POROSITY AND DIMENSIONAL CHANGES IN Cu AND Cu-Ni SYSTEM

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المسامية والتغيرات الحجمية في النحاس
وفي نظام النحاس ـ النيكل

بقلم
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خلاصة المقالة

في هذا البحث درست المسامية التي تتكون خلال الانتشار ما بين النحاس (خال من الاوكسجين وموصل عالي) ونيكل بعد لحامهما لتكوين زوج انتشاري وكذلك المسامية التي تتكون في نفس النوع من النحاس المحضر على شكل اقراص واسطوانات بسبب الهيدروجين •

بعد التلدين الانتشاري تحت نفس الشروط في الفراغ وفي غاز الاركون (ضغط جوي واحد) كانت نتائج حجم المسامات والتغيرات الحجمية مختلفة وعند لحام النحاس المذكور اعلاه والمحتوي على مسامات مع نيكل ، ثم تلدينه انتشاريا ، اثر على تكوين المسامية • كما ان استعمال ضغط قبل التلدين ادى الى زيادة المسامية وتقليل حجم المسامات •

ان هذه الملاحظات تخلق كثيرا من المشاكل في مجالات هندسية مختلفة مثلا في طلاء سطوح المعادن ، لحام معادن مختلفة ، واستعمال معادن مركبة •

POROSITY AND DIMENSIONAL CHANGES IN Cu AND Cu-Ni SYSTEM

ABSTRACT:

The porosity formed during interdiffusion in OFHC Cu/Ni diffusion couples, and in OFHC Cu discs and cylinders due to hydrogen have been studied. Different volumes of porosity and dimensional changes were obtained after diffusion annealing in vacuum and in 1 atm argon gas under similar conditions. Porosity introduced previously in OFHC Cu prior to welding to Ni affected the subsequent porosity during diffusion annealing. Prestraining of specimens showed extensive porosity but with reduced sizes. These observations can creat problems in many engineering areas such as coating of materials, welding of dissimilar materials, composite materials and where fine tolerances are required.

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1. INTRODUCTION :

Porosity and swelling have been observed in many systems due to hydrogen effect[1, 2, 3]. Copper is one of the metals which can be disrupted due to this effect. If copper is heated in hydrogen atmosphere at high temperature, then Cu_2O will be reduced and water vapour is formed, that causes porosity and blistering, because copper can not withstand the water vapour pressure created, which has a value of about 10^4 atm. at 850°C. This effect is known as steam embrittlement[4]. At low temperatures of 130°C and probably below, hydrogen diffuses into the copper and reacts with cuprous oxide particles to form water without disrupting the copper, but when heated to higher temperatures for a short time the trapped water will vaporize and expand causing disruption[5]. Steam embrittlement has several aspects, e.g. cracks on the surface, change of dimensions, blisters near the surface, series of holes along grain boundaries and within the grains. Density measurements show that the density of copper can be reduced to 6 g/cm^3 [6]. The porosity and the cracks form according to the concentration of Cu_2O particles. Steam embrittlement can take place if the enviroment contains water vapour in the presence of some reducing elements, that have higher affinity to oxygen

than copper, e.g. chromium steels, which act as reducing media and form oxides and the atomic hydrogen is left free to diffuse into the copper. Also oil damp can cause disruption in copper, where atomic hydrogen is obtained in a similar manner at high temperature from oil vapour. Heating copper in the absence of a reducing element, such as quarz, will cause no distuption. Using moist argon as a protective gas by heating of copper causes microcracks and no cracks in those treated with argon of dry quality[7]. Water can act as a source for hydrogen[8]. There must be some elements to reduce the H_2O according to this equation:

$$x\,M + H_2O \longrightarrow M_xO + 2H_{at}$$

The more active metal than copper reacts with H_2O that can come from any source, even from the air. This reaction produces the oxide of the active metal and the atomic hydrogen diffuses along the grain boundaries and cause the disruption of copper at high temperature according to:

$$Cu_2O + 2H \longrightarrow 2Cu + H_2O$$

To produce the observed effect only few parts per million of hydrogen is needed[9].

