J. Am. Chem. Soc. **1982**, *104*, 5390–5394

NMR results of his student, M. A. Leparulo.[41] We are grateful to the National Science Foundation for support under Grant No. CHE 76-05887.

Registry No. $H_4[GeW_{12}O_{43}]$, 12207-33-9; $H_6[ZnW_{12}O_{40}]$, 82679-05-8; $H_3[PW_{12}O_{40}]$, 1343-93-7; $H_4[SiW_{12}O_{40}]$, 12027-38-2; $Na_6[H_2W_{12}O_{40}]$, 12141-67-2; $Na_6[D_2W_{12}O_{40}]$, 82752-42-9; $H_5[BW_{12}O_{40}]$, 12297-12-0; $Na_8[SiW_{11}O_{39}]$, 82691-59-6; $Na_6[P_2W_{18}O_{62}]$, 82797-11-3; α-Na_{10}-$[P_iW_{17}O_{61}]$, 82797-10-2; α_2-$Li_7[P_2W_{17}VO_{62}]$, 82797-09-9; $Li_7[PW_{11}O_{39}]$, 82691-60-9; ^{183}W, 14265-81-7.

Determination of the Onset of the Dezincification of α-Brass Using X-ray Photoelectron (ESCA) Spectroscopy

T. L. Barr* and J. J. Hackenberg[†]

Contribution from the Corporate Research Center, UOP Inc., Des Plaines, Illinois 60016.
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Abstract: The initial effect observed during the dezincification of air-passivated α-brass in simulated seawater is the migration of Zn^{2+} from the alloy, through the passivation layers, to form an overlayer of ZnO. Subsequent layer thickening, selective oxide dissolution, and island formation are also documented. A general mechanism is proposed.

Dezincification of Cu–Zn brasses is a classic corrosion problem[1] for which the mechanism is still not entirely understood.[2] Extensive studies during the early part of this century indicated two possible mechanisms for the process:[2] (1) the preferential migration of zinc to the surface of the brass with its subsequent removal by fluid flow[3] and (2) the uniform dissolution of the alloy into the fluid with subsequent selective precipitation of Cu onto the alloy surface as a porous (spongy) Cu, leaving the Zn behind in solution.[4] The present consensus appears to favor mechanism 2.[5] However, it has been proposed that both may sometimes occur in sequential fashion.[1] In any case, the area of the brass affected by dezincification is known to exhibit a loss of Zn and the retained Cu, a spongy morphology. The surface in this region often exhibits a white appearance,[1,2] as opposed to the golden yellow characteristic of the unaffected brass. The former occurs primarily when dezincification is achieved in saltwater, and the color change has been attributed to the formation of Cu_2Cl_2.[2] In order to elucidate the mechanism for this process, we studied the onset of the dezincification of α-brasses (percent Cu >70) by using X-ray photoelectron spectroscopy.

Experimental Section

The process was activated by immersing coupons of thin α-brass foils into a simulated seawater solution (3% NaCl by weight), hereafter referred to as "the salt solution". The preimmersion composition of the high-purity foil was determined by X-ray microprobe to be Cu $\simeq$ 74.5% and Zn 24.5 ± 1.0%. Prior to immersion, the foils were permitted to experience "natural passivation" in clean air, i.e., the natural conversion (tarnishing) of the surface Cu(0) and Zn(0) to a thin film of the corresponding oxides (and hydroxides).[6] The details of this natural oxidation have been documented and published elsewhere.[7] Figure 1a demonstrates the layering structure typical of that resulting from the exposure of the α-brasses in question to ambient air. This preliminary process was permitted because "real"-use situations for brass (e.g., condenser tubes, etc.) will invariably expose the passivated rather than the zero-valent surface to the onset of dezincification. The existence of an outer surface rich in copper is a particularly important feature of passivation. This passivated surface should affect the temporal aspects of the onset of dezincification.

Individual coupons of the brass were removed from the salt solution at periodic intervals, rinsed clean (to "fix" the process), dried, examined in an optical microscope, and inserted into the vacuum chamber of the Hewlett-Packard 5950A ESCA X-ray photoelectron spectrometer. The entire transfer process (solution to 1×10^{-9} torr vacuum) was accomplished in a few minutes—a relatively short period compared to the hours of immersion needed to affect significant changes. The present study was accomplished mainly in a static salt solution at 25 ± 2 °C. ESCA profiles were obtained of the coupons during the study (outer dezincified surface to the bulk of the zero-valent alloy) by ion milling using high purity argon. The potential ill effects of ion etching have been noted[6b,7,8] and monitored in this study. No problems significant enough to endanger the general conclusions of this study were found. The details of this aspect of the study will be presented elsewhere.[9a] The fortuitous similarity in the atomic masses of Cu and Zn assisted in this aspect of the study.

