The Structure of Metal Deposits Obtained by Electrochemical Displacement upon Zinc[1]

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ABSTRACT

An attempt is made to identify the composition and the structure of nonadherent immersion deposits of noble metals on zinc. For this purpose Cu, Au, Ni, and Ag deposits, obtained by electrochemical displacement from their salt solutions in $1N$ sulfuric acid, were examined by x-rays. All of them contained redeposited Zn. Cu deposits contained approximately 9 to 13 atom per cent in solid solution, and Ni deposits contained 17 to 20 per cent in solid solution; Au deposits large amounts and Ag deposits below 0.5 atom per cent. The grain size of the deposits was very small because their growth was hampered by codeposited Zn. During the displacement of Ag, zinc deposited mostly as a very thin layer on the surface of the grains. The other three metals absorbed Zn readily, forming α-phases. The displacement of the noble metal occurs because of the activity of the local cells; Zn acts as anode and the noble metal forms very small cathodes. The redeposition of Zn on these cathodes is possible because it is deposited in form of a solid solution, the free energy of which is reduced.

Introduction

Highest purity zinc dissolves very slowly in dilute acids ($1N$ to $4N$ hydrochloric or sulfuric acid) (1). On adding to the solution a small amount of a salt from which a metal with low overvoltage can be displaced upon the zinc, the rate of dissolution is increased greatly (2). Not all metals more noble than Zn increase its dissolution rate in the same order as their hydrogen overvoltages decrease (3). Among the exceptions are Cu, Au, and especially Ag. A large increase in the rate of dissolution of Zn might be expected for Ag since it has a low overvoltage. However, this is not realized. It was suspected that the small effect of the dark deposits of Ag (also of Cu and Au) thus formed on Zn (4) might be caused by coprecipitated Zn which exhibited a high overvoltage. Indeed, Mylius and Fromm could show that Ag and Cu displaced from neutral solutions on Zn contained up to 50 per cent of Zn (5).

The intention of the present paper is to prove that even in acid solutions the deposits of Cu, Au, Ni, and Ag contain Zn and that, therefore, the assumption of a high overvoltage on these deposits is justified. Further, the structure of the deposits and their grain growth are discussed in connection with the x-ray photographs obtained.

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The question of the structure of the deposits produced by electrochemical displacement is now of some importance, as propositions have been made to cover metals with more noble ones using this process [Fe with Ni (6, 7) Al with Zn, Cd, Sn (8)]. No references concerning x-ray investigation of such metallic deposits could be found in the literature.

Experimental Procedure

The following operations were used in all tests to obtain the deposits, separate them from Zn, and to prepare them for the further investigation:

(1) A piece of C.P. Zn rod was treated for 15 to 30 seconds in 1.42 sp gr nitric acid to remove all sharp edges; it was then washed in distilled water and introduced into a test tube containing 3 ml of $2N$ sulfuric acid; 3 ml of a $0.1M$ salt solution of the metal in question were added to this giving a $1N$ acid solution.

(2) After the deposit had formed in an amount sufficient for further experiment (in 5 to 30 minutes), the tube was shaken to separate the deposit from the Zn. The solution was then quickly poured off and the precipitate washed in distilled water. Removal of the acid prevented the dissolution of Zn which otherwise might be distributed in the deposit of the nobler metal. Several decantations of the deposit with distilled water and tests for SO_4^{--} (with $BaCl_2$) followed to assure that the deposits did not contain soluble substances, e.g. $ZnSO_4$.

(3) Finally, the wet Ag deposits were washed

with alcohol and dried at room temperature, while the others were dried by gentle heating at approximately 50°C.

To study each deposit, the sample was divided into three parts:

(*a*) An x-ray photograph of the dark, dry deposit was made.

(*b*) One part of the precipitate was treated for a prolonged time with acid and the residue was analysed by x-rays. The presence of Zn^{++} in the acid solution after this treatment was confirmed.