The observations related to the hydrogen effect have been encountered in diffusion couples made of copper and nickel. The porosity and dimensional changes which

occur in diffusion couples made of OFHC Cu and Ni are affected due the presence of hydrogen[10]. This study was designed to investigate further the hydrogen effect on the Kirkendall diffusion which leads to void formation, dimensional changes and property degradation, which vary in severity depending on temperature, time, composition, hystory of the component, pressure, vibration and etc.[11, 12, 13, 14]. In Kirkendall diffusion, e.g. in a binary system, flow of material occurs in opposite direction across their contact interface and imparts a velocity to any object in the lattice which does not take part in the diffusion process[15]: which is

$$V = (D_1 - D_2) \frac{\partial N_1}{\partial X} = \frac{\Delta X_m}{2t}$$

The chemical diffusion coefficient is related to the partial diffusion coefficients as follows :

$$\tilde{D} = D_1 N_2 + D_2 N_1$$

2. EXPERIMENTAL PROCEDURE :

To study the porosity by hydrogen, experiments were carried out using OFHC specimens, in form of disc and cylinders. The discs were of 6.5 mm diameter and 22 mm length, a size which gave suitable weight for density measurements. Diffusion couples were made in form of

sandwichs of Cu/Ni as shown in Fig. 1. The OFHC Cu was available in 6.5 mm as extruded bars. The nickel rods were available in larger diameter, which were then swaged down to 6.5 mm diameter bar. Small mechanical saw was used to cut discs of 2-3 mm thickness. All discs were ground slightly and then polished using a double sided mould that allowed them to be polished on both sides without remounting. Before mounting the discs, grooves were cut in the Ni sections to assist the winding of the tungsten wire of 23.5 μm diameter which were used to determine the Kirkendall shift. The diffusion couples were pressure welded at 750 °C.

The specimens were annealed for various times at different temperatures in vacuum using horizontal silica tube furnace and in 1 atm. argon using a pressure vessel. A micrometer was used to measure the dimensional changes after annealing. Many specimens were pre-strained by compression at room temperature and then annealed in vacuum and in 1 atm. The pre-straining was 18%. Ratcliffe's hydrostatic comparative technique was employed to follow the density changes[16]. The balance was a stanton "Unimatic CL 43". The liquid was diethylphthalate $C_6H_6(COOC_2H_5)$.

The fractional density change according to Ratcliffe is given by :

$$\frac{\Delta \rho}{\rho} = \frac{W_{a1}\,(w_{a1} - w_{L1})}{w_{a1}\,(W_{a1} - W_{L1})} - \frac{W_{a2}\,(w_{a2} - w_{L2})}{w_{a2}\,(W_{a2} - W_{L2})}$$

A microscope with two micrometers attached to it was used to determine the distance between the marker pairs before and after annealing treatment. The vacuum furnaces were capable of providing a vacuum of 10^{-5} mm Hg. The mean linear intercept method used for grain size determination. The solution used for etching was hydrogen peroxide (20 vols), 8/80 ammonia and water in the ratios 2:5:5 respectively by volume. The analysis of void distribution were obtained from optical photographs enlarged to sizes suitable for measurements using the Zeiss particle size analyser.

3. RESULTS :

The results of specimens exposed to hydrogen effect are listed in Table 1, 2, and 3. The pure OFHC Cu discs and cylinders annealed in 1 atm. argon showed a volume increase, that could be measured by micrometer or density measurements in case of cylinders. The OFHC Cu discs and cylinders annealed in vacuum showed no significant changes

in either length and diameter, Table 1 and 2. Experiments of the same sort but specimens pre-strained to 18% at room temperature in compression showed extensive void formation after annealing in argon, Table 1 and 2. The parameters such as mean void diameter and void volume per unit area were calculated from the number of voids and individual void diameters.

From the areal analysis of the photographs the total area of the voids per unit length of the interface was calculated from :

$$A / L' = (\pi \sum r_i^2 N_{vi}) / L'$$

then it was assumed that A/L could be taken as equal to V/S, where V is the total void volume per unit area S of interface. The average void diameter was calculated from:

$$\bar{r}^2 = (\sum N_{vi} r_i^2) / N_{tot}$$

where $\bar{r}^2$ is the mean value of r^2. The geometric mean value of r and hence the geometric mean void diameter were then calculated from $\bar{r}^2$.