The pH of the immersion solution was monitored during these experiments and found to remain slightly acidic, pH 6.0 ± 0.5, throughout. The pH will, of course, affect the mobility and type of ions formed in solution and also at the interfaces, particularly if the principal process is electrochemical. Under the latter circumstances, it would be instructive to try to identify the parts of the metal surfaces functioning as the electrodes and also to monitor the distribution of products under various pH settings, since extreme variations could dramatically effect the reported results. These feature are left for future studies.

The results to be described were generated from ESCA observations of selected 5 × 1 mm regions on the surfaces of the aforementioned polycrystalline alloy foils. The results were thus selective and yet deemed to represent a *statistical average* of those realized by the *total* alloy surface. This assumption is based, in part, upon the microscopic observation that the grain size of the alloys employed was found to be extremely small (<4 μm) and relatively uniform. The materials were also periodically examined by optical microscopy (during treatment), and no preferential sites of reaction were detected in the area of observation. Thus, it should be realized that any preferential metallurgical events (e.g., grain boundary migration vs. mobility inside of the grains) that no doubt occur are undetected in this study *but* should be uniformly weighted in the results by the relatively large field of observation. For this reason,

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[†] Present address: Harris Semiconductor Group, P.O. Box 883, Melbourne, FL 32901.

(1) Evans, U. R. "The Corrosion and Oxidation of Metals"; Arnold: London, 1960; pp 471–80.

(2) Gilbert, P. T. "Corrosion"; Shreir, L. L., Ed.; Butterworths: London, 1976; Vol. 1.

(3) Pickering, H. *J. Electrochem. Soc.* **1970**, *117*, 8.

(4) Lucy, V. F. *Br. Corros.* **1965** *1*, 9; **1965** *1*, 52.

(5) Boyer, H. E., Ed. "Metals Handbook", 8th ed.; American Society for Metals: Metals Park, OH, 1975; Vol. 10, pp 175–77.

(6) (a) Barr, T. L. *J. Vac. Sci. Technol.* **1977**, *14*, 660. Barr, T. L. "Quantitative Surface Analysis of Materials"; McIntyre, N. S., Ed., ASTM: Philadelphia, PA, 1978; STP 643, pp 83–104. (b) Barr, T. L. *J. Phys. Chem.* **1978**, *82*, 1801.

(7) Barr, T. L.; Hackenberg, J. J., *Appl. Surf. Sci.*, in press.

(8) Greene, J. E.; Klinger, R. E.; Barr, T. L.; Welsh, L. B. *Chem. Phys. Lett.* **1979**, *62*, 46.

(9) (a) Barr, T. L., to be submitted for publication. (b) The term "surface" refers here to the outer layers of a solid with thickness of ~30 Å, i.e., the approximate "observation depth" of the ESCA.

