THE EFFECT OF BENZOTRIAZOLE ON THE MICROHARDNESS OF COPPER ELECTRODEPOSITS

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The Microhardness of copper electrodeposited from an acid sulphate bath with and without the addition agent Benzotriazole (BTA), has been investigated.

From a pure acid bath, the microhardness of deposit varies from 94 VHN to 10 VHN as c.d. is changed from 6.5 mA/cm^2 to 39 mA/cm^2 When BTA is added, the microhardness varies from 200 VHN to 379 VHN as c.d. is changed from 6.5 mA/cm^2 to 39 mA/cm^2 It is seen that profound increase in microhardness is brought about by the use of BTA as an addition agent.

There are many factors which can affect hardness of metals eg. Internal stress, grain size, banded structure, dispersion of fine particles etc. The role of these in hardness of electrodeposited copper, has been discussed in detail. The present investigation points out that grain size is by far the most important factor.

Though a considerable amout of work has been done on electrodeposition and electrodeposits, the mechanical properties of electrodeposits and the effect of plating conditions on them, have received attention only in recent times. Among the mechanical properties, hardness has been studied to a greater extent especially in the case of copper. It has been reported that the use of addition agents like gelatin [1], Thiourea [2], rochelle salt [3], β - naptho-quinoline [4], benzatriazole (BTA) etc., in acid copper bath results in harder deposits. Of these addition agents, BTA has been studied extensively [5-11] in recent years. A survey of the literature on the properties of BTA copper deposits (copper deposits obtained from baths containing BTA) shows that (1) the deposits are very hard, i.e., 3-4 times harder than that from simple acid bath (2) they exhibit a self annealing effect i.e., decrease of hardness with time at room temperature. Similar self-annealing has been reported in the case of copper deposited from a bath containing β -naphthoquinoline [4] and silver deposits [12].

Macnaughtan and Hothershall [13] and Askarov and Nemenonov [14] have suggested that the high hardness of electrodeposits, often noticed, could be due to fine grain size. Walker and Benn [15] have investigated the effect of grain size on hardness in the case of deposits from acid copper bath. They concluded that the hardness-grain size correlation is better expressed through an empirical semilogarithmic relationship rather than by the Hall-pètch [16,17] equation which has a theoretical basis. Hofer and Hintermann [18] have measured the grain size and hardness of copper deposited from acid bath containing thiourea. They did not attempt at a quantitative correlation between hardness and grain size but observed qualitatively that the hardness increased with decrease in grain size. Walker and Benn [11] have suggested that the, high hardness of BTA copper may be due to fine grain size and perhaps banded structure.

In this communication the results of a systematic study to understand the causes that contribute to the high hardness of BTA copper are presented.

EXPERIMENTAL TECHNIQUE

Preparation of Specimen

All the experiments were conducted with a bath of following compositon

$CuSO_4 .5H_2O$	-	125 g/l (0.5M)
H_2SO_4	-	49 g/l (0.5M)
Benzatriazole	-	0.119 g/l (0.001M)

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For each experiment the bath was prepared fresh using analytical reagent grade chemicals and twice distilled water, to avoid the ageing effect that has been observed [6] with BTA. The anodes consisted of BDH 'Analar' grade copper foil. The same grade foil was used as cathode in most of the experiments. However, the specimens for microhardness measurements were prepared by using deoxidised copper discs.

The pretreatment consisted of polishing, degreasing in trichloroethylene, stopping off with 'Americo' lacquer, cathodic cleaning at 0.1 A/cm^2 in an alkaline solution (5% NaOH + 5% Na_2CO_3) at 30°C for one minute, rinsing in water, a 30 sec dip in 5% H_2SO_4 and rinsing in distilled water. Plating was conducted at 30°C in a divided rectangular perspex cell of one litre capacity. A regulated D.C. power-supply 30V; 3A regulation 0.005%, ripple < 1mV was used. To measure reproducibility three specimens were prepared simultaneously by having three cells in series. The measurements were done on all of them and the average was taken.