The volume change and the number of voids were larger, but the average void size was smaller than in specimens without pre-straining, Table 1 specimens 2, 2.1 and 2.2. The pre-strained specimens annealed in vacuum did not show any significant change in volume (specimen 6.3).

in case of specimens annealed in vacuum, Table 2 specimen 7.1.

In order to study the hydrogen effect on mutual diffusion, sandwich type diffusion couples were annealed at 800°C in 1 atm argon and in vacuum for the same time. The results are given in Table 3, specimens 8.1 and 8.2. The length increase of the couple in vacuum was about 1/3 of that annealed in 1 atm. of argon. To show the effect of prior annealing in 1 atm. argon on diffusion, the OFHC Cu discs were annealed for 140 hours in argon which caused extensive void formation. Then the discs were welded to Ni discs. The results are given in Table 3 specimen 11. Comparing these results with those obtained from a diffusion couple annealed in vacuum at the same temperature and for the same time (specimen 10) show that the length increase and the marker movement are smaller in the former.

Figs. 2 and 3 show the hydrogen effect after annealing at 800°C for 240 hours in 1 atm. argon. Fig. 2 is from a pre-strained OFHC Cu discs for 18% in compression at room temperature, which showed more voids of smaller sizes than the former. This can be clearly seen in Figs. 4 and 5. The OFHC Cu discs annealed in vacuum are not affected by hydrogen. They are free of voids. Figs. 6 & 7

which are from specimens annealed at, 750°C and 1000°C respectively. Figs. 8 and 9 show the differences in porosity formed in sandwich type diffusion couples annealed in 1 atm. argon and in vacuum for 16 hours at 800°C. The porosity in the former is more than in the latter. Voids are in the whole section of the Cu subjected to the hydrogen effect.

4. DISCUSSION OF THE RESULTS :

The atomic hydrogen may form as described in section 1, and causes porosity in OFHC Cu which leads to volume changes. The possible sources are the wet air or the moist argon that act as sources for atomic hydrogen in the pressure vessel used which was made of Ni-Cr-Mo steel. The chromium reduces the vapour and produces the atomic hydrogen. In OFHC Cu discs exposed to hydrogen effect, the grain sizes are smaller than those of not exposed ones, Table 1 specimens 2, 2.1 and 6.1 - 6.3. This means that the void inhibits the grain growth by acting like anchors on the grain boundaries. The anchoring effect was reported by many authors[17, 18]. The distribution of the voids was mainly on grain boundaries, which suggests that the oxide particles find themselves mainly on grain boundaries and occasionally in the grains, Fig. 3. Prestraining at room

temperature for 18% in compression increased the porosity where as the void size is reduced Figs. 3. 4. This observation suggests that pre-straining may increase the number of nucleating sites such as grain boundaries and dislocations.

In diffusion couples annealed for the same time and at the same temperature, the length change of the couples exposed to hydrogen effect was larger. The ΔL in unexposed one agrees with void volume V/S, Table 3, specimen 8.1, but in the exposed one the ΔL agrees with void volume calculated from diffusion zone and outside the diffusion zone. Table 3 specimen 8.2.

In a diffusion couple in which the OFHC Cu discs were exposed to the hydrogen effect and then welded to the nickel, ΔL is smaller than that of an usual couple annealed in vacuum for the same time and at the same temperature. Table 3, specimen 10 and 11. This observation suggests that the voids formed in OFHC Cu discs before diffusion annealing have reduced the number of nucleation sites which are in this case most probably oxide particles, and therefore less porosity and smaller ΔL. The smaller marker shift may suggest as well that diffusion of the vacancies was occuring in opposite direction at the start of diffusion, that is from Cu to Ni.