(*c*) To determine quantitatively the amount of Zn present, the deposit was put into a narrow-necked quartz tube which was evacuated, sealed, and heated to 800°–900°C to homogenize the powder. As no reducing agents were present in the powder (the filtration of the deposits was also omitted in order not to contaminate them with filter paper fibers), reduction processes could not occur during annealing. If a trace of $ZnSO_4$ were still present it would be converted into ZnO and SO_3 which would not be reduced by the noble deposit. Thus, any Zn present would have had to come by co-deposition. The homogenized powders were used to obtain x-ray patterns. The films were measured and the lattice constants computed. From these data it was possible to determine the total Zn content of the deposits. The method is sufficiently precise (9) so that there was no need for quantitative chemical analyses, for which the amount available was too small. The photographs for comparison and for determination of the lattice parameters were made by the asymmetric method (10). A minus 400-mesh sample of the powder was attached with Cello-Seal[2] to a practically nonabsorbing Li-B-glass hair of 0.08–0.12 mm diameter. The powder mount had a diameter of about 0.18 mm. For such a tiny sample, the corrections due to absorption by the specimen were reduced to a minimum, using the last lines in the back-reflection region for the parameter calculations. Therefore, no absorption corrections were applied (11).

All metals and chemicals used were of highest purity available.

Experimental Results

Displacement of copper.—Using a 0.1*M* $CuSO_4$ solution a dark red, spongy deposit appeared on the Zn. When washed, dried, and examined under the microscope, the deposit was still dark red with some particles of faint red and yellow brass color. If the powder was rubbed or ground the color of brass was unmistakable.

The precipitate that peeled off the Zn piece during deposition gradually became copper-red in the acid solution and, simultaneously, a slight evolution of gas (hydrogen) could be observed on the surface of the precipitate. The same was true when the dry powder was treated with hydrochloric acid. Zn was identified in the solution by qualitative analysis (12).

The x-ray patterns of the dark Cu deposits differed from that of pure Cu (Fig. 1*a*) and were not the same in all experiments. The last lines, (331) and (420), were broad, faint, and considerably shifted from their old positions, especially when $ZnSO_4$ was added to the solution, indicating very fine grain size and lattice expansion.

The dark Cu deposit treated with cold 2*N* sulfuric acid gave an x-ray pattern of broad lines of nearly the same lattice parameter as pure Cu, but the inner edges of the last lines were sharper (Fig. 1*c*), indicating that part of the Zn was already dissolved. When the deposits were boiled in 2*N* sulfuric acid or treated with the cold acid for several days, the lines appeared normal again except that they remained broad.

The dark deposits, when heated in vacuum, turned yellow. The copper lattice simultaneously expanded still more in most cases because of the dissolution of particles rich in Zn, which had formed on separate points of the deposits and which were not always indicated by the x-ray patterns. The lines became sharper, due to increase in grain size and to more even distribution of Zn throughout the deposit. The Zn diffusion process, therefore, was completed at elevated temperatures, α-brass was formed, and an increase in the Zn content was observed after heating (Fig. 1*d*). In Table I are shown the lattice constants obtained with different Cu deposits and the computed Zn content using previously published α-brass x-ray data (14). The accuracy of determination for the case of sharp lines was ± 0.0008 kX (Fig. 1*a* and *d*), and for the case of broad lines it was only ± 0.002 kX. Nevertheless, the picture and the tabulated data show unmistakably the expansion of the lattice, caused by the dissolution of appreciable amounts of metallic Zn in the deposited Cu.

Displacement of gold and nickel.—For the displacement of gold by zinc, a $HAuCl_4$ solution was used. The reaction proceeded rapidly. The x-ray pictures showed that the grain size of the Au deposits was very small (10^{-5} to 10^{-6} cm) and that they contained Zn in solid solution (contraction of the Au lattice) (15). If annealed, a new phase was formed beyond the α-region of the solid solution Au-Zn, indicating that large amounts of Zn were absorbed by the gold deposit.

[2] Fisher Scientific Company, Pittsburgh, Pennsylvania.

The Zn from the dark deposits could be removed quickly only by boiling in nitric acid. Sulfuric acid acted very slowly. No recrystallization of the deposit took place at room temperature.