Measurement of Stress

(a) Stoney's Flexible cathode method [19]: These experiments were performed with a copper foil [3.2 thou thick and area 2 sq. cm] as cathode. The deflection was measured with a travelling microscope to an accuracy of ±0.01 mm. The stress was calculated by using stoney's formula [19]. The stress measurements were made on deposits of thickness 36 μ (1.44 thou) so that these could be compared with those of x-ray results.

(b) X-ray method: The photographic method described by Balasingh and Singh [20] was used. The procedure is as follows: A back reflection photograph of the deposit of thickness 36 μ (which is 1.3 times greater than the penetration depth of x-rays) was taken using a Rigaku Denki back-reflection camera. Keeping the angle of incidence of x-rays normal to the specimen, one of the segments was exposed. The other segment was exposed with an angle of incidence of 45°. In both cases the distance between film to specimen was 6.5 cm. After developing the photograph, radius of the 420 ring in the two segments were measured with the help of a microphotometer (Carl Zeiss, Jena). The stress was calculated by the equation:

$$\sigma = \frac{E\left\{S_i - S_n\right\}}{2D(1+\nu)\ \sec^2 2\theta\ \tan\theta\ \sec^2\psi}$$

where

S_i is the distance of the diffraction maxima from the centre of the film when the reflecting plane normal is set at an angle 45° with the incident x-ray beam, S_n is the distance of the diffraction maxima from the centre of the film when the reflecting plane normal coincides with the x-ray beam, D is the distance between film and the specimen in Cm, ν is the poisson ratio, E is the young's modulus of the deposit in Kg/cm^2, θ is the Bragg angle and ψ is the angle between the reflecting plane normal and the incident x-ray beam.

Microhardness Measurements

Microhardness measurements were made with deposits 36 μ thick (i.e. 20 times thicker than the depth of indentation) plated on to deoxidised copper discs 1 cm dia and 6 mm thick. The deposits were smooth and bright. They were lightly polished with ν -alumina, etched very lightly in ammonium persulphate, rinsed in water followed by alcohol, dried and

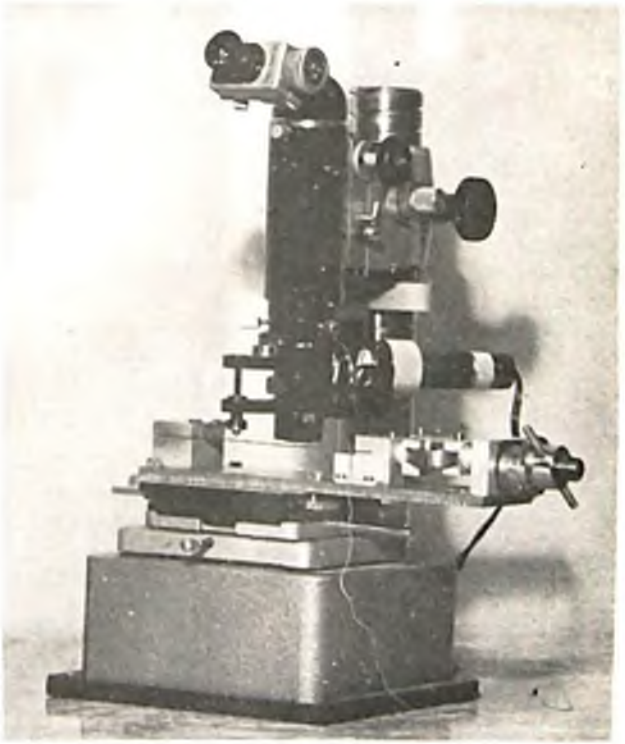


Fig. 1b Strain guage with Specimen on the stage.

used for measurement. Hardness was measured immediately after plating to avoid errors due to the ageing effect [6]. These were determined with the microhardness tester (π MT-3 USSR) using 20 gms load. For each specimen, a minimum of six determinations were made and their average was taken.