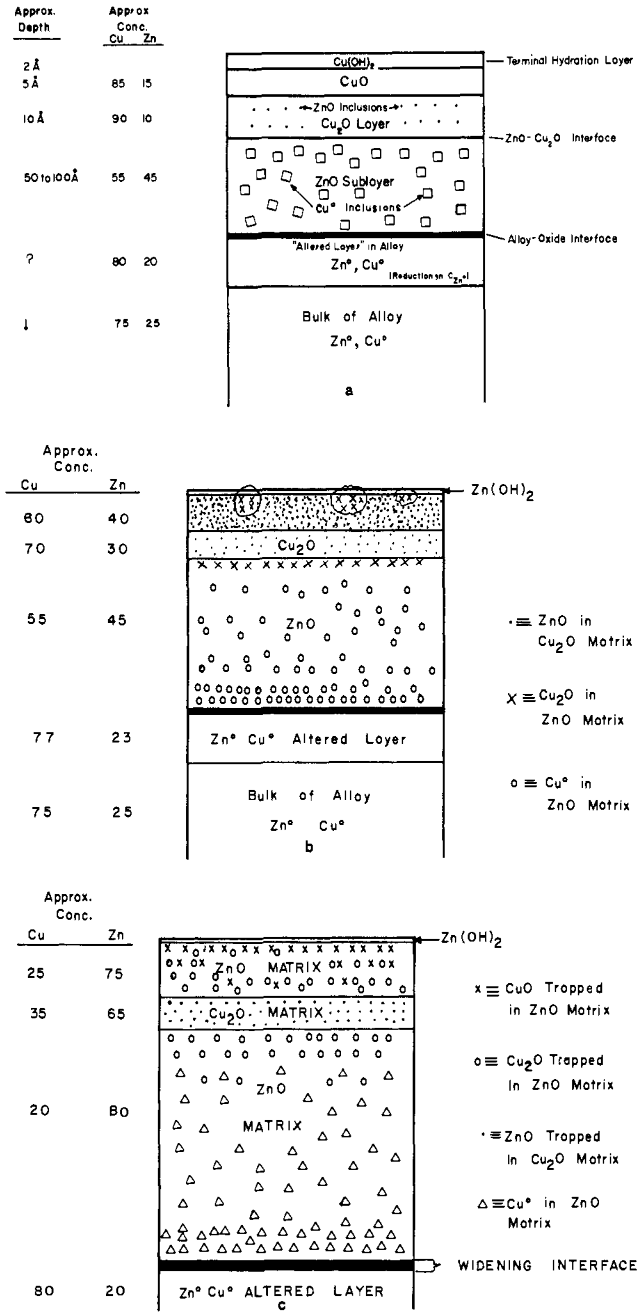

Figure 1. Generalized oxide-layer schemes for α Cu–Zn: (a) air passivated; (b) after several hours in simulated seawater; (c) after several days in seawater.

any considerations as to the specific *metallurgical* aspects of these results (grain boundary migration, etc.) must be viewed as *speculations* based largely upon other experiences.

Results

Immersion of the α-brass produced a relatively rapid, persistent change in the surface[9b] and subsurface of the passivated alloy. Deciphering all the ESCA results was complicated by several confusing features inherent to some of the spectra. The most difficult feature was the lack of a definitive chemical shift in the principal (2p) photoelectron lines of Cu and Zn when the chemical status changed from oxide to zero-valent material. Considerations of these complications and their circumvention have been discussed in detail elsewhere;[7,9,10] suffice it to say that the problem may be solved by studying the X-ray-induced Auger lines for selective qualitative chemical analysis (e.g., Figure 2a) and the near-valence-band (3d) lines for relative quantitative analysis (e.g., Figure 2b). Monitoring the total spectrum for the possible anions (e.g., O, Cl) greatly assisted in this analysis. A list of the most important binding energies and line widths utilized in this study are contained in Table I. Readers interested in more of the XPS details should consult ref 7 and 9.

