

high solute alloys of this kind, therefore, seems to provide a useful method of alloy hardening which might lead to the development of new engineering materials, especially in the case of the chromium-tungsten system. From this point of view the aluminium-zinc system may also be of interest. Its phase diagram is more complex than those of the three systems discussed here, but it also allows the possibility of studying age-hardening in alloys of equiatomic composition.

This work is being continued and extended to the systems gold-platinum, chromium-tungsten and aluminium-zinc. We thank Mr. J. Varon for his assistance with the experimental work.

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Plating Radioactive Zinc-65

THE radioisotope zinc-65 is often used as a tracer element for investigations of transport phenomena in metals. It is conveniently introduced by electroplating the zinc on to a cathode made of one of the components of the material to be investigated. Unfortunately, no simple and flexible plating procedure has yet been used for this work. Shirn, Wajda and Huntington¹ developed the procedure used for their own self-diffusion studies, and Jaumot and Smith² used the same procedure. However, this requires a rotating cathode, a zinc anode, and a relatively high concentration of zinc-65. Also, the plating efficiency is low—about 6 per cent.

My own plating solution is based on the composition given by Shteinberg and Bogakovskii³. However, where these authors have used the sulphate, I have chosen the chloride, since zinc-65 is commonly available as a solution of the chloride in nitric acid (Oak Ridge National Laboratory, Isotope Sales Dept., P.O. Box X, Oak Ridge, Tenn.). The bath composition is 0.05 g ZnCl₂, 2 g NH₄Cl, 0.3 g NaC₂H₃O₂, 0.01 g gelatine, and 10 ml. water. The effects of the small amount of nitric acid present in the tracer stock solution may be neglected, since the sodium acetate buffer is sufficient to maintain the proper pH.

For electrodes, I used a platinum anode separated from a cadmium or tin cathode by 1 cm. The platinum has the advantage of allowing a plate with a higher specific activity than that which is obtained using a zinc anode. This could be important for those cases in which zinc has only slight solubility in the material being studied. On the other hand, if smaller concentrations of tracer are desired, then the solution may be partly mixed from reagent grade zinc chloride.

A current density of 1-2 m.amp/cm² is satisfactory. Masking is unnecessary, because throwing power is low. However, efficiencies are fairly high, ranging from 40 to close to 100 per cent. The highest efficiencies are obtained for higher initial concentrations of zinc ion and for current densities near 2 m.amp/cm². All plates are bright and adherent.

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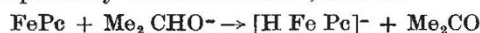
Reduction of Metal Phthalocyanines

THERE has been interest recently in oxidation and reduction reactions of metal phthalocyanines¹⁻³. Ferrous phthalocyanine (FePc) dissolves in alcohols such as MeOH, EtOH, iso-PrOH and *t*-BuOH, each containing sodium hydroxide (0.1 per cent). The solutions in these alcohols have the characteristic visible absorption spectrum of FePc (Table 1)⁴. However, on refluxing the solutions in basic EtOH and iso-PrOH under nitrogen the colours change from blue to red. The red solutions are stable in the absence of oxygen, but react rapidly with traces of oxygen, giving solutions with the same visible absorption spectrum as before the colour change, except that the peak intensities are reduced by about 20 per cent. The sequence can be repeated. Acetone (about 0.0014 moles) was detected by V.P.C. from the reaction of FePc (0.0035 moles) with iso-PrOH containing sodium (0.1 per cent). The solutions in MeOH and in *t*-BuOH, both containing sodium hydroxide (0.1 per cent), do not change colour on refluxing.

The red solution obtained by refluxing FePc in EtOH containing sodium hydroxide was too sensitive to traces of oxygen to allow its visible absorption spectrum to be recorded. However, the same colour change, from blue to red, occurs when FePc is reduced by excess sodium borohydride in MeOH containing sodium hydroxide, and in this case the visible absorption spectrum could be measured (Table 1). The spectrum observed depends on the sodium borohydride concentration. Again the red solution reacts with traces of oxygen to give a solution which has the same visible absorption spectrum as before reduction, but with the peak intensities reduced by about 20 per cent.

FePc in MeOH containing NaOH is also reduced by stannous chloride and by formaldehyde. The spectra of the red solutions are the same as those obtained after reducing FePc with a low sodium borohydride concentration (Table 1).

The reduction by basic EtOH and iso-PrOH probably proceeds via a hydride ion abstraction mechanism of the type proposed by Chatt and Shaw⁵, that is:



The mechanism accounts for iso-PrOH reacting to give acetone, and for there being no reduction by *t*-BuOH, in which there is no α C-H bond, and by MeOH, in which the α C-H bond is more stable than in EtOH and iso-PrOH. The hydrido-ferrous phthalocyanine may be an unstable intermediate leading to iron in a lower valency state and/or hydrogen added to the Pc ring system. The marked change in the visible absorption spectra suggests that the Pc group is modified in the reduced forms of FePc.

Table 1. VISIBLE ABSORPTION SPECTRA OF FEPC SOLUTIONS

Solvent	λ_{max} (m μ) with relative peak heights in parenthesis
Unreduced FePc	
FePc (0.004%) in MeOH + NaOH (0.1%)	657 (1.00), 600 (0.26), 375 (0.07)
Reduced FePc	
FePc (0.004%) in MeOH + NaOH (0.1%) + NaBH ₄ (0.2%)	830 (0.30), 690 (0.35), 610 (0.32), 515 (1.00)
FePc (0.004%) in MeOH + NaOH (0.1%) + NaBH ₄ (0.2%)	780 (0.12), 618 (0.49), 492 (1)
FePc (0.004%) in tetrahydrofuran + EtMgBr (see Note)	700 (0.48), 635 (0.45), 512 (1.00)

Note: 5 per cent by volume of the Grignard reagent, EtMgBr, added; the Grignard reagent was about 2 M, based on the concentration of halide used in its preparation.

The low solubility (generally 10⁻⁴ M) of FePc in alcohols containing base and in other solvents together with the extreme reactivity of the reduced FePc with oxygen makes it difficult to establish the precise nature of the reduced species. Sulphonated FePc and also sulphonated CoPc can be titrated potentiometrically with sodium stannite. The end-point corresponds to the colour change.