Microhardness Measurements as a Function of Stress

For making these measurements, a special tensile loading stage (Fig. 1a) was fabricated and used. An annealed copper strip was milled to yield a specimen (15 mm long, 13 mm wide and 1 mm thick). This was electropolished in phosphoric acid bath. For measuring strain, a KB-3A1 strain gauge was fixed on the back surface of the specimen; Grips G_1 and G_2 (Fig. 1b) were used to grip the specimen. Load was applied through a ring R by tightening the nut N. The strain produced was measured using a BLH-SR-4 strain indicator. Microhardness measurements were made at 50 gms load for each value of strain. To check whether the specimen bends during indentation, one of the edges of the specimen was observed through a microscope fitted with an eyepiece graticule capable of measuring 0.005 min. This did not show any measurable defection.

Grain Size Measurements

This was accomplished by the x-ray method. In this method, the grain size is obtained from the broadening of the diffraction ring. It has been shown [21] that coherent domain size (taken to be equal to grain size) is a function of integral breadth,

$$\beta(2\theta) = \frac{\text{area of the diffraction profile}}{\text{width of the base}}$$

To apply this method, a diffraction pattern of the deposit was recorded using Cu K_α radiation and a diffractometer (General Electric). The diffraction pattern of annealed copper (grain size very large and assumed to be infinite) was also recorded using the same settings of the instrument. The profiles in the latter pattern represents only broadening due to the diffractometer geometry.

To get the integral breadth, one has to calculate from these data the stokes corrected Fourier coefficients, C_n since

$$\beta(2\theta) = \frac{2\theta_2 - 2\theta_1}{\sum C_n}$$ where $2\theta_2 - 2\theta_1$,

is the Fourier interval.

De Angelis [22] has given a computer programme for the evaluation of C_n from the experimental diffractograms in Fortran language. This was translated into Autocode and used with the Ferranti Sirius computer for getting C_n and hence $\beta(2\theta)$. The grain size L was then obtained from $\beta(2\theta)$ by using the expression [23].