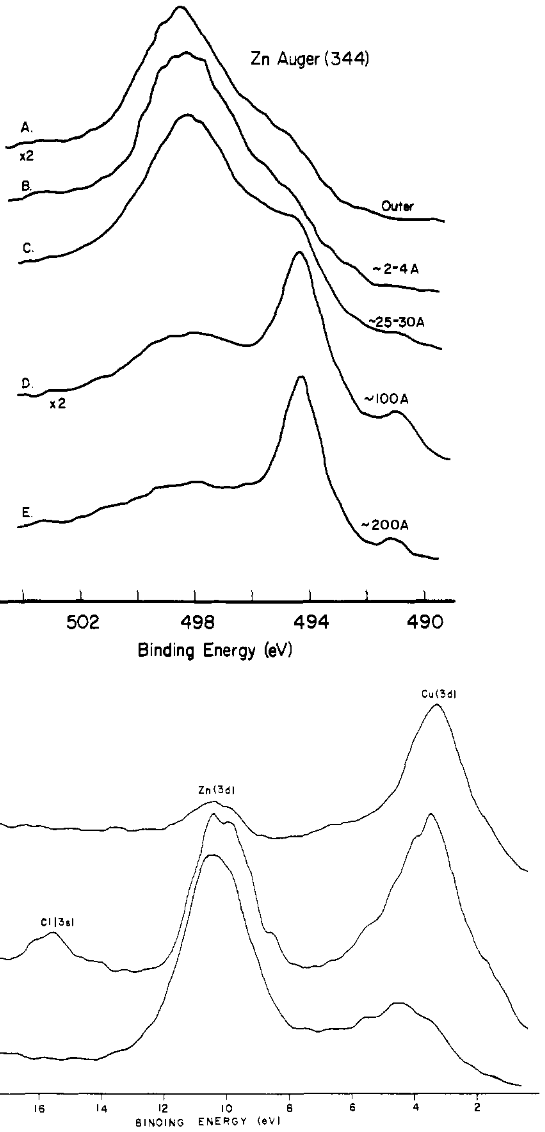

Figure 2. (a) Zn (Auger) lines for α Cu–Zn during natural passivation. Note relative extent of the ZnO layer. (b) Representative Zn(3d) and Cu(3d) lines during progressive Zn precipitation. (I) Before immersion; (II) after 18 h in salt solution; (III) after 240 h in salt solution. Note changes in Cu chemistry and Cl⁻ impurity following incomplete rinse.

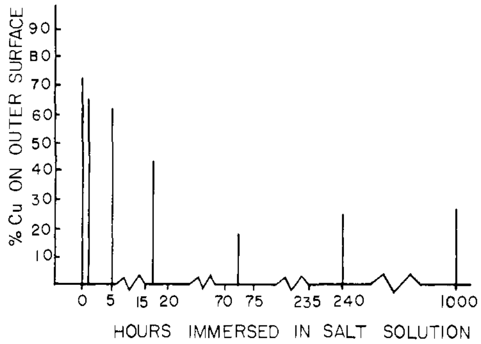

Figure 3. Relative percent Cu detected on the outermost surface of Cu_{75}–Zn_{25} vs. hours of immersion in salt solution.

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(10) Wertheim, G. R.; Compagna, M.; Hilfner, S. *Phys. Condens. Matter* **1974**, *18*, 133.

Table I. Selected Binding Energies and Line Widths (in Parentheses) in Electronvolts for Reference Systems

	polycrystalline Cu(0)	Cu_2O	CuO	$Cu(OH)_2$	Zn(0)	ZnO	$Zn(OH)_2$	α Cu–Zn outer (totally) passivated	α Cu–Zn ~ 200 A sputter cleaned
$Cu(2p_{3/2})$	932.47 (1.01)	932.5 (1.2)	933.7	934.75				932.6 [5][a] 934.3 [2] 935.2 [1]	932.75
$Zn(2p_{3/2})$					1021.6 (1.78)	1022.1	1022.3	1021.9 (2.15)	1021.5
Zn(344) Auger					494.3	497.8	498.5	498.4	494.25
O(1s)		530.3	530.3	531.7		530.3	531.35	531.8 [5] 530.4 [2]	530.8 [small]
C(1s)		285.4	285.5	285.5	284.5	284.4	284.4	285.0	
oxidation states of major components								$Cu^{2+} + Cu^{+}$ $Cu^{2+}/Cu^{+} \simeq {}^{3}/_{5}$ Zn^{2+}	Cu(0) Zn(0)

[a] [ ] = selected relative intensities.

A number of surface and subsurface features changed dramatically during the onset of dezincification. Foremost among these changes was the near-exponential decrease in the outer surface Cu/Zn ratio, Figure 3. During the drop in this ratio from 7/2 to 1/5, the color of the outer surface changed from light yellow to a mixture of yellow and white-gray. The previous attribution of a similar color change to the appearance of (white) Cu_2Cl_2 seems in error since no significant Cu_2Cl_2 (surface or solution) was ever detected during the present study. Rather, it is here proposed that this surface discoloration was due to the appearance on the surface of substantial quantities of (white) ZnO. The "leveling off" of the decrease in surface Cu/Zn eventually stunted this color change.

Immersion of the alloy into pure H_2O produced only slight changes in the ratios and chemical compositions of the layers. Immersion of the coupons into the NaCl solution, on the other hand, rapidly produced the previously mentioned Zn-rich outer surface. Initially (after 5 and 18 h) this outer ZnO surface not only covered the (relatively) thin copper oxide rich layer but also continuous exposure to the salt solution seemed to progressively deplete some of the Cu in the latter layer. This process of Cu removal eventually stopped, however, and the Cu-rich layer began to rethicken in an inward direction, i.e., the point of maximum percent copper oxides gradually moved further into the subsurface of the alloy. In general, depth profiles into the oxidized layers of the various coupons revealed extensive and progressive migrations and growths, apparently brought on by the presence of the salt solution.

