Notes on Etching and Microscopical Identification of the Phases Present in the Copper-zinc System

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A large amount of time has been devoted to the microscopical study of the copper-zinc alloys, emphasis naturally being placed upon the commercially important alloys of the system. Suitable methods are available for microscopically recognizing the two phases richest in copper, but none appear to have been developed for the positive identification of the other phases. This is, however, accomplished, for the phases normally encountered, by an electrolytic method described in the following pages.

Five phases of the copper-zinc diagram (Fig. 1) are considered for the purpose of this paper: the solid solution of zinc in copper, alpha (α); the intermediate phases, beta (β), gamma (γ), and epsilon (ε); and the solid solution of copper in zinc, eta (η). Beta prime is not considered a separate

phase, since, according to Phillips and Thelin, it is probably not a true polymorphic modification of beta. Delta is stable only between the temperatures of 555° and 695° C., and has not been observed in this work.

Identification of Alpha and Beta.—Unstained alpha and beta are easily recognized by their natural colors. The color of alpha varies under the microscope, according to zinc content, from that of pure copper to what may be described as a light flesh color. Beta is pure lemon yellow. The other phases are all white and identification by color is not possible.

Identification of Gamma, Epsilon and Eta.—In some early work (1928) on annealed copperplated zinc, mixtures of Superoxol (30 per cent H₂O₂) and ammonia were partially successful in developing the structure of the alloy layers. Attention was therefore turned to this reagent as a possible means of identifying the white copper-zinc phases. It was found that the staining that occurred could be somewhat reduced by pouring a mixture of one part of Superoxol and five parts of ammonia over the specimen; washing; rinsing in a 17 per cent solution of chromic anhydride (200 grams CrO₃, 1000 c.c. H₂O), then washing in running water. The chromic rinse reduces staining somewhat but does not etch the specimen. Where staining does not occur, this etchant reveals the alloy layers (Fig. 2). When tried upon specimens containing but one or two phases, however, the action was found to depend upon the associated phases, even when various proportions of Superoxol and ammonia were used.

Although this (as well as Vilella’s reagent, which was also tried) is useful in developing the microstructures of known alloys, it does not help in identifying the white phases. Etching methods were therefore sought to make this identification possible.

Electrolytic etching in a 17 per cent aqueous solution of chromic anhydride was found to be a positive means of distinguishing between gamma and epsilon. The polished specimen is made the anode while a small coil of platinum wire in the bottom of the dish or beaker serves as the cathode. The specimen is connected to the source of current before immersion in the etching solution. At 1.5 amp. per square inch, gamma

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The apparatus finally adopted for this work consisted of a 12-volt storage battery, connected through a rheostat and ammeter to the specimen. The specimen
and epsilon are about equally attacked. At higher current densities\(^4\), gamma is preferentially attacked; at lower current densities, epsilon is preferentially attacked. The recommended procedure for identification is as follows:

Polish, and etch anodically at 5 amp. per sq. in. Gamma, if present, will be attacked, but epsilon will not be attacked. Repolish, and etch at

\(^4\)Current densities over about 10 amp. per sq. in. were not tried in this work.
1 amp. per sq. in. (Current densities less than 0.4 amp. per sq. in. are not recommended, because of uneven etching.) The effects will be reversed (Figs. 3 and 4). The reversal serves as a positive identification. No confusion with eta (η), the solid solution of copper in zinc, should occur, since it is attacked under both conditions.

The effect of anodic etching at high current densities in 17 per cent CrO₃ on annealed copperplated rolled zinc, containing 1 per cent copper, is shown in Fig. 5. Four phases are visible, alpha, gamma (dark due to strong etching), epsilon, and eta (the base material). The effect of low current density on this same specimen is shown in Fig. 6. The four first mentioned phases are again visible, but epsilon, which is etched this time, is seen to be made up of two layers. A faint line, indicating the double layer, will also be seen in Fig. 5, and the effect is quite marked in Fig. 2. The reason for the double layer is not understood, although it is possible that one layer may indicate diffusion of copper into zinc, the other of zinc into copper. The beta phase has not been observed microscopically on this type of specimen, although X-ray studies by M. L. Fuller, of this laboratory, on similar material have revealed its presence along with the other four phases. It seems that the amount of beta formed must be very small, since the structure of alpha-beta brasses is nicely revealed by this etching method (although on pure alpha brass grain boundaries are not well developed).

**Discussion of Results**

At low current densities the five phases are attacked roughly in the order of their zinc contents. At high current densities, epsilon is not attacked. The suggestion is made that this reversal may be explained by a selective polarization of epsilon at high current densities.

Electrolytic methods of etching deserve wider application than they have enjoyed in the past. G. A. Ellinger⁵, working in the National Bureau of Standards, has found electrolytic etching in oxalic acid a superior method of developing stainless-steel structures. A mild reagent, oxalic acid, is used instead of strong mixed acids, which are difficult to handle. W. A. Mudge⁶ has recommended electrolytic etching for obtaining contrast with nickel. In the present work, a high-copper phase (gamma) may be etched in the presence of high-zinc phases (epsilon and eta). Other problems that might possibly be solved by electrolytic etching with a suitable reagent suggest themselves. It is difficult to etch steel structures adjacent to a galvanized coating, because of the strong reactivity of the coating. Etching of nickel or chromium plate on zinc

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is almost impossible, owing to the strong selective etching action on zinc. It is for such problems as these that electrolytic etching may provide an answer.

**Summary**

The alpha and beta phases of the copper-zinc system are easily identified by their distinctive colors. A method has been described whereby gamma and epsilon may be identified by anodic etching in 17 per cent CrO$_3$. At current densities over 1.5 amp. per sq. in., gamma is attacked, epsilon not attacked. At low current densities the reverse is true. Eta is attacked under both conditions. Positive identification of the five important phases is thus secured.

The flexibility of electrolytic etching as a method and its possible wide application are stressed.

**Acknowledgment**

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