Ultrafine particulate reinforcement to improve the corrosion resistance of brass, polyaniline and metal-metalloid deposits

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Abstract

In general, anodic gain boundaries, voids, inclusions and other stress concentration points, like dislocation, vacancies, etc. are the most preferential sites for metallic corrosion to take place. Incorporation of ultrafine ceramic particulates in lower concentration range, in metals and alloys, may be effective in the formation of a cathodic coverage on these anodic sites, such that the galvanic relationship between the anodic boundaries and other defects with the cathodic grain properties is somewhat reduced. This results in an effective reduction of the galvanically induced dissolution, from the surface of metals and alloys. This paper, has discussed all these aspects, in the light of their roles in the improvement of their surface properties. The physico-chemical properties of the particulated Cu 60% Zn 40% brass and polyaniline matrix, have been discussed, along with those of the ultrafine particulate reinforced copper-manganese class of marine alloys and nickel based metal-metalloid class of deposits on carbon-steel surface. Some correlations have also been made between the grain structure and the concentration of ultrafine particulates, stressing on their role in the reduction of surface corrosion including pitting. It is assumed that a particular metallic matrix has a quantified anodic sites, such that it can accommodate a critical amount of ultrafine particulates within these sites. It has been further observed that ultrafine boron carbide incorporated Cu60Zn40 matrix revealed very low leaching of both Cu and Zn – ions.

Introduction

Anodic sites, like grain boundary, void, inclusion and other stress concentration points like dislocations, vacancies, etc. are the preferential sites for corrosion [1-10] to take place on the surface of metals and alloys. Under such circumstances, incorporation of ultrafine particulates in lower concentration range may be effective in the formation of a cathodic coverage on these anodic-sites, such that the galvanic relationship between the anodic boundaries and other defects with that of the cathodic grain proper is somewhat moderated. It results in an effective reduction of the galvanically induced dissolution and anodic current of the surface [1-4]. The excess particulates which do not find any entry within these anodic micro-features of the surface, are normally dispersed in a random manner, creating stress, concentration points and galvanically induced surface dissolution. As the total anodic sites are limited, there is a limit, upto which the ultrafine particulates may be accommodated on the matrix anodic sites.

De-alloying or dezincification of brass is a well known process [1], where one of the components of either copper or zinc or both may undergo leaching. Attempts have been made to prevent such selective leaching, employing the conventional surface modification techniques and also using suitable inhibitors, resulting only in the marginal reduction of de-alloying [1-4]. Incorporation of ultrafine ceramic particulates of matching galvanic activity and in lower

concentration, may eventually improve the resistance to such de-alloying process.

Literature survey revealed that systematic studies in the field of ultrafine particulate reinforced matrices for the improvement of corrosion resistance of metals and alloys is lacking.

The author in this paper has therefore, taken a different approach, to address this problem. Studies have revealed that proper selection of ultrafine particulates and their application in lower concentration range may block the removal of both Cu and Zn-ion and the Zn-ion in particular.

Experimental

Pure metals like Cu, Zn, Mn used in this study, are of 99.9% purity. Ultrafine particulates like SiC, BC, WC, Al_2O_3 and TiO_3 are used for making the composite matrices of $\alpha - \beta$, brass, Cu-Mn alloy and Ni-P-B metal metalloid deposits, are of the particle size-range of 0.5 to 2mm, are of AR. Quality.

Description of test results

Table 1 reveals the correlation of ultrafine ceramic particulates and the anodic micro-defect sites, like grain-boundaries, dislocations, micro-voids, etc. in Zn-Al-SiC and Zn-Al_2O_3 composite alloys. It is seen that the total volume equivalent of grains and grain boundary areas and the volume equivalent of other effects (II) are more or less the same in

both these cases and also the values of the particle trapping capacity. However, the residual particle trapping capacity is different in these two cases, due to the difference in the value of the volume equivalent of the particulates (III). The Zn-Al-Al_2O_3 matrix reveals a higher residual particle trapping capacity, due to the fact that it is associated with a lower volume equivalent value of the reinforcing particulates, such that the excess matrix volumes remain vacant for further particulation.