The identities of the constitutents formed on the naturally passivated surface are contained in Figure 1a.[7] Most of the compounds formed following immersion in the salt solution were chemically the same as those formed on the alloy after exposure to air; i.e., little evidence of chemical reaction between alloy and NaCl was observed. The differences observed were largely those of layer ordering and thickness. Thus, for example, both the Zn-rich layers formed on the other surface and that located in the subsurface contained almost exclusively ZnO as the sole Zn compound (some $Zn(OH)_2$ on the outer surface may be present!). The aforementioned subsurface Zn–rich layer, containing predominately ZnO, thickened dramatically with increasing exposure to the salt solution. Interestingly, the presence of ZnO continued to be observed as one sputtered into the subsurface until unoxidized alloy was reached, where the Cu/Zn ratio first appeared somewhat larger than and finally equal to that for the bulk zero-valent [Cu(0)Zn(0)] alloy.

The interface between the oxidized and zero-valent species was never a sharp discontinuity, and this overlap of layers grew dramatically with increasing exposure to the salt solution; see, for example, Figure 4.

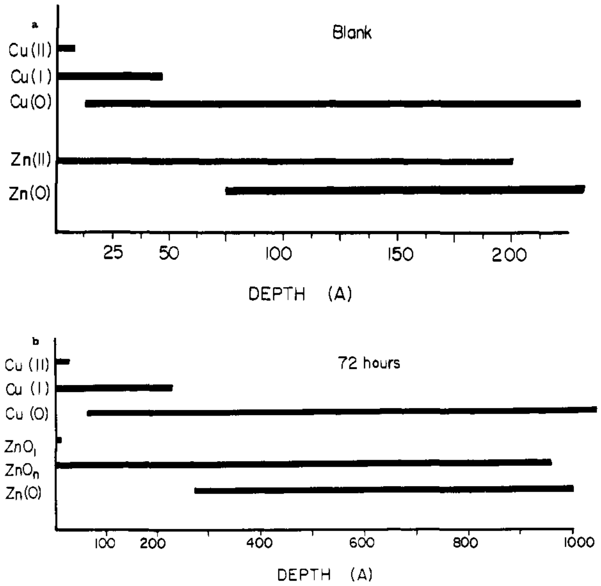

Figure 4. Relative layer thicknesses and their overlaps for (a) air-oxidized Cu–Zn and (b) after extensive exposure to the salt solution.

The copper species found in the oxidized layers changed with depth in the coupons and exposure to the salt solution. The outer surface Cu(II) species that formed on the naturally passivated coupon seemed eventually to dissolve when exposed to saltwater and perhaps pure H_2O. However, a Cu(II) outer layer began to form again after exposure for >18 h to the salt solution. This new Cu(II) layer was apparently due to precipitation of Cu from solution and perhaps oxidation of Cu(I) (see below). In both cases, the Cu(II) species on the outer surface seemed to be mainly $Cu(OH)_2$[11] covering small amounts of CuO. The total amount of CuO had to be small, due to the relatively light color of the outer surface, even after extensive exposure to salt solution. The subsurface Cu(I) layer (mainly Cu_2O) seemed to thicken gradually with exposure to the salt solution (Figure 4). The red spots seen on the outer surface of the coupon after extensive exposure were probably Cu_2O. The interface between Cu(I) and Cu(0) also seemed to overlap more and more significantly with increasing exposure to the salt solution, Figure 4.

Certain changes in the observed binding energies due to charge shifts[12] were used to provide a crude index of the progressive structural changes being experienced during the lateral growth of the oxides on the outer surfaces of these coupons.[13] The copper oxides (particularly Cu_2O) are sufficiently good conductors to prevent significant charging during photoelectron ejection. The ZnO, on the other hand, is generally less receptive to surface electronic conductivity, and in the H. P. (Hewlett-Packard) ESCA, this species may produce binding energy shifts as large as 3 eV. As a result of these various effects, mixings of the structural arrangements of the copper and zinc systems may result not only in charging shifts but also in *differential* charging shifts.[12] Thus,

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(11) Larsen, P. E. *J. Electron Spectrosc. Relat. Phenom.* **1974**, *4*, 214.
(12) See, for example: Barr, T. L. *Am. Lab.* (*Fairfield, Conn.*) **1978**, *10*, 65. Barr, T. L. *Ibid.* **1978**, *10*, 40.
(13) Barr, T. L. *Chem. Phys. Lett.* **1976**, *43*, 89.