The process of the displacement of Au on Zn proceeds, therefore, in the same manner as in the case of Cu.

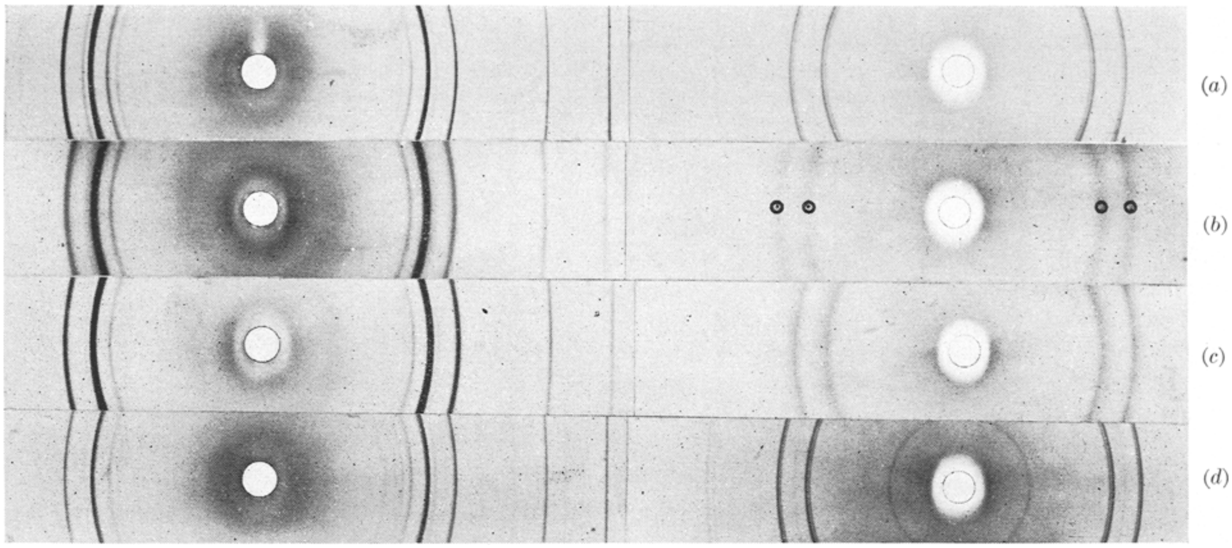

FIG. 1. X-ray patterns of Cu deposits obtained by electrochemical displacement on Zn. (a) pure Cu, (b) dark red Cu deposit (α-brass), (c) dark deposit treated with sulfuric acid, (d) dark deposit annealed in vacuum to 800°–900°C (α-brass).

The same is true concerning Ni deposits. The grayish black deposit of Ni on Zn, obtained from a $NiSO_4$ solution, could be separated from Zn only with difficulty, and it showed an x-ray pattern without back reflection lines. Even the front reflections were broad indicating a very small grain size (approximately 10^{-6} cm). The deposit could be dissolved entirely in cold $2N$ sulfuric acid in 10 minutes. Annealed in vacuum, a new phase was formed, showing the presence of large amounts of Zn in the deposit (approximately 17–20 atom per cent).

Displacement of silver.—The formation of the silver deposit using $0.1M$ $AgNO_3$ differs in some respects from the previous three cases. The deposit on the Zn grew to a velvety black sponge and occasionally black sponge particles were detached from the Zn surface by hydrogen bubbles. These particles changed color from black to white. This same effect was achieved by treating the sponge with $2N$ sulfuric acid solution, which action was accompanied by slight liberation of hydrogen. A much darker sponge resulted if $ZnSO_4$ was initially added to the solution. In the dry state the deposit aggregates to particles, the outside of which are darker than the inside.