. CONCLUSIONS :

Hydrogen effect in copper is a phenomenon that can cause disruption and serious defects in the structure. A reducing media is necessary to get this effect. Prestraining increases the number of voids, probably by increasing the number of nucleation sites, such as grain boundaries and dislocations. Interdiffusion (or chemical diffusion) leads to porosity, which can be serious, specially in materials which are designed for use at high temperatures. In both cases, volume changes occur, which are large if compared with fine tolerances in engineering designs. In Cu/Ni diffusion couples where Cu was porous, the marker movement, void volume and the volume increase were smaller.

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NOTATIONS :

V = Marker Velocity

D_1, D_2 = Intrinsic Diffusion Coefficients

N_1, N_2 = Atomic Concentrations

X_m = Marker Shift

t = Diffusion Time

$\tilde{D}$ = Chemical Diffusion Coefficient

$\Delta\rho/\rho$ = Fractional Density Change

W = Specimen Weight

w = Dummy Weight

$a, L, 1, 2$ = Refer to Air, Liquid, before and after annealing

A = Total Area of the Voids

L' = Length of the Interface

r_i = Void Radius

N_{vi} = Number of Voids of Concerned Radius

N_{tot} = Total Number of Voids

V/S = Void Volume per Unit Area

TABLE 1

Specimen Number	T (°C)	Time (hr)	Dimensions L (mm)	Dimensions D (mm)	ΔL (μm)	ΔD (μm)	N_v / mm²	$\bar{d}$ (μm)	Grain size before treatment (μm)	Grain size after treatment (μm)
2 1 atm argon	800	240	2.665	6.34	6.0	17.0	60	31.6	25.7	110
2.1 1 atm argon	800	240	2.687	6.34	6.0	18.0	60	31.0	25.7	112
2.2 1 atm argon 18% prestrained	800	240	2.377	7.08	16.0	29.0	138	22.6	24.3	99.8
3.1 vac.	950	1	2.65	6.32	0.0	0.6	-	-	25.7	145
3.2 vac.	950	4	2.74	6.32	0.4	0.9	-	-	25.7	245
3.3 vac.	950	16	2.824	6.32	1.0	-1.0	-	-	25.7	282
4 vac.	1000	1	2.687	6.3	-4.0	-1.0	-	-	25.7	151.4
6.1 vac.	750	377	2.883	6.32	0.0	-0.3	-	-	25.7	152
6.2 vac.	750	472	2.83	6.32	-0.3	-2.0	-	-	25.7	160
6.3 vac. 18% prestrained	750	24	3.244	6.6	1.1	0.75	-	-	25.7	128

TABLE 2

Specimen Number		T (°C)	Time (hr)	Dimensions (mm) L	D	$\Delta\rho/\rho$
7.1	1 atm argon	800	6	22.1	18.2	2.7×10^{-5}
7.2	vac.	800	6	22.3	18.09	-0.812×10^{-4}

TABLE 3

Specimen Number		T (°C)	Time (hr)	ΔX_m (μm)	ΔL (μm)	ΔD (μm)	$\bar{d}$ (μm)	V/S(μm) diffusion zone	V/S(μm) outside zone
8.1	vac.	800	16	7.0	9.0	3.0	7.0	10.05	-
8.2	1 atm argon	800	16	6.0	25.0	6.0	8.05	11.0	9.0
			16	9.0	10.0	2.0	7.5	9.2	-
10	vac	800	36	13.0	17.0	4.0	-	-	-
			68	21.0	23.5	8.0	11.7	26.0	-
			16	3.0	4.0	1.0	-	-	-
11	1 atm argon	800	36	7.0	7.5	3.0	-	-	-
			68	15.0	11.0	6.0	11.51	15.2	9.4