if the principal arrangement of surface species is such that conductive contact to the spectrometer is maintained through copper oxides and all (or nearly all) of the zinc oxides are uniformly (and relatively lightly) dispersed throughout this copper oxide matrix, then *no* significant charging shifts will be observed. This was indeed the case obtained for the outer surface of naturally passivated α-Cu–Zn (Figure 1a) and also for the alloy after exposure to a static salt solution for less than 18 h. After 18 h of exposure to the salt solution, the buildup in ZnO concentration on the surface was apparently too large for *all* of it to be dispersed uniformly throughout the conductive copper oxide matrix. Stable clusters of insulating ZnO were apparently formed. This feature was indicated by the appearance of a differential charge shift; i.e., the ZnO that was relatively well distributed in the copper oxides exhibited no appreciable charge shift, whereas the ZnO that had clustered displayed a charge shift. As more and more ZnO was isolated to the surface, a larger and larger percentage of the ZnO began to experience charge shifts. After ~240 h of exposure to the salt solution, essentially all of the ZnO ESCA spectra revealed charge shifts, i.e., total island growth.[13] The small amount of copper oxides on the surface must at that point have been encapsulated by the ZnO clusters; thus the former also lost its surface conductivity as a result of being surrounded by an insulator and exhibited a charge shift.[13] In all cases, application of the H. P. Electron Flood Gun completely removed the above-mentioned charge shifts. Details of this aspect of the study will be published elsewhere.[9]

The 3% NaCl solution was also analyzed at several points during use to try to determine the amount and relative percentage of Cu and Zn that were dissolving off of the surface of the coupons. It was discovered that the amounts of Cu and Zn detected were never greater than several parts per million. The relative concentrations were difficult to determine exactly; however, the values obtained indicated that initially either (1) a small amount of the surface Cu–Zn alloy was dissolving "uniformly" with exposure to the salt solution or (2) slightly more Zn was dissolving than Cu. After extensive exposure to a coupon (~1200 h), the salt solution revealed a 1:10 Cu/Zn ratio, thus verifying the preferential removal of Zn.

No significant impurities other than Na^+ and Cl^- were detected during the ESCA analysis. No pattern arose for retention of those ions. When Na^+ and Cl^- did occur, they appeared in ~1:1 ratios, indicating little or no selective chemical involvement with other species and that their presence was probably due to incomplete washing of the coupons.

Discussion and Conclusions

General Summary. Many of the features of the *initial stages* of dezincification of α-brass may be delineated from these results. In general, one may conclude that exposure of a naturally passivated α-brass to the aforementioned salt solution rearranges and thickens the various oxidized layers but does not produce any significant amount of new products. Thus, during these initial stages of dezincification, *no* metal halides or unusual oxidation states for oxides or hydroxides were observed.

The thickening and rearrangement of the oxidized products produced by the salt solution are extensive, as can be seen by examining the summary depicted in Figure 1c. These features have been shown to result mainly from the presence of the 3% NaCl in the "attacking" solution, wherein the saline solution seems to produce an (anodic) field gradient rather than entering directly into the chemical process. The rearrangements mentioned above are primarily characterized by the appearance on the outermost oxidized surface of relatively large quantities of ZnO. The switch of the outer oxidized surface from one primarily composed of copper oxides (naturally passivated surface) to one primarily of ZnO (beginning after a few hours and essentially completed after 72 h of exposure to salt solution) is continuous and fairly rapid. Despite the growth of a zinc-rich cover, the visible copper near the outer surface of the alloy remains oxidized, and where this oxidized Cu appears, it generally exists in a layer in which the Cu/Zn ratio is at a maximum for the oxidized layers. A sublayer of oxidized ZnO mixed with small amounts of Cu(0) is found to exist below the oxidized Cu in both naturally passivated and dezincified brasses. In addition, the thickness of all layers (particularly the sublayer ZnO) and the overlap of the layers increase dramatically with increasing exposure to salt solution. The ZnO that formed on the outer surface eventually exhibits sufficient clustering to form insulating islands that produced charge shifts appearing in the ESCA spectra of both the clustered ZnO and the encapsulated copper oxides.

There is evidence that some of the copper oxides present in the outer (protective) passivation layers are initially dissolved by both the water and the salt solution. The cupric salts seem to completely dissolve (see the results after 5 h of exposure to the salt solution) whereas the relatively insoluble Cu_2O is generally retained on the coupon. This effect must, however, eventually cease, as further exposure of the coupons to the salt solution produces an apparent re-formation and thickening of all copper oxides, with a relatively thick layer of Cu(II) formed mixed in with the newly formed outer surface of ZnO, see Figure 4.

