Dezincification of Alpha Brass*

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Dezincification of α -brass, which is one of the most prominent cases of selective corrosion, has been investigated by the electron diffraction method. To explain the process of the dezincification, two hypotheses are considered, one of which can very likely explain our experimental results.

In the early stage of the dezincification, sharp diffraction rings from copper begin to appear together with those from the α -brass which is the initial specimen. With the progress of the dezincification, the intensities of the copper diffraction rings increase gradually and those of α -brass decrease. The dezincified α -brass layer composed of pure copper has a textural property similar to, but not strictly the same as, that of the initial specimen.

It is concluded that the process of the dezincification is the result of dissolution of α -brass into corrosive solutions followed by re-deposition of copper on the specimen surface.

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I. Introduction

It has so far been reported by a number of investigators that some alloys are subject to selective corrosion in a corrosive atmosphere, for example, selective dissolution of magnesium from copper-magnesium-tin alloys and copper-magnesium-cobalt alloys⁽¹⁾, selective corrosion of cobalt from stellite No. 1⁽²⁾ and dealuminification of aluminium bronze⁽³⁾. The most prominent case of selective corrosion is dezincification of copper-zinc-alloy systems.

For the industrial use, care must especially be taken to prevent the dezincification of brass. When the dezincification occurs, the surface of the brass is replaced by a porous mass of copper which, though retaining the shape of the original surface, has virtually no strength. There have been many previous discussions⁽⁴⁾ as to whether the process occurs by selective corrosion of zinc in the brass leaving copper behind or by complete dissolution of the brass followed by re-deposition of copper. However, no concrete conclusion has ever been obtained for the process of dezincification.

The dezincification phenomenon has been studied in the present experiment by the electron diffraction method. A definite conclusion for the process of the dezincification has been obtained from a consideration of the compositions of both the substrate alloy and the dezincified layer, and their mutual crystallographic relation.

II. Experimental Procedure and Results

Specimens employed were α -brass, the chemical analysis of which showed 31.28 % zinc content. The

specimens were rolled to a thickness of about 1 mm. The investigation about the mechanism of the dezincification was started by observing the surface structure by means of the reflection electron diffraction method. A clear conclusion, however, was difficult to be drawn from this observation, since strong background intensity and diffuse diffraction rings impeded a clear resolution of the diffraction rings from α -brass and copper. Thus the transmission electron diffraction method was adopted instead of the reflection method. α -Brass of the above-mentioned composition was rolled to a thickness of about 10 μ and then chemically thinned with a solution of 50 % 6 N-HNO₃ and 50 % CH₃OH until films of several hundred angstrom in thickness were obtained.

Photo. 1 Electron diffraction pattern of alpha brass (31.28 % Zn). Lattice constant ; 3.680 ± 0.005 Å.

An electron diffraction pattern from this alloy film shown in Photo. 1 indicates a f.c.c. structure with a remarkable rolling texture. Employing gold as standard

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(1) W. W. Mitchell : Metal Progress, 28 (1935), 40.

(2) M. G. Fontana : Ind. Eng. Chem., 39 (1941), 87 A.

(3) M. Shussler and D. S. Napolitan : Corrosion, 12 (1956), 107 t.

(4) cf. U. R. Evans : "Metallic Corrosion Passivity and Protection", London, Ed. Arnold & Co. 1946. F. W. Fink : Trans. Electrochem. Soc., 75 (1939), 441. E. P. Polushkin and H. L. Shuldener : Trans. Am. Inst. Mining Met. Engrs., 161 (1945), 2104.

* Weak deffraction rings were observed besides those of the alloy. The former seem to be caused by unknown corrosion products.

substance (lattice constant : $4.078 \text{ \AA}$), the lattice constant obtained from Photo. 1 was $3.680 \pm 0.005 \text{ \AA}$, which was in good agreement with the value of $3.688 \text{ \AA}$ which was calculated from the alloy of the same composition from the relation between the lattice constant and composition determined by the X-ray diffraction method⁽⁵⁾. Therefore, Photo. 1 was confirmed to be the electron diffraction pattern from α -brass with 31.28 % zinc content. The same alloy as that which gave this electron diffraction pattern was employed as the initial specimen throughout the present experiments. When the initial specimen was etched with a 2 % NH_4Cl aqueous solution at room temperature, a part of the surface assumed a red color, whereby the occurrence of the dezincification was recognized. Photo. 2 shows an electron diffraction pattern from the specimen in this

Photo. 2 Electron diffraction pattern of dezincified alpha brass, showing the first stage of dezincification. Rings of copper appear with weak intensity on the outside of those of alpha brass.

state. It is noted that diffraction rings of a f.c.c. structure appear on the outer sides of diffraction rings from α -brass, that is, a new substance with a lattice constant slightly smaller than that of α -brass is formed. When the dezincification proceeded further, the two sets of diffraction rings appeared to have comparable intensities as shown in Photo. 3, and finally the diffraction rings of the new substance became predominant as shown in Photo. 4. The lattice constant of this substance obtained from Photo. 4 was $3.610 \pm 0.005 \text{ \AA}$ and was in good agreement with that of copper ($3.6147 \text{ \AA}$) which was obtained by the X-ray diffraction method⁽⁶⁾. In addition, the two lattice constants obtained from Photo. 3 were $3.680 \pm 0.005 \text{ \AA}$ for the inner rings and $3.615 \pm 0.005 \text{ \AA}$ for the outer ones. These values indicate that the outer rings are due to copper and the inner ones to α -brass of the initial specimen. A schematic representation of these electron diffraction patterns from dezincified α -brass is shown in Fig. 1. The electron diffraction patterns composed

of two sets of diffraction rings from α -brass and copper were obtained from 20 specimens dezincified. Relative intensities of the two sets of diffraction rings, however, varied from specimen to specimen depending on the grade of dezincification.