$$L = \frac{\lambda}{\beta(2\theta)\cos\theta}$$

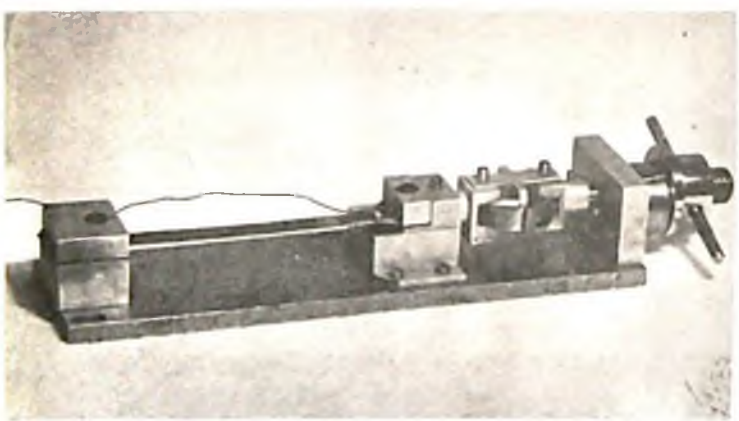


Fig. 1a Tensile loading stage fabricated in the lab

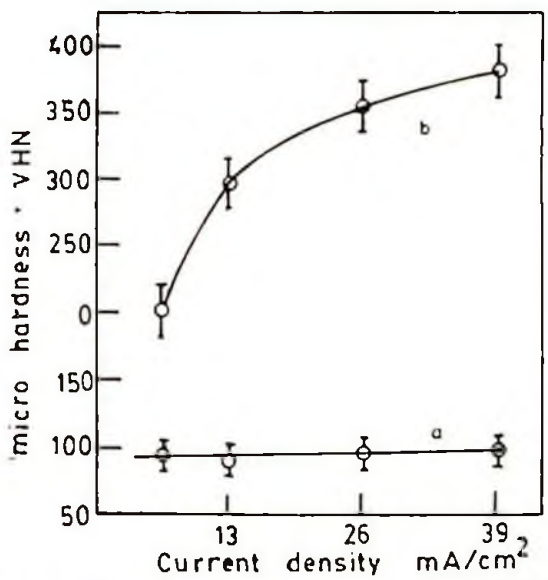


Fig. 2 Microhardness vs c.d. for electrodeposited copper from
a) acid copper bath with no BTA
b) acid copper with BTA

where λ is the wavelength of the radiation, θ is the Bragg angle. The profile of (220) reflection was used for calculating the grain size.

RESULTS AND DISCUSSION

Fig. 2 shows the variation of microhardness H_m with current density (c.d.) for pure acid copper bath and that containing BTA as an addition agent. It is seen that H_m increase with c.d. and tends to attain a constant value in the case of BTA copper deposits.

The variation of internal stress (obtained by the x-ray and Stoney's methods) with c.d. is shown in Fig.(3) It is seen that the values of stress obtained from the flexible cathode method is lower than that obtained by the x-ray method in the region of tensile stress whereas an opposite behaviour is noticed in the compressive stress region. The difference between the two methods, however, is of the order of experimental error. But the error is systematic. The precise reason for this is not clear, at present. It has been shown recently that preferred orientation affects the value of stress measured by the x-ray method [24]. This may perhaps be responsible for the difference noted above.

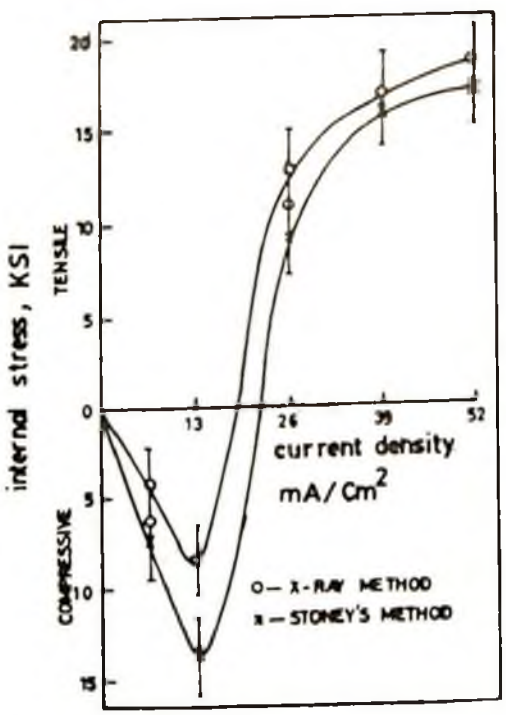


Fig. 3 Internal stress vs c.d. of plating.

The pattern of variation of stress with c.d. and the magnitude of stress values are in good agreement with the result reported by Walker [9]. As for the hardness values, it must be pointed out that although the pattern of variation is similar to that of Walker and Benn [11], the values reported here are higher. This difference is perhaps due to the fact that the results reported here pertains to a bath not purified by treatment with H_2O_2, activated carbon and pre-electrolysis. However the values are in agreement with those of Walker [6]. It is known that the hardness of copper from a bath containing BTA, changes with time. A change of 60 to 80 units is not uncommon. The values reported here corresponds to the values obtained immediately after plating.

Following are the established causes that increase hardness of metals.

(a) "Locked-in" stress
(b) Cold working
(c) Small grain size
(d) Dispersion of fine particles

We discuss below the relevance of each of these factors in relation to the high hardness of BTA copper deposit.

