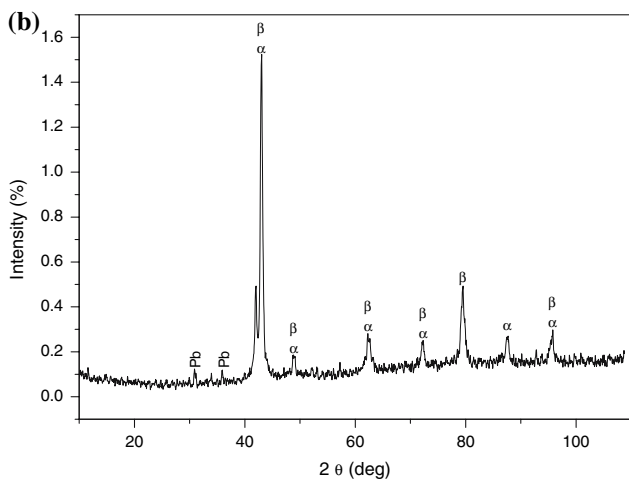
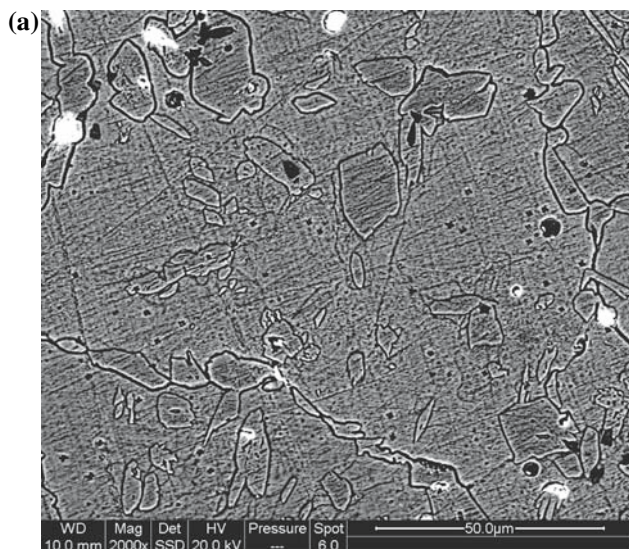
Microstructure and XRD analysis

Figure 1a shows a typical SEM microstructure of the alloy 60Cu–39Zn–1Pb. The microstructure consists of α and β phases, as anticipated from the phase diagram [20]. The lead, which was added to promote machinability, was insoluble in brass and observed as a separate phase in the form of globular particles. The XRD pattern also revealed α and β phases, in addition to lead (Fig. 1b).

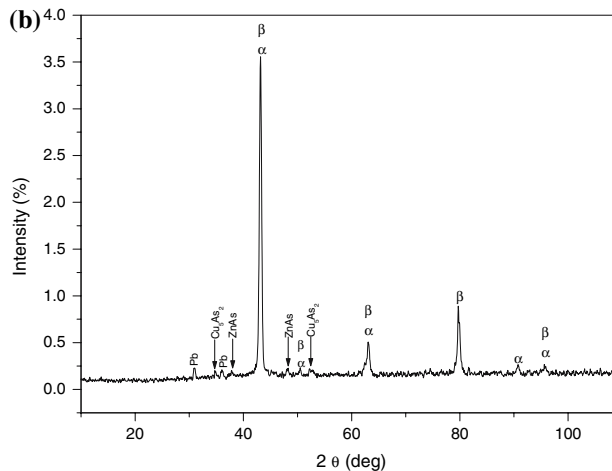
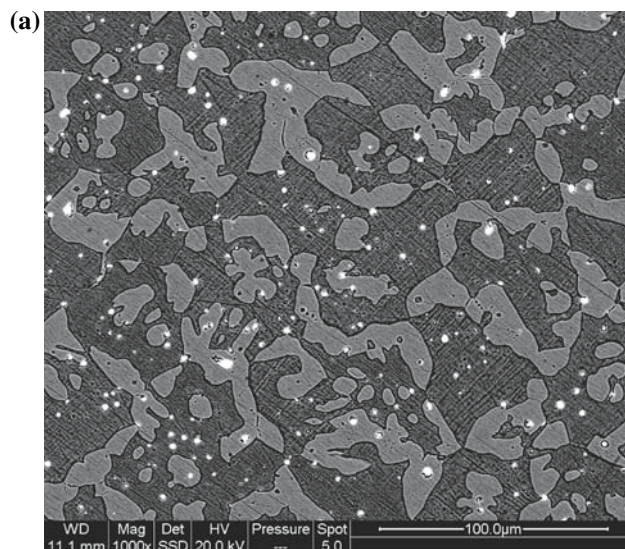
The SEM microstructure of the alloy 48.95Cu–45Zn–5Pb–1Sn–0.05As has been presented in Fig. 2a. The microstructure consists of α and β phases. Image analysis