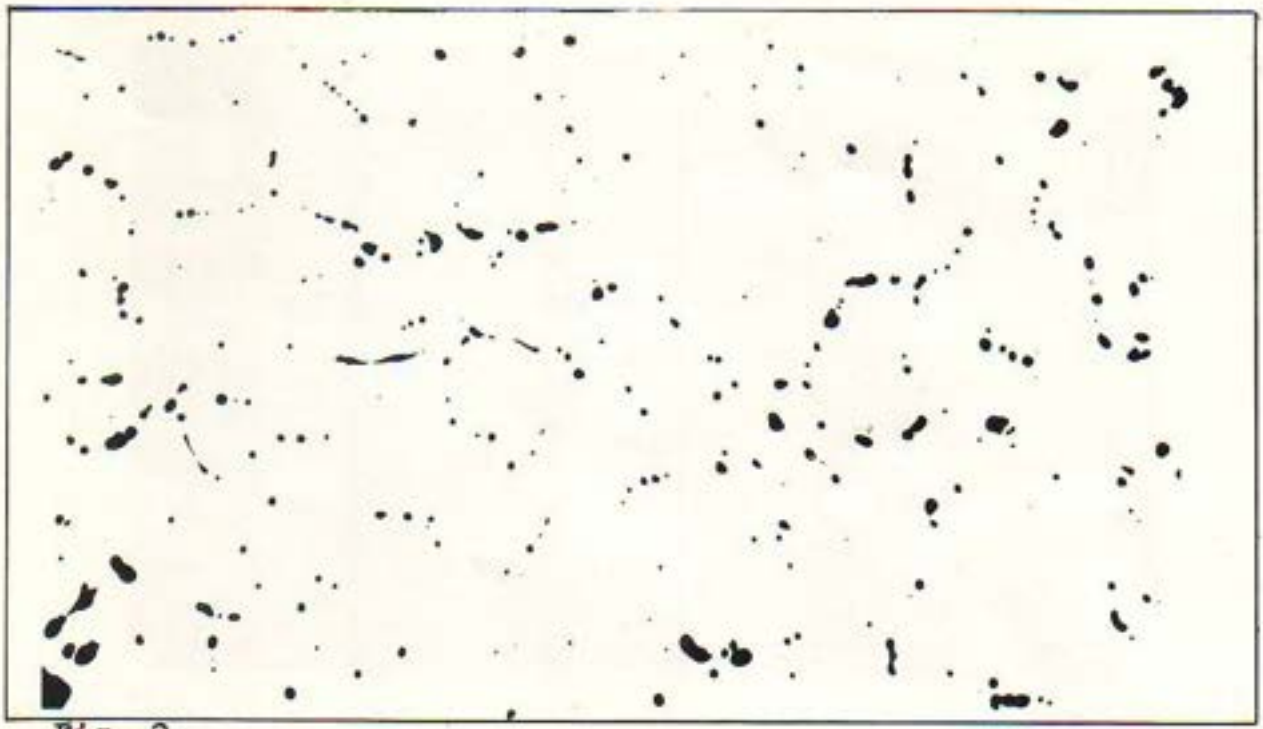


Fig. 2

Porosity in OFHC Cu caused by nydrogen at 800°C after 240 hours. Magnification x 54

