

**Procedure.**—Transfer an aliquot of the sample solution which contains from 20 to 200  $\mu\text{g}$  of Ru(III) to a 25 ml volumetric flask. Add sufficient sulphuric acid so that the final solution will be 1.5 N in sulphuric acid. Add 5 ml of 0.2% TH. Dilute to volume with double distilled water. Measure the absorbance vs a reagent blank at 640 nm after 10 minutes. Compare the absorbance with a standard curve to calculate the amount of ruthenium (III).

#### Results and Discussion

TH forms a blue coloured species with ruthenium(III) instantaneously at room temperature (22°–25° C) in sulphuric or hydrochloric acid. The sensitivity in the four acid media (1.5 N) is in the order—HCl > H<sub>2</sub>SO<sub>4</sub> > H<sub>3</sub>PO<sub>4</sub> > HAC. The maximum colour development takes place in 10 minutes after mixing the reagents. The stability of the blue colour in 1.5 N H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub> and HAC is 30, 20, 8 and 5 minutes respectively. Hence sulphuric acid medium has been selected. Nitric acid medium cannot be used as it oxidises TH.

The maximum colour intensity is observed in 0.1–2.5 N H<sub>2</sub>SO<sub>4</sub>. Above 3.0 N precipitation of the reagent takes place. A fifteen-fold molar excess of the reagent was necessary for the full development of the colour intensity. The blue coloured species assumed to be a radical exhibits absorption maximum at 640 nm at which the reagent does not absorb. The absorbance values remained constant for 30 minutes and were insensitive to temperature in the range 5–50° C. The order of addition of reagents was not critical. Beer's law is obeyed from 0.8 to 8.0 ppm of ruthenium. The optimum concentration range evaluated by Ringbom's method<sup>7,8</sup> is 1.5 to 7.0 ppm. The Sandell sensitivity of the colour system was found to be 0.0222  $\mu\text{g}$  Ru(III)  $\text{cm}^{-2}$ . The molar absorptivity was  $4.58 \times 10^3$  litre mole<sup>-1</sup>  $\text{cm}^{-1}$ .

With the help of this reagent, as little as 4 ppm of Ru(III) can be determined in presence of 1000 ppm of the ions of Zn(II), Mg(II), Ca(II), Ba(II), Sr(II), fluoride, chloride, bromide, nitrate, sulphate, phosphate, oxalate, acetate; 100 ppm of Ni(II), Co(II), Cu(II), UO<sub>2</sub>(II) and EDTA. However the ions of other platinum metals, Au(III), Ag(I), V(V), Ce(IV), thiosulphate and iodide were found to interfere at all concentrations.

**Analysis of synthetic samples.**—In one phase of the processing system devised for experimental Breeder reactor-II (EBR-II), molten zinc and zinc-magnesium alloy are used as solvents in the separation of uranium from ruthenium and other fission products. The results of analysis of ruthenium in

the synthetic mixtures corresponding to zinc-magnesium alloy composition are given in Table I.

TABLE I  
Determination of ruthenium in zinc-magnesium alloy

Zinc added, mg	Magnesium added, mg	Ruthenium		No. of determinations
		added $\mu\text{g}$	found av. $\mu\text{g}$	
30	..	4.00	3.98	5
..	30	4.00	3.99	5
15	15	4.00	3.97	5
15	15	2.00	1.99	5

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#### THE EFFECT OF ULTRASOUND ON THE CATALYTIC ACTIVITY OF COPPER

THE reported work-hardening of fcc metals<sup>1</sup> and a 30–100 fold increase in the rate of recrystallisation, in oxygen-free, high-conductivity copper<sup>2</sup>, both induced ultrasonically, and the variation of the velocity of ultrasound and attenuation in copper under varying static stress<sup>3</sup>, when viewed in the light of Hutchison's review<sup>4</sup> on ultrasonic absorption in solids, clearly indicate the existence of a definite interaction between ultrasound and dislocations in a solid. If the ultrasound can also bring about an alteration in the catalytic activity of a metal, that will, indeed, provide a new evidence in favour of Cratty and Granato's hypothesis<sup>5</sup> that the surface terminations of dislocations are one type of active centres. A survey of the literature does not reveal any attempt made in this direction, hence, the present investigation.