A Mechanism for the Initial Stages of Dezincification. Before suggesting a mechanism for this process, it is necessary to try to determine how the resulting oxides may be formed. In particular, one must select from among several possible atomic migrations that may occur, e.g., (1) oxygen, (2) zinc, (3) copper, or (4) some combination of the first three. It is impossible to make an unequivocal selection, but a combination of the results obtained strongly suggests the following conclusions:

(1) The thickening of the oxidized layers demands that oxygen and bulk zero-valent metal (particularly zinc) must be getting together in an environment conducive to oxidation.

(2) The environment mentioned above must include an extensive pattern of ionic and/or possible atomic (Wagner type)[1,2,14a] diffusion through the intervening oxide layers.

(3) A migration of oxygen (primarily ionic) to the Zn(0)[15] will not produce the outer layer of ZnO unless the initial process is the dissolution of the protective copper oxide layers. Analysis of the salt solution indicates, however, that more Zn is dissolving than Cu.

(4) A preferential migration of oxygen to the Zn(0) will produce a thickening of the sublayer ZnO *but* will also retain at the surface the existing (~3:1) ratio of Cu/Zn, *unless* this process is accompanied by a migration toward the outer surface by Cu. No evidence exists either in the form of copper oxide layers or dissolved copper to support the preferential inward migration of oxygen.

(5) *There is apparently no extensive migration of Cu to the surface.*

(6) *Therefore, the extensive, preferential migration of Zn through the oxide layers is predicted by the results of this study.*

(7) A secondary mechanism may be necessary to explain the migration of either Zn or ZnO through the copper oxide layer to the outermost surface of the dezincified brass. The latter process may occur before the thickening of the sublayer of ZnO begins. *All of this suggests that Zn(II) is the (primary) migrating species during these processes.*

(8) The migration of zinc to the outer surface during this initial phase of dezincification seems to desist after the Cu/Zn ratio has dropped to ~1:4.

(9) *On the basis of these results, one cannot preclude the possibility of the simultaneous incursion (inward migration) of some oxygen into the alloy layers accompanying the outward migration of Zn.*

(10) Although Zn migration is preferred, metastability suggests some outward migration of Cu. The latter is required in order to maintain the presence of Cu and copper oxides in the growing ZnO layers.

These results and their analysis permit the development of a probable "summary" mechanism for the *initial stages* of the

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[14] Wagner, C. *Z. Phys. Chem., Abt. B* **1933**, *21*. Wagner, C. *J. Electrochem. Soc.* **1956**, *103*, 627.

[15] The term Zn(0) is employed to symbolize the Zn at the alloy–oxidized-layer interface.

Table II. Stages of Development of Dezincification of Naturally Passivated Cu_{75}–Zn_{25} in 3% NaCl

(1) Migration to subsurface and surface of Zn^{2+} from bulk alloy to form ZnO.
(2) Dissolution of some of the protective (passivating) oxides: (A) all Cu^{2+} quickly dissolved (~5 h, 3% NaCl); (B) a little of the Cu^+ may dissolve; (C) some of (original) ZnO also dissolves
(3) Extensive thickening of ZnO sublayer.
(4) New, thicker Cu oxide layer forms below surface layer of ZnO.
(5) Overlap of layer boundaries increases dramatically.
(6) Termination of surface secretion of Zn.
(7) Island growth of clusters of ZnO at outer surface incapsulating some Cu oxides.

dezincification of α-brass under these conditions. The stages of this process are expressed in Table II. Detailed arguments for the above conclusions will appear elsewhere.[9]