It has been shown [25] that locked in compressive stress increases hardness whereas tensile stress decreases it. To examine the magnitude of this effect, micro hardness as a function of stress was measured, and the results are shown in Fig. 4. Since the applied stress is tensile, H_m decreass in the elastic region of stress and tends to increase

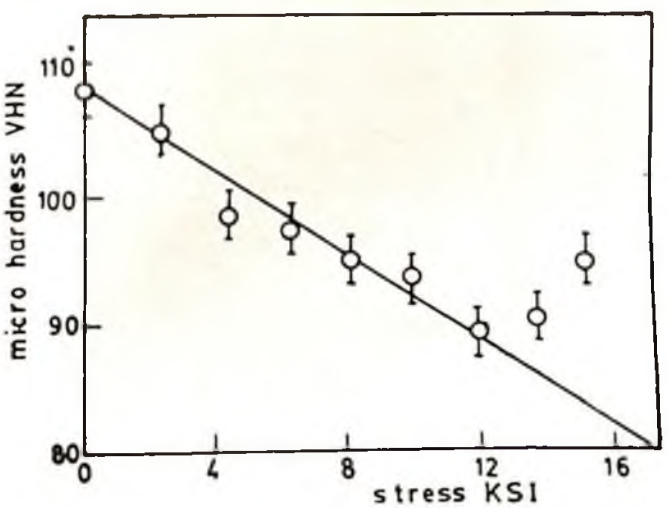


Fig. 4 Microhardness vs stress.

at high stress presumably dut to cold working. For a compressive elastic stress, H_m would increase. The slope of H_m vs, compressive stress would be the same as that of Fig. 4 except that its sign will be positive. From the results, it is seen that for a strain corresponding to a third of the strain at breaking, H_m changes only by 20 units which is too small compared to the difference between the microhardness of plain acid copper deposit and BTA copper deposit (Fig. 2). There is another reason in favour of discarding the stress hypothesis of hardness. Since compressive stress increases hardness and tensile stress decreases it, one would have expected that H_m vs c.d. curve should have increased upto 13 mA/cm^2 (since the compressive stress increases upto this c.d.) and then decrease continually till such a value of stress where work hardening starts. No such behaviour is noted.

It is known that work hardened metals are harder because of an arrangement of dislocation substructure could be present in electrodeposited metals. If this argument is true, then we would expect that the heardness of electrodeposited copper should be nearly the same as that of cold-worked copper. O'Neill and Cuthbertson [27] showed that the hardness of copper increases from about 60 to 120 Kg/mm^2 when the thickness of the specimen is reduced by 60%. This shows that the dislocation sub-structure brought about by severe cold-working changes hardness by only 60 units. Hence the hardness of BTA copper deposit cannot be ascribed solely to a dislocation substructure similar to that induced by cold working.

A correlation between high hardness of electrodeposits and small grain size has been suggested [13,14]. The extent to which this factor contributes to the hardness of BTA copper deposit can be evaluated by attempting a quantitative correlation between grain size and H_m using Hall-Petch equation [16,17]. Tabor [28] showed that for copper $H_o = 3\sigma$ where H is hardness and σ is the yield stress. Using this in Hall Petch equation one gets $H = Ho + 3Kd^{-1/2}$ where d is the grain size, Ho is the hardness when $d^{-1/2} \to 0$ and H is the hardness at any grain size and K is constant. Felthan and Meakin [29] report a value of 0.36 for K in the case of copper. In table 1, the grain size, hardness measured and that expected on the basis of Hall Petch equation are shown at three typical current densities. The results show that at low c.d., the hardness of the deposit could be explained on

TABLE 1

c.d. mA/cm	d grain size in mm x 10	H VHN measured	H, calculated from Hall petch relation*
6.5	0.569	200	213
13.0	1.329	298	164
26	1.44	355	160

*H = 70 + 3 x 0.36 d.

the basis of fine grain size. At higher current densities only a portion of tne hardness increase could be due to grain size effect.