Table 1 Thickness reduction, micro-hardness and phase volume fraction of the brass alloys studied

Sample	Chemical composition (%)	Thickness reduction	Microhardness (kg/mm ²)	Volume fraction (%)	
				α phase	β phase
1	60Cu–39Zn–1Pb	0.212 ± 0.12	165 ± 08	79	21
2	48.95Cu–45Zn–5Pb–1Sn–0.05As	0.037 ± 0.03	277 ± 42	65	35
3	48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb	0.048 ± 0.02	337 ± 45	38	62
4	48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P	0.071 ± 0.05	443 ± 45	12	88

**Fig. 1** (a) SEM morphology and (b) XRD pattern of the alloy 60Cu–39Zn–1Pb

revealed that the β phase fraction was higher (35%) than that for the reference alloy (21%) (see Table 1). Interestingly, this alloy provided improved corrosion resistance compared to the alloy 60Cu–39Zn–1Pb with lower β phase (Table 1) and this brought out the beneficial aspects of Sn and As addition on improving corrosion resistance. XRD analysis also indicated the presence of intermetallic com-

**Fig. 2** (a) SEM morphology and (b) XRD pattern of the alloy 48.95Cu–45Zn–5Pb–1Sn–0.05As

pounds of Cu and As, Zn and As (Fig. 2b). The enhanced hardness of 48.95Cu–45Zn–5Pb–1Sn–0.05As can be attributed to the presence of higher fraction of β phase and intermetallic compounds of As in the alloy.

The volume fraction of β phase was higher in the As + Sb and As + Sb + P containing alloys (Table 1). SEM microstructure (Figs. 3a, 4a) clearly brought out this

feature. The alloy 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P essentially consisted of β phase (88% of the volume fraction) with only a small amount of α phase. Therefore, even relatively small additions of Sb and P drastically altered phase distribution. The main effect of these additions appears to be the stabilization of the β phase.

Bowers [16] proposed that the β phase dezincifies more readily than α phase. Thus, the comparatively lower corrosion resistance of 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P than 48.95Cu–45Zn–5Pb–1Sn–0.05As may be due to the increased volume fraction of β phase in these alloys. The combined addition of As + Sb and As + Sb + P also resulted in the formation of precipitates. Interestingly, these precipitates were observed essentially in the β phase, as indicated by the microstructures in Figs. 3a, 4a.

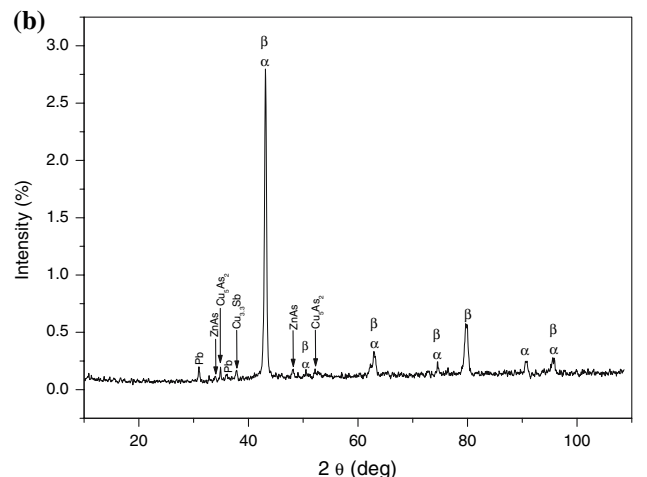
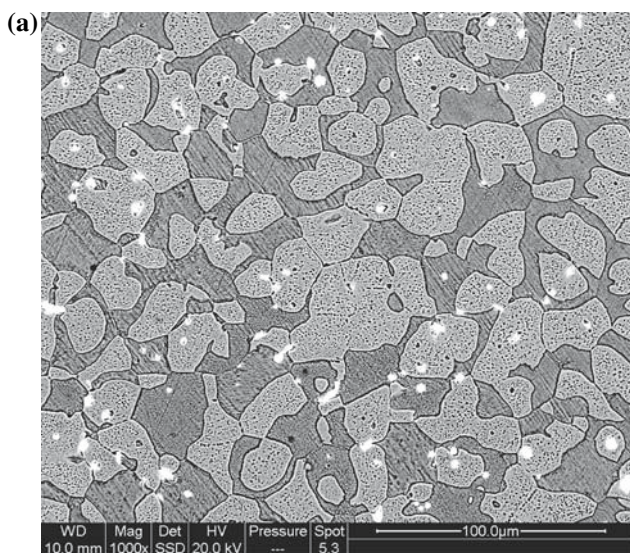