An important, as of yet unanswered, question concerns the *source* of the oxygen that produces the extensive growth of oxidized Zn (and Cu) revealed during the onset of dezincification. As mentioned above, this oxygen, no doubt, also plays a major role in the diffusion of the ions (or atoms) that necessarily precedes oxide formation. Unfortunately, at present, no definite conclusion may be drawn concerning this question; however, the experimental features do permit reasonable speculations about the oxygen source. First, it is apparent that the oxygen in question must arise during one (or more) of three possible periods: it is (1) adsorbed before immersion, (2) picked up during immersion, or (3) adsorbed following immersion but before insertion into the spectrometer. The first source is probably not important since there is too little unreacted oxygen on the outersurface of the passivated alloy to produce the relatively thick oxide layers realized after immersion. The progressive thickening of the oxide layers formed during increased exposure to the salt solution would seem to exclude both (1) and (3) as major sources of the reactive oxygen. In addition, dramatic variations in the exposure of the coupons to oxygen during stages 1 and 3 did not seem to affect any of the dezincification growth features. It seems certain, therefore, that most (if not all) of the oxygen producing the oxides formed during the onset of dezincification comes into contact with the passivated brass during the immersion in the salt solution. This does not answer the question of the *source* of the reactive oxygen, which may come from either dissolved O_2 or the electrochemical breakdown of H_2O. It has already been demonstrated that the dezincification process in question is of electrochemical rather than chemical origin. Thus, the NaCl solute is needed in order to produce the reactions (in the time frame of the present study). Crude attempts to simulate real seawater by agitating the solution during immersion altered the rate of growth and apparent thickness but not the ordering of the layers. These observations seem to favor a reaction based upon dissolved oxygen; however, further, more carefully controlled experiments (during which the amount of dissolved O_2 is both measured and varied) are needed to unequivocally establish the source.

In addition to the uncertainty as to the source of the oxygen, it should be noted that the present study concerns only the behavior of naturally passivated α-brass during the *initial* stages of dezincification as produced under conditions that crudely simulate *static* seawater. The results and proposed mechanism may be significantly different if (1) the zero-valent [Cu(0)Zn(0)] surface is the one exposed to the salt solution; (2) other types of Cu–Zn brass (e.g., α-β, β, Admiralty, etc.) are employed in the process; (3) a controlled turbulent solution (more representative of true seawater) is employed; (4) single-crystal Cu–Zn faces or large grain-sized surfaces of the polycrystalline brass are used; (5) other metallurgical aspects such as the number of defects and the state of cold working are markedly varied; and/or (6) the pH and temperature of the solution are varied. Studies in these various areas are needed before a completely general mechanism for the onset of dezincification may be realized.

Registry No. α-Brass, 82823-80-1; ZnO, 1314-13-2.

A New Type of Trinuclear Cluster Compound: The Incomplete Bicapped (or Hemicapped) Structure in $[W_3O(O_2CCH_3)_6(H_2O)_3]ZnBr_4{\cdot}8H_2O$

Michael Ardon,*[1a] F. Albert Cotton,*[1b] Zvi Dori,*[1c] Anne Fang,[1b] Moshe Kapon,[1c] George M. Reisner,[1c] and Miriam Shaia[1c]

Contribution from the Department of Chemistry, The Hebrew University, Jerusalem, Israel, The Technion-Israel Institute of Technology, Haifa, Israel, and the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received December 29, 1981*

Abstract: Small amounts of a new, dark blue, tritungsten cluster cation have been obtained as a byproduct in the preparation of the well-known $[W_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion. This new species has been isolated in the form of the isomorphous $[W_3O(O_2CCH_3)_6(H_2O)_3]MBr_4{\cdot}8H_2O$ compounds (M = Fe, Zn), and the structure of the zinc-containing compound has been fully determined by X-ray crystallography. The crystals belong to space group $C2/c$ with the following unit cell dimensions: a = 13.218 (4) Å, b = 16.231 (5) Å, c = 17.722 (5) Å, β = 105.34 (3)°. The calculated density, 2.711 g cm^{-3}, for the above formula (Z = 4) agrees well with that measured, 2.717 g cm^{-3}. The trinuclear cation has crystallographic 2 (C_2) symmetry, but approximates closely to C_{3v} symmetry, with the following average principal dimensions (Å): W–W, 2.710 [4]; W–O(cap), 1.96 [2]; W–O(acetate), 2.07 [1]; W–O(H_2O), 2.16 [1]. The electronic structure of the hemicapped species can be considered similar to that of the bicapped species except that in place of three bonds to a second capping atom there is an empty e orbital and a filled a_1 orbital that has a moderate bonding character with respect to the W_3 triangle.

Work in these laboratories[2-7] and elsewhere[8-11] within the past few years has shown that the elements molybdenum and tungsten,[12] in oxidation states of IV or thereabouts, have a marked predilection to form trinuclear cluster species. What is even more

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(1) (a) The Hebrew University. (b) Texas A&M University. (c) The Technion-Israel Institute of Technology.

(2) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.

(3) Bino, A.; Cotton, F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L133.

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