It would be worthwhile to make some observations on the grain size determined by the x-ray method. This method really gives only the coherent x-ray domain size. The grain size is expected to be equal to or greater than the coherent domain size. From the results of Hofer and Hintermann [18] who measured grain size by electron microscopy and coherent domain size by x-ray diffraction, it is seen that the two are practically equal. In this present work, the coherent domain size (taken as equal to the grain size) has been calculated from integral breadth without correcting for strain and stacking faulty broadening. Since the deposit did not give sufficient number of diffraction lines, these corrections had to be omitted. Judging from the results of Hofer and Hintermann [18], there is no need to correct for the above factors since the total domain size agrees with the grain size. However even if they are important, we would have underestimated the grain size by about 10 to 20% and hence the main conclusion drawn above is still valid.

A comparison of the effects of thiourea and BTA on the H_m of copper leads to very interesting results. For this purpose Hofer and Hintermann's [18] data on copper deposited from an acid bath containing thiourea are presented in Fig.(5) as Hm vs $d^{-1/2}$. From the graph one finds that Ho = 100 VHN and K = 0.363 $Kg/mm^{3/2}$. It is seen that though Ho is higher (100 instead of 70), the value of K agrees very well with the value of 0.36 $Kg/mm^{3/2}$ quoted by Feltham and Meakin [29]. Therefore it can be concluded that the hardness of copper deposited from thiourea containing bath can be attributed to small grain size whereas the hardness of BTA copper deposits is not only due to grain size but also due to some other factors.

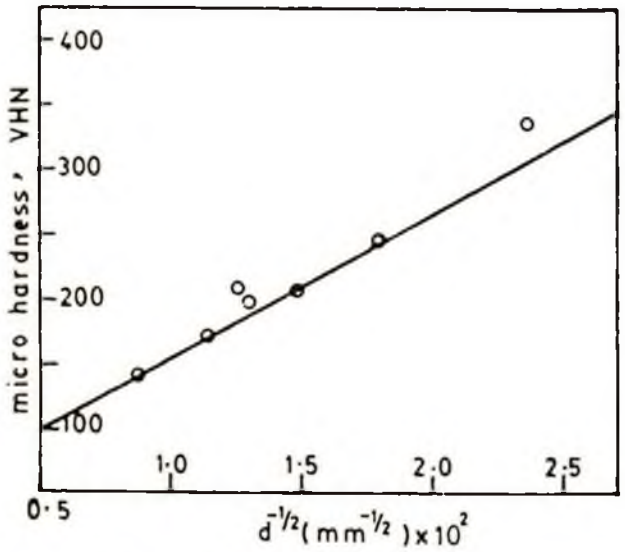


Fig.5 Hofer and Hintermann's data

Perhaps there is a dispersion hardening effect since it is known that cuprous benzotriazolate is incorporated [5]. However an anomaly should be pointed out. Prall and Shreir showed that the amount of incorporation decrease with c.d. since dispersion hardening effect increases as the inter particle distance is descreased [30], it may be expected that the hardness (if it is due to dispersion hardening) should decrease with increase in c.d. unless the particle size itself is affected by c.d.

It has been assumed [31] in the case of Iron-Nickel deposits that the banded structure is responsible for high strength; but no theoretical arguments have been given in this paper and in others for exoepting a higher strength in the case of banded-structured-deposits. The recent work of Koehler [32] makes one suspect that there could be some correlation between laminar structure and strength.

From the above discussion it is concluded that though a substantial fraction of the hardness of BTA copper deposits can be explained by grain size, the contribution from dispersion hardening and perhaps banded structure of the deposit are also significant.

ACKNOWLEDGEMENTS

The authors thank Mr. Narayana Iyer for fabricating the tensile loading stage, Mr. B.S. Dasannacharya for help in regard to strain gauge instrumentation, and Dr. A.K. Singh for advise regarding stress and grain size measurement. They thank Dr. S. Ramaseshan for his keen interest and discussions.

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