Table 2 reveals the physico-chemical properties of the composite brasses. It is seen that the 4 a-b, brass

containing 1% BC reveals the lowest corrosion rate value by weight loss, technique. This is supported by the lowest l_{corr} value and lowest oxidation rate of the 1% BC containing a -b brass and is attributed to the finer particle size (0.5 μm) compared to W_c (1.5 mms) and TiO_2 (1.5 μm) particulates. The higher hardness of the boron carbide brass is attributed to the higher hardness of boron carbide brass is attributed to the higher hardness of boron carbide particulates, which appear to undergo degeneration during the heat treatment of this class of brass – matrices, resulting in oxidation of boron and reduction in surface hardness.

Table 1. Correlation of the ultrafine ceramic particulates and the grain boundary features in the Zn-Al-SiC and the Zn-Al-Al_2O_3 composite alloys (Particulates ultrafine; SiC = 2 μms and Al_2O_3 = 1.5 μms.)

S.No.	Description of the matrix	Total volume of Grains (C:C)	Vol. Equivalent of total grain boundary area & (C:C) I	Vol. Equivalent of other defects (C:C) II	Vol. Equivalent of particulates (C:C) III	Particulates trapping capacity (C:C) (I+II)	Residual particulate trapping capacity of the matrix (C:C) (I+II) – (III)
1	Zn 95.5 Al3 Sic 1.5	0.693	0.032	0.275	0.1340	0.307	+0.1730
2	Zn 95.5 Al3 Al1203	0.617	0.029	0.354	0.911	0.383	+0.2919

Table 2. Physico-chemical properties of the composite α-β, brass [α-β, = Cu 60 Zn 40, particulates = ultrafine: TiO_2 = 1.5 μm and Al_2O_3 = 1.5 Bc = 0.5 μm]Wc = 1.5 μm.

S.No.	Materials under test	Hardness (BHN)		Icorr (mA/cm^2)		Oxidation Rate (gm/cm^2/hr] (As cast alloy)	Corrosion rate by weight loss [mg/cm^2] (period of exposure = 72 hrs) [As cast]
		As cast	Heat treated [200° C] 2 hrs	As cast	Heat treated [200 C] 2 hrs		
1	α-β, brass	376	359	0.01	0.01	11.4	0.07
2	α-β, brass + 1% Bc	570	533	0.001	0.02	0.31	0.04

Table 3. Electrochemical properties of polysilicone matrices with and without fine fraction and course fraction of metallic alloy (M.G) reinforcement, along with cladding of Pb-Sn alloy [Electroyte = 3% NaCl].

S.No.	Description of the matrix	Proportional mass – loss index of the polyaniline matrices
		Cladding material = Pb=Sn alloy
1	Pure polyaniline fraction M.G (1mm) reinforced PA	5.3
2	Fine fraction M.G (1 mm) reinforced PA	1.0

Table 4. Corrosion rate (I_{corr}) values of Cu70 Mn30 composite alloys, as a function of the type of reinforcements,
[particulate = ultrafine; SiC = 2 μm and Al_2O_3, = 1.5 μm, TiO_2 = 1.5 μm].

S.No.	Description of the matrix	Icorr (mA/cm²) [Electrolyte = 3% NaCl, w.r.t. S.C.E]
1	Cu70Mn30	0.900
2	Cu70Mn30 + 1% Al_2O_3	0.0072
3	Cu70Mn30 + 1% TiO_2	0.0074

Table 5. Physico-chemical properties of the amorphous Ni-P-B coated m.s. substrate with an without Co-deposition of ceramic particulates [Particulate = ultrafine, SiC = 5 μm WC = 5 μm; Al_2O_3 = 1.5 μm]

S.No	Description of the matrix	Average Hardness (V.P.N)	Average thickness (μm)	Average weight loss value (mdd) [3% NaCl]
1	Amorphous Ni-P-B (No particulate)	1200	40	1.33
2	Amorphouse Ni-P-B (Particulates, 5 Sic 5 Wc 1.5 Al_2O_3	1400	32	0.22