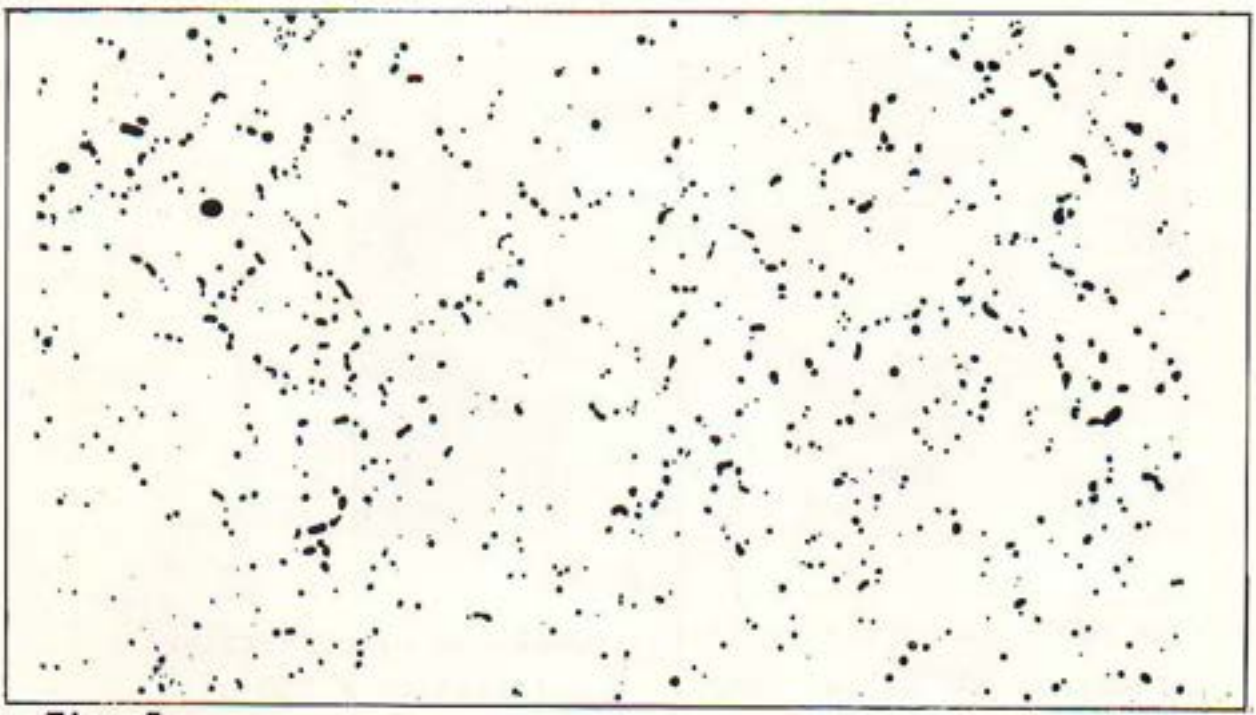


Fig. 3

Porosity in OFHC Cu caused by hydrogen at 800°C after 240 hours. The specimen was prestrained at room temperature for 18% in compression. Magnification x 54

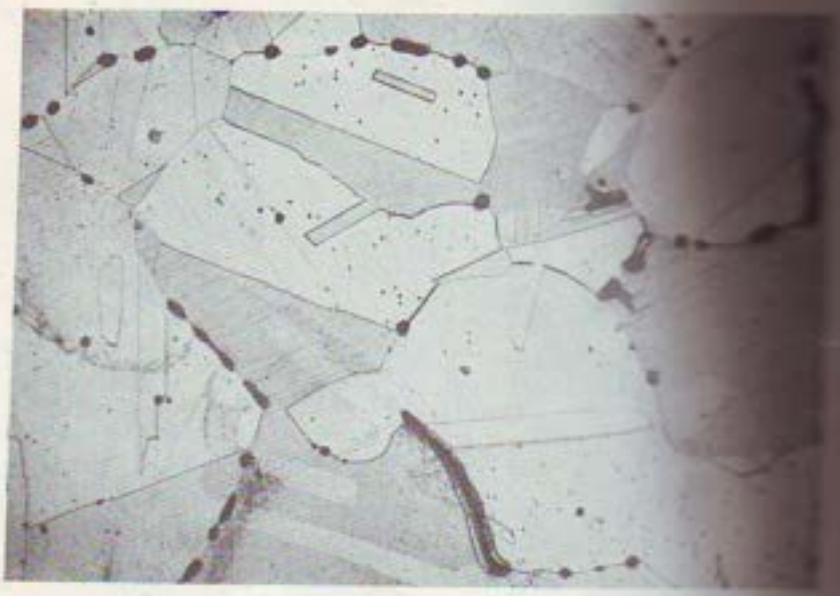


Fig. 4
The hydrogen effect in etched condition 800°C, [illegible]
Magnification x 130