Square pieces (3.0 cm  $\times$  3.0 cm) of copper foils (99.9%, B.D.H.) were used; the gm. equiv. of hydrogen peroxide (0.25 N) decomposed per

unit surface area of the foil during the initial 10 min. of the reaction at  $69.5^\circ\text{C}$  at a stirrer speed of 200 rpm was taken as a measure of the activity,  $a$ , of the foil.

In one set of exploratory experiments the copper foils were first annealed in air for one hour at  $T_A = 150^\circ\text{--}480^\circ\text{C}$  and then subjected to the following sequence of treatments:

I (a) [QD], I (b) [QID], I (c) [QDID] where Q, quenching the annealed foil in water at  $25^\circ\text{C}$ ; D, dipping the foil in 2 N  $\text{H}_2\text{SO}_4$  for 3–4 min. until it regained its shine, *i.e.*, the surface oxide dissolved out; I, insonating the foil at frequency 80 kHz ( $60\text{ W/cm}^2$ ) for 30 min. at  $25^\circ\text{C}$ . The apparatus for insonation consisted of an ultrasonic cleaner (Type 1201, Systronics) fitted with an electrical-to-mechanical power transducer at the bottom of the tank; the foil was placed in contact with the transducer with water (at  $25^\circ\text{C}$ ) standing to a height of 9 cm above it; as there was warming up of the water during insonation, it was carried out with interruptions.

In another set of experiments the unannealed copper foils were immersed in 0.25 N hydrogen peroxide for 20 min. at  $69.5^\circ\text{C}$  to oxidise the surface and then subjected to either [ID], II (a) or [DID], II (b) treatment.

Figure 1 shows the variations of  $(a/a_0)$  with  $T_A$ ,  $a_0$  being the catalytic activity of the untreated foil ( $1.14 \times 10^{-4}$  gm. equiv. of hydrogen peroxide decomposed  $\text{cm}^{-2}$  in 10 min. at  $69.5^\circ\text{C}$ ).

The results of

I (a) simply confirm the earlier findings of the authors<sup>6</sup>.

I (b) and I (c), though different from those of I (a), are new and significant; they clearly reveal that while in the presence of surface oxide, ultrasonic annealing of activity does occur, in the absence of the surface oxide, however, the activity, apparently, remains unchanged.

II (a) and II (b) showed that even without previous annealing the oxide-coated foils lost about 30% of their activity ( $a_0$ ) while the 'oxide-free' ones lost no activity.

Incidentally, the observed absence of activity decay at  $T_A < 200^\circ\text{C}$  can, now, be attributed to negligible or partial oxidation of the metal at low  $T_A$ . [see curve I (b) in Fig. 1].

This observation assumes special significance when it is recalled that surface oxide has also been found to affect such of the bulk properties as internal friction<sup>7</sup> and steady state creep rate<sup>8</sup> of copper and other metals. Thus, it is clear that the effect of ultrasound on the catalytic activity of copper is independent of  $T_A$  but, dependent on the coverage

of the metal surface by its oxide, no matter how the surface oxidation is brought about; a detailed correlation between this effect and the extent of surface oxidation is under investigation.