Table 3 reveals the electrochemical properties of the polymeric matrices with and without fine fraction of metallic glass reinforcement. These data clearly reveal that the proportional mass – loss values of the polyaniline matrices, claded to Pb-Sn alloy, undergo a progressive reduction as a result of metallic glass reinforcement. It is explained by the fact that Met-glass reinforcements improve surface passivity, due to their inherent surface metastability and the associated passive nature. The finer fraction Met-glass reinforced matrix is associated with lower porosity and higher met-glass surface area resulting in lower corrosion rate value.

Table 4 reveals the corrosion rate (I_{corr}) values of the Cu70 Mn30, Cu70 Mn29 Al_2O_3 12, and Cu 70Mn 29 TiO_2 12 alloy composites, as a function of the type of reinforcements employed in lower concentration range. It is seen that the corrosion rate values come down abruptly as a result of 1% TiO_2 and 1% Al_2O_3 addition.

Table 5 reveals the physico-chemical properties of the amorphous Ni-P-B coated mild steel substrate, with and without ceramic reinforcements. It is seen that reinforcement of the amosphous Ni-P-B matrix with ceramic particulates, like SiC, BC, WC ad Al_2O_3, have resulted in an increase of the surface hardness level, along with a drastic decrease of surface corrosion rate and a reduction of the deposit thickness values. The amorphous Ni-P-B coating obtained, is associated with a lot of micro-porosities due to the very high level of hydrogen generation at the cathode. Incorporation of ultrafine particulates, help in the filling up of these porosities and brings down the mass – loss value drastically obviously, the hard ceramic particulates are responsible for the increase of

surface hardness values. Filling up of the micro-voids by the particles, also consolidates the void-spaces, within the deposit thereby reducing the layer thickness. Macro-porosities and micro-voids are anodic sites and their filling up results in surface ennoblement in terms of lower corrosion-rate values.

Fig. 1 and 2 reveal respectively the impedance diagram of the a-b brass, with and without 1% BC particulate. It is clearly observed that the Rct value increases as a result of reinforcement of the a-b , brass matrix with 1% BC ultrafine particulate. Fig. 3, reveals the micrograph of Zn + 1 SiC. Al_2O_3 matrix, while Fig. 4 reveals that of Zn + 1% SiC. It is seen that a typical wearing pattern is observed on the brass – SiC, surface, while the brass – Al_2O_3 surface reveals linear dispersion of the particulates, over the matrix micro – structures. The lower particulate trapping capacity of the brass – SiC matrix, appears to be the reason behind the patterned net-work structure on the surface of Zn-1% SiC composite due to the fact that a good amount of the particulates do not find access within the anodic micro-defect sites on the surface of the composite. On the other hand, excess particulates are less on the Zn + 1% Al_2O_3 matrix, due to its higher particulate trapping capacity. Moreover, the size factor of SiC particulates (2μm) in higher than that of the Al_2O_3 (1.5 μm), making the easy entry within the anodic micro-defect sites, more difficult.

Conclusion

An objective analysis of all the data, projected in Table 1 clearly indicates that ultrafine particulation of a-b brass, alters its physico-chemical properties. Particulation of the a-b brass matrix with 1% BC improves the corrosion

resistance properties to a considerable extent. Further, it is observed that polyaniline matrix reinforced with finer fraction metallic glass, reveals superior corrosion resistance properties. This trend is also observed in copper-manganese alloys, reinforced with 1% TiO_2 and 1% Al_2O_3. It has also been observed that reinforcement of the amorphous Ni-P-B matrix with ultrafine powder mix of SiC, WC, BC and Al_2O_3, results in the drastic reduction of the corrosion rate value, along with an increase in the level of surface hardness. It is assumed that ultrafine particulates are trapped inside the anodic surface micro-features, like, grain-boundary channels, dislocations, vacancies and micro-voids, etc. thereby reducing the surface anodic current.

Acknowledgement

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