The x-ray picture of the black silver deposit showed the pure silver pattern but with broad lines. The grain size of such silver is, therefore, very small. However, the lattice constant was the same as that of pure silver. The dark deposits turned white after annealing in vacuum. The x-ray pictures of the white deposits were sharp and the lattice constants nearly the same as for pure Ag. The black silver deposit contained small quantities of Zn since: (a) in sulfuric acid the deposit evolved small amounts of hydrogen and turned white (the x-ray pictures showed that the deposit had recrystallized); (b) the presence of Zn^{++} was detected in the solution just mentioned (12) but not in blank tests; (c) darker deposits were obtained when the deposition occurred from sulfuric acid solutions containing $ZnSO_4$ originally. The process of Ag deposition was very similar to that of Cu deposition, except that zinc did not diffuse into silver at room temperature. The amount of

TABLE I. *Lattice constants and composition of different copper deposits*

Cu-radiation; the line 420 was used for the measurements. Room temperature.

Copper	Annealing		in kX	Atom % Zinc
	Temp °C	Time hr		
Pure	—	—	3.6075	—
Dark red	—	—	3.629*	10
Dark red	—	—	3.625*	9
Dark red → red**	—	—	3.608*	—
Dark red‡	—	—	3.635*	13
Dark red → yellow	788	1	3.6490	19.2
Dark red → yellow	900	3	3.6536	21.4

* Rough measurements of marked points.
** Treated with H_2SO_4.
‡ Deposited in the presence of $2M$ $ZnSO_4$ solution.

Zn present in the Ag deposit, therefore, must be small, below 0.5 atom per cent, corresponding to the error limit of determination (± 0.0008 kX for the sharp lines of the heated deposits) (13).

Discussion

There are at least two possible explanations for the presence of Zn in the noble metals:

(1) The metallic Zn could be present in the deposit as fragments or as very small particles which were undermined and then separated from the original metal by the dissolution process.

(2) Zn could be redeposited in form of a solid solution together with the nobler metal by the emf of Zn itself.

If Zn particles were left in the deposits mechanically, the x-ray patterns of the unheated deposits would have shown separate Zn lines, unevenly blackened (because the quantity of the separated grains could not be large). Such lines could not be observed. The only Zn lines, sometimes present on a film, were faint and very uniform, indicating that the particle size of Zn was very small. Even if small, discrete zinc particles were present, the formation of a Zn-Cu solid solution would require a different explanation because even colloidal Zn in contact with solid Cu would not dissolve at room temperature. Since the presence of solid solutions was proved in all Cu-, Au-, or Ni-deposits by the x-ray, the second mechanism seems more probable.

The Displacement Process

In order to understand the Zn redeposition achieved by the emf of Zn itself, the electrochemical displacement upon Zn must be considered first.

According to observations, the precipitation of the nobler metal starts on discrete points of the Zn surface, where there are evidently some discontinuities. If the first nuclei, consisting of the nobler metal, are formed, the precipitation then continues from these nuclei as starting points, because this growth requires less energy than the formation of new nuclei (16, 17). A Cu particle grows simply by cathodic deposition. Zn acts as anode and after the deposit forms, it acts cathodically. The electrolyte contains not only sulfuric acid and sulfates, chlorides, or nitrates of the nobler metals but also Zn ion, especially in the limiting layer. A current is supplied by Zn that goes into solution and at a potential limited by that of Zn in $1N$ sulfuric acid (ca. -0.71 volts) (19). The electrons flow from the Zn piece into the Cu deposit. The potential of the cathode (Cu deposit) (18), ϵ_c, is given by the equation:

$$\epsilon_c = \epsilon_a + ir + \eta \qquad \text{(I)}$$

where ϵ_a is the anode potential, i the current in the particle of the noble metal, r its resistance, which can vary considerably in the different parts of the particle, causing different rates of deposition (see Fig. 2), and η the polarization due to the hydrogen discharge on the surface of the particle. This potential is