Fig. 3 (a) SEM morphology and (b) XRD pattern of the alloy 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb

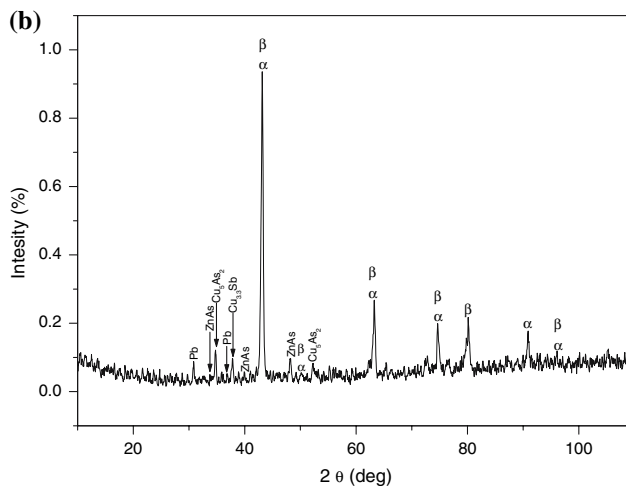
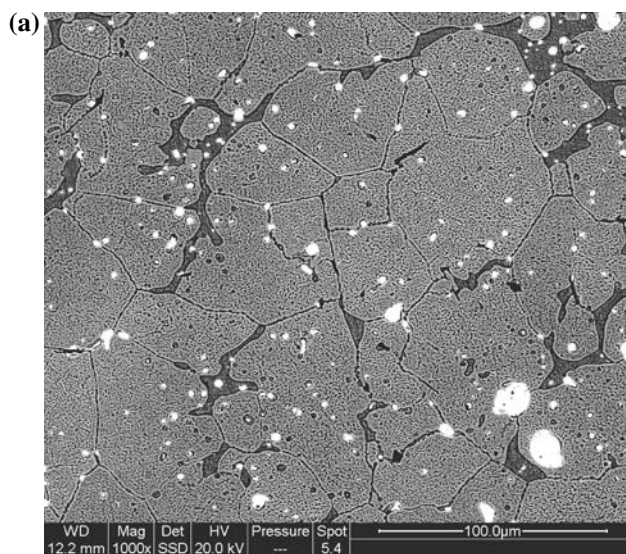


Fig. 4 (a) SEM morphology and (b) XRD pattern of the alloy 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P

XRD analysis indicated the existence of intermetallic compounds Cu_5As_2 , $ZnAs$ and $Cu_{3.3}Sb$ in the alloys containing As + Sb and As + Sb + P (Figs. 3b, 4b). The intermetallics Cu_5As_2 and $ZnAs$ were also detected in the alloy containing only As. Therefore, $Cu_{3.3}Sb$ is the additional intermetallic that precipitated in these two alloys. The structural imperfections resulting due to the precipitation of intermetallic compounds could affect the corrosion resistance of the alloys [21].

The increased micro-hardness of these alloys (Table 1) could be related to precipitation hardening and higher volume fraction of the β phase. The intermetallic precipitates establish strain fields in the matrix. The strain fields and the interactions between fields hinder dislocation motion and thus lead to a decided increase in hardness [22].

Conclusions

The corrosion behavior and microstructures of brass alloys containing minor additions of As, Sb and P were studied. The alloy 48.95Cu–45Zn–5Pb–1Sn–0.05As exhibited higher corrosion resistance compared to reference alloy, 60Cu–39Zn–1Pb and 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P alloys. The alloys 48.90Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb and 48.85Cu–45Zn–5Pb–1Sn–0.05As–0.05Sb–0.05P revealed improved corrosion resistance than 60Cu–39Zn–1Pb. The lower corrosion resistance of these alloys as compared to 48.95Cu–45Zn–5Pb–1Sn–0.05As was attributed to the increased fraction of β phase and precipitation of intermetallic compounds in the β phase. The enhancement in the fraction of β phase and precipitation of intermetallic compounds also increased the hardness of As, Sb and P containing alloys.

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