

On the Ordering Effects in the Corrosion of Cu_3Au by Aqueous Ferric Chloride

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SINCE it can be shown both theoretically¹⁻³ and experimentally⁴⁻⁶ that disordered Cu_3Au has a greater internal energy than the ordered alloy, it might be expected that its chemical reactivity would be greater. Experiments were initiated⁷ to test this hypothesis. This note will describe some recent results obtained in the study of the rates of corrosion of ordered and disordered polycrystalline Cu_3Au by aqueous FeCl_3 . The work of Robertson⁸ has indicated that the attack by such solutions is intergranular and highly orientation dependent. It was of interest to see whether the order-disorder effect was great enough to overcome the variations from specimen to specimen which would arise from this type of attack.

The polycrystalline alloy specimens (0.020 in. wire, 1 3/4 in. long) were preannealed in 1/2 atm H_2 at 700°C for 2 hr. The subsequent heat treatments to produce order and disorder were performed in 1/2

Table I. Reactivity Rates for Cu_3Au in Aqueous Ferric Chloride at 30°C

FeCl_3 concentration, mol per liter	0.125	0.250	0.500	1.000
Rate for ordered specimens, mg per min	0.052	0.083	0.145	0.340
Rate for disordered specimens, mg per min	0.062	0.099	0.262	0.475
$R_{\text{disordered}}/R_{\text{ordered}}$	1.2	1.2	1.8	1.4

atm He . Disordered specimens were obtained by heating at 450°C for 2 hr and quenching in water. Ordered specimens were produced by heating for 2 hr at 450°, furnace cooling to 380°, and soaking at 380°C for 80 to 90 hr. Room temperature was reached by cooling to 150° at a rate never exceeding 7° per hr, and water quenching from 150°C. The specimens so produced exhibited electrical resistivities characteristic of the two states; of the order of 11.27×10^{-6} ohm-cm for the disordered, and 4.28×10^{-6} ohm-cm for the ordered specimens.

The corrosion rates were studied at 30°C in ferric chloride solutions of several concentrations (1/8, 1/4, 1/2, and 1 molar). The specimens were attached to a stirrer during the tests. Tests were interrupted at intervals, and the specimen weight change was determined after washing and drying. Analysis of the solutions showed that the attack was limited to the copper.

The higher corrosion rate for the disordered alloy, as illustrated in Fig. 1, is typical of the results obtained. The effect of variation in ferric chloride concentrations is indicated in Table I for typical specimens. The variations in the ratio of reactivity for disordered and ordered specimens at the different concentrations are within experimental error, and the best value is estimated to be near 1.4. The

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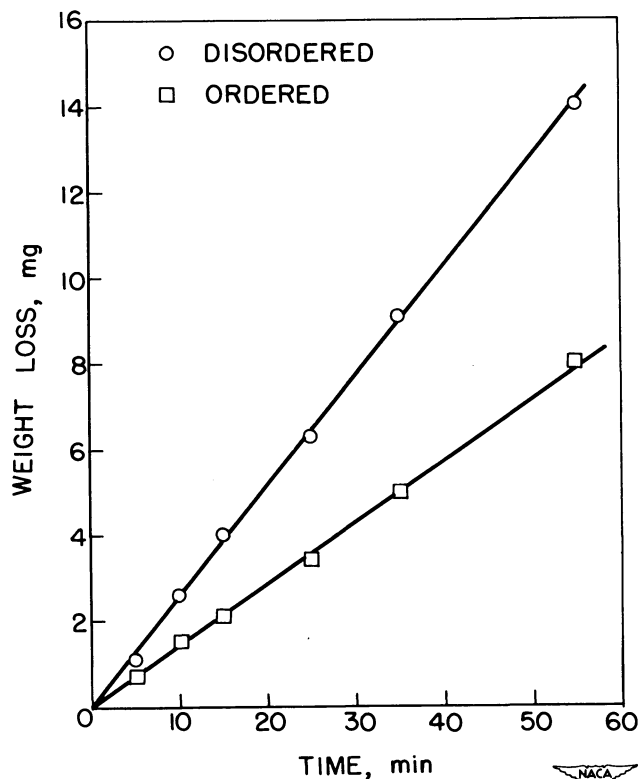


Fig. 1—Reactivity of ordered and disordered polycrystalline Cu_3Au in 0.5 molar ferric chloride.

experimental variation was due in part to the mode of attack, as mentioned, and in part to the fact that films were formed on the specimens under some conditions. Electron diffraction patterns of the films were very complex and indicated the presence of metallic iron, as did chemical analysis. In an attempt to eliminate the difficulties arising from the mechanism of attack, single crystal specimens were used. A greater reaction rate was again measured for the disordered specimens, but the reproducibility was no better than that for the polycrystalline metal. This would indicate that film formation was primarily responsible.

It was concluded that the reaction with aqueous ferric chloride served to demonstrate that the reactivity of disordered Cu_3Au is greater than that of the ordered alloy. However, the difficulties with film formation did not permit determinations of a precision great enough to warrant extension of the study to partially ordered alloy systems.

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