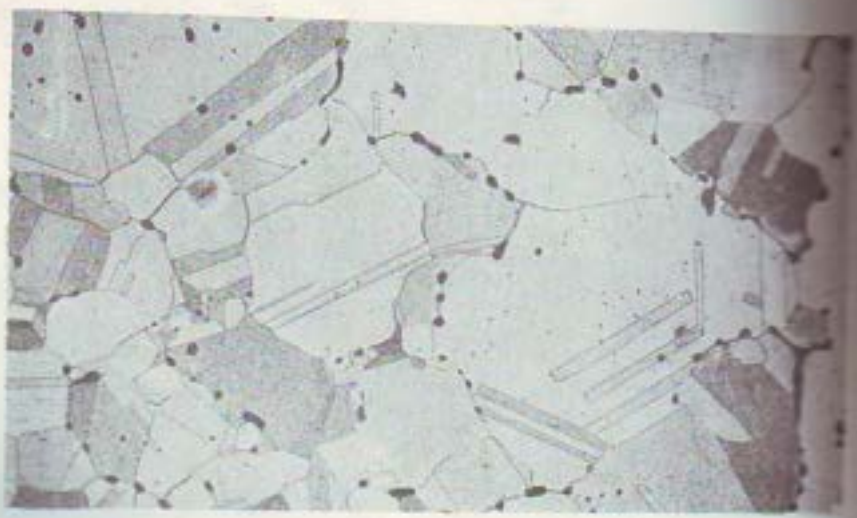


Fig. 5
The hydrogen effect in etched condition of [illegible] specimen. 800°C, 240 hours. Magnification x 130

" CORRECTION : Interchange Fig: 6, by Fig : 7".

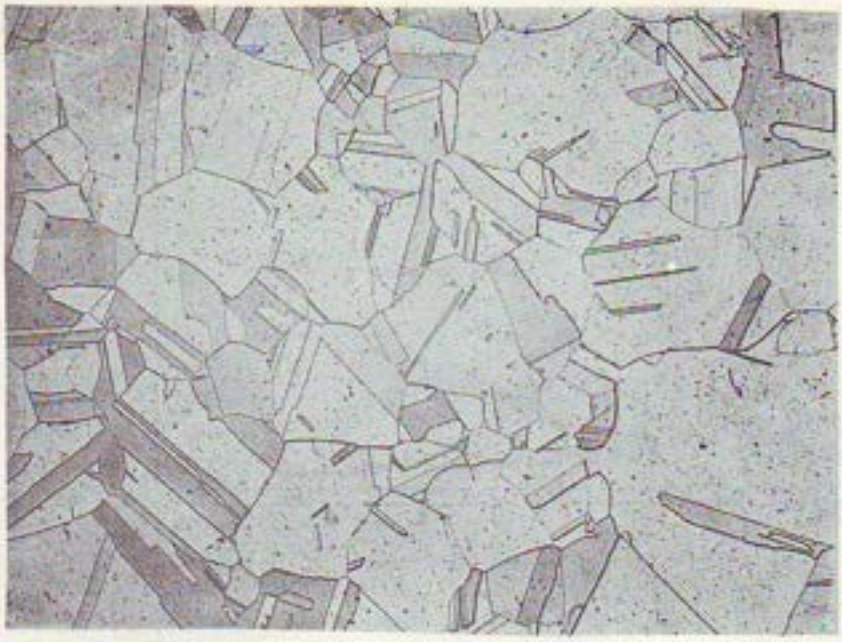


Fig. 6

No porosity in OFHC Cu annealed in vacuum after 24 hours at 750°C. Magnification x 30