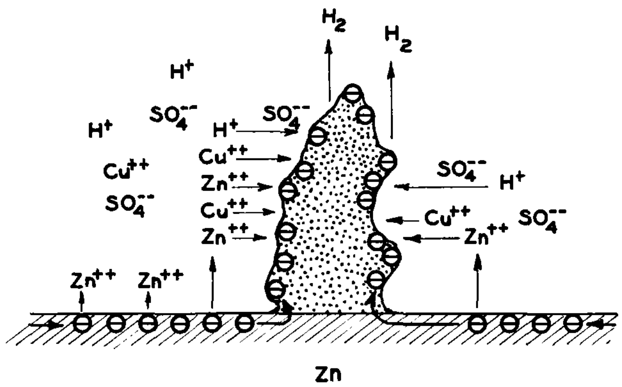

FIG. 2. Cu displaced upon Zn. The tiny Cu particle on the Zn surface acts as cathode; Cu^{++}, H^+, and finally a mixture of Cu^{++} and Zn^{++} are discharged on it. In the latter case a solid solution is formed.

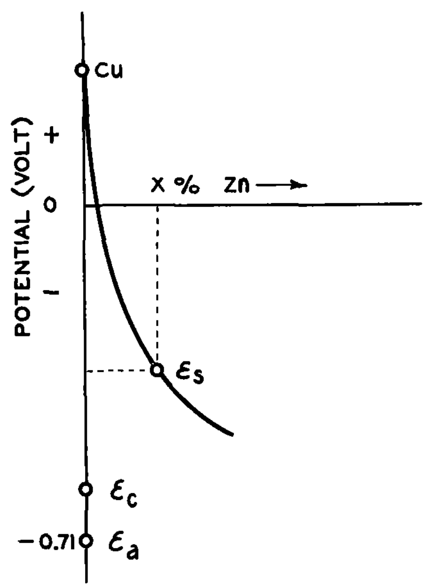

FIG. 3. Potential of a Cu-Zn solid solution versus per cent Zn. ϵ_a—dissolution potential of Zn (-0.71 volt), ϵ_c—potential of the Cu cathode (eq I), ϵ_s—potential required for desposition of a solid solution containing x per cent Zn.

quite insufficient to deposit Zn from the same solution, if the nature of the cathode is not considered.

It is well known that zinc forms solid solutions with copper and the reversible potential of a solid solution generally lies between those of the pure constituents (20, 22). Tammann (21) gives a formula for the potential of a solid solution, provided that it is in equilibrium with its ions and the diffusion in the solid is rapid (25), as schematically represented by Fig. 3, showing the anodic and cathodic potentials of a local cell during the formation of a solid solution (containing Zn) by electrochemical displacement. The curve shows that the deposition potential of the solid solution ϵ_s is less anodic than that of the anode (Zn) and, therefore, Zn in solid solution can be deposited by the emf of Zn itself. The same relates also to the Au and Ni deposits (23, 24).

The codeposition of Zn hampers the growth of the deposits and, as a result, a very fine-grained deposit is obtained (17).

If the components do not form solid solutions, as is the case in the displacement of Pb^{++} or Cd^{++} by Zn, the deposits are pure and coarse crystalline, because the cathodic crystallization process is not disturbed by the discharge of Zn^{++}.

The process of Ag displacement is somewhat different. Although Ag forms solid solutions with Zn, only small amounts of Zn could be found in the deposits. It is believed that the low Zn content may be explained by the low rate of diffusion of Zn into Ag at room temperature and by the simultaneous action of the acid. The whole deposit consists, therefore, of tiny Ag particles (diameter approximately 10^{-5} cm) covered with a very thin Zn layer, not detectable by x-rays. The deposit has a black appearance because of the fine grain size. The deposit is fairly stable if it is in contact with Zn. If some black particles separate, the Zn on these particles dissolves quickly in the acid solution because the Ag acts as a large local cathode (contrary to the behavior of Cu- or Au-deposits under the same conditions). The silver grains grow even at room temperature and turn white (recrystallization, sharp x-ray pattern). In neutral solutions, such a dissolution is impossible and the Ag deposits show a high Zn content as already observed by Mylius and Fromm (5).

Since the noble metal deposits contain Zn in solid solution, and the Ag deposit has Zn on its surface, the hydrogen overvoltage of the deposits must be high. This confirms the assumption made earlier and explains the low activity of the deposits with respect to the dissolution of solid Zn in acids.

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

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