Photo. 3 The middle stage of dezincification. Diffraction rings of alpha brass and copper appear with comparable intensities.

Photo. 4 The last stage of dezincification. Diffraction rings of copper are dominant.

Besides these results, photomicrographs of these specimens in Photo. 5 showed that remarkable boundaries were present between the brass and the red-colored dezincified layer. Based upon the above facts, it is evident that, when the dezincification has occurred, both α -brass of the initial specimen and pure copper free from zinc are found in the specimen, and α -brass with a smaller amount of zinc than the initial specimen was not found in the boundaries.

It is of interest that the pure copper layer formed by the dezincification showed a textural property resembling that in the initial specimen. However, the intensity

(5) E. A. Owen and E. W. Roberts : *Phil. Mag.*, **27** (1939), 294.

(6) M. Straumanis and O. Mellis : *Z. Phys.*, **94** (1935), 184.

curve of diffraction rings (Fig. 2) measured by a microphotometer along the direction of the arrow in Photo. 3 indicated that the ratio of the diffracted intensity from α -brass to that from copper in a couple with the same indices varies from couple to couple.

Fig. 1 Schematic representation of the electron diffraction pattern from dezincified alpha brass.

Photo. 5 Microstructure of dezincified alpha brass.

Fig. 2 Variation of diffraction intensities measured from Photo. 3.

This fact shows that the textural properties in the copper and the initial specimen are slightly different from each other.

It has been reported⁽⁷⁾ that the dezincification can not be verified in α -brass whose zinc content is less

than 15 %. This was also confirmed by the present experiment, because no diffraction pattern from the copper was observed when a specimen containing 10.00 % zinc was corroded for 7 days in a 3 % NH_4Cl aqueous solution. On the other hand, the specimen

Photo. 6 Diffraction pattern of dezincified alpha brass (20.04 % Zn).

with about 20 % zinc showed the diffraction rings from both copper and α -brass, as shown in Photo. 6.

III. Discussion

As known by Vegard-Dale's law for binary solid solutions, the lattice constant changes almost linearly with variation of concentration. In the α -brass region of a f.c.c. structure, the lattice constant changes with the variation in zinc content as shown in Fig. 3⁽⁵⁾⁽⁶⁾.

Fig. 3 Variation of lattice constant with zinc content.

For the processes of the dezincification, the following two hypotheses have been proposed : (1) Selective dissolution of zinc from α -brass into the aqueous solution, (a) leaving copper behind and (b) followed by surface

(7) G. T. Colegate : Metal Ind., **73** (1948), 483.

(8) G. D. Bengough and R. May : J. Inst. Met., **32** (1924), 81.

migration of atomic copper and formation of a copper crystal lattice at energetically stable sites. (2) Complete dissolution of α -brass, followed by re-deposition of copper on the specimen surface.

It has so far been confirmed that the dezincification does not occur during the rapid flow of a solution. Therefore, the process (1) is improbable, because this process includes only dissolution of zinc and hence is not inhibited by stirring of the solution. The process (1-a) especially contradicts the experimental evidence, because, according to this process, the zinc contents of α -brass decrease with dissolution of zinc, and then the lattice constant becomes smaller than that of the initial specimen. With the progress of the dezincification, therefore, the lattice constant gradually change with the value corresponding to the initial specimen towards that of copper along the line in Fig. 3, or since the concentration of zinc varies in α -brass from place to place, alloys of various concentrations would exist in the specimen. This fact would cause broad diffraction rings due to the continuous change of the lattice constant. In the present experiment, however, two sets of sharp rings appeared simultaneously in the early stage of the dezincification, and only the relative intensities of two sets of diffraction rings changed with the progress of the dezincification.

If the dezincification follows the process (2), the specimen surface will be composed of two parts separated by clear boundaries with the progress of the dezincification. One of these is α -brass of the initial specimen and the other is that formed by re-deposited copper. Therefore, only two sets of diffraction rings from the initial specimen and re-deposited copper are expected to be found in the electron diffraction pattern. Furthermore, it is more likely that, with the progress of the dezincification, the diffraction rings from copper become more and more intense than those from α -brass. As mentioned above, the present experimental results well coincide with such expectations. It follows, furthermore, from the process (2) that copper ions are always accumulated in the vicinity of the specimen

surface. If this is the case, the stirring of the solution will inhibit the dezincification. As already stated, this is also supported by the experimental evidence. Consequently, it may be concluded that the dezincification of α -brass proceeds following the process (2) i.e., complete dissolution of α -brass from the specimen surfaces into a corrosive solution takes place, followed by re-deposition of copper on the specimen surfaces. This conclusion is in agreement with a previous investigation carried out electrochemically by Bengough and May⁽⁸⁾. They reported that copper was re-deposited with a surface structure similar to that of α -brass before dissolution. In the present experiments, a texture similar to that of α -brass of the initial specimen also appeared in the copper formed after complete dezincification, but the two textures were slightly different from each other. This difference also supports the process of re-deposition of copper.

IV. Summary

The transmission electron diffraction method is effective for investigating selective corrosion.

In the early stage of dezincification, sharp electron diffraction rings from copper begin to appear with rings from α -brass of the initial specimen. With the progress of the dezincification, the intensities of the diffraction rings from copper increase gradually and those from α -brass decrease. The copper layer, dezincified from α -brass has a textural property similar to, but not strictly the same as, the initial specimen.

It is concluded that the process of the dezincification is a complete dissolution of α -brass into corrosive solutions, followed by re-deposition of copper on the specimen surfaces.

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