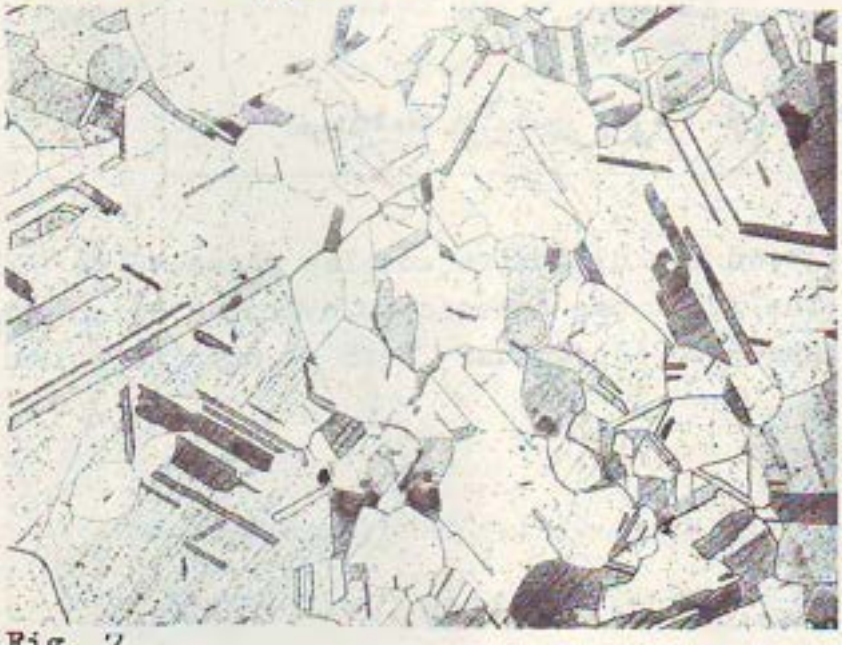
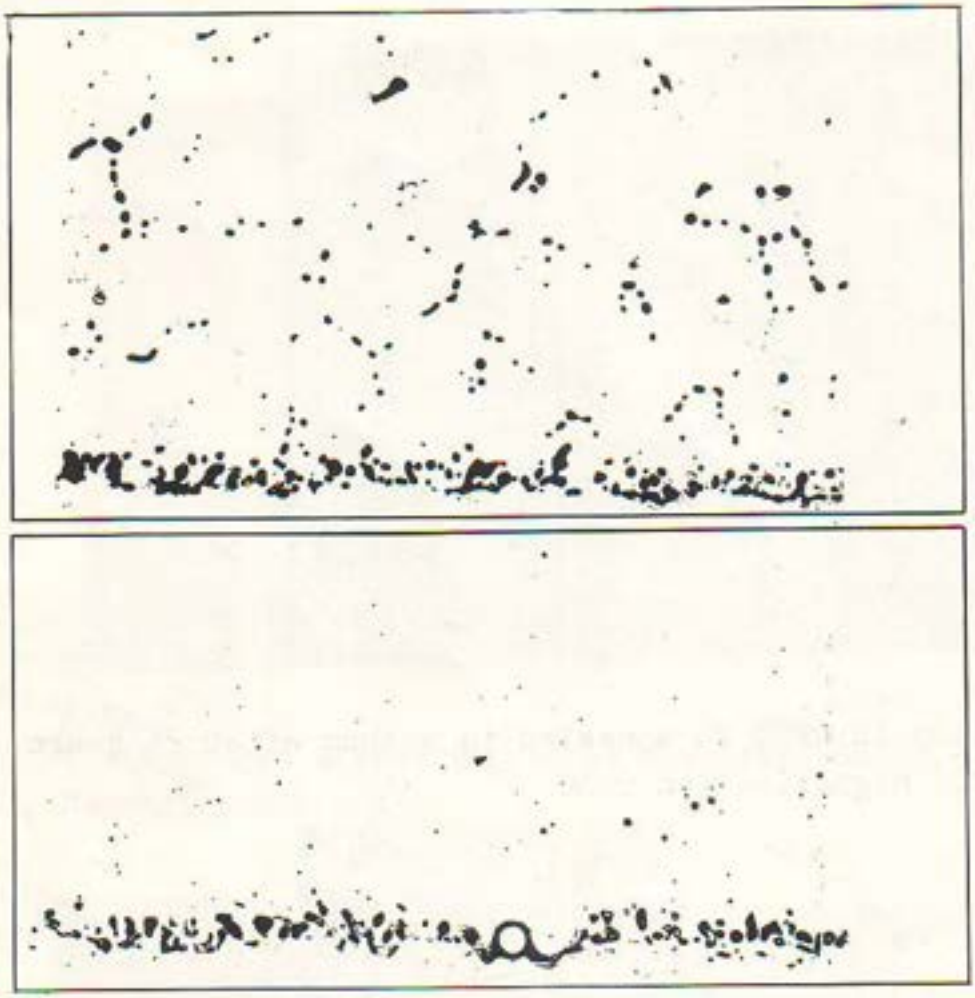


Fig. 7

No porosity in OFHC Cu annealed for 1 hour at 1000°C. Magnification x 30



Figs. 8-9

A comparison between two diffusion couples annealed at 800°C for 16 hours. The first one exposed to hydrogen effect and the second one annealed in vacuum. Both at magnification of x 176