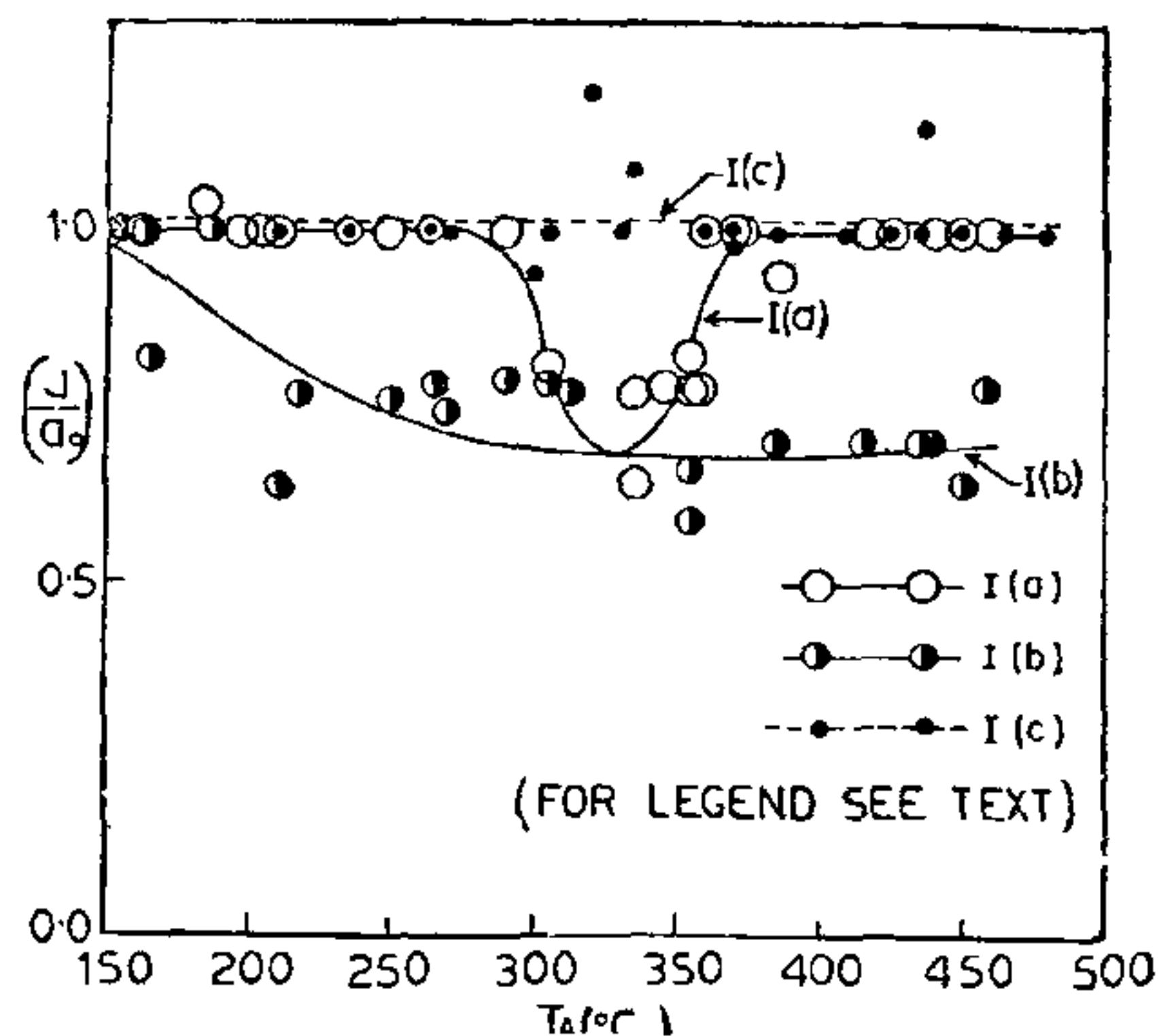


FIG. 1.

Anyway, the present investigation succeeds in providing not only a new and strong evidence in favour of Cratty and Granato's hypothesis<sup>5</sup>, but also, a new insight into the possible relationship between the problem of active centres (on the surface of a metal catalyst) and such of the physical properties as internal friction, creep, recrystallisation, hardness, etc. Further studies are in progress.

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