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X-Ray Diffraction Line Broadening Studies of Raney Copper and Nickel

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X-Ray diffraction line broadening analysis has been used to determine crystallite sizes, microstrains and stacking fault probabilities in Raney nickel and Raney copper catalysts prepared by different methods. The data for the Raney catalysts were compared with those for ball-milled copper and nickel powders.

Time and temperature of digestion of the Raney alloys affect the defect structures. The crystallite size in the ⟨111⟩ direction was mainly determined by the digestion temperature.

On aging a highly active Raney nickel, a rapid decrease of microstrain was observed. This was followed by a steady growth in the ⟨100⟩ direction, while little change occurred in the ⟨111⟩ direction. Aging the catalyst and increasing the digestion time of the Raney alloy were shown to cause similar changes in defect structure.

The microstrain and stacking fault probability were observed to be inversely related to crystallite size.

INTRODUCTION

Uhara *et al.* (*1*) have shown that plastic deformation increased the specific catalytic activity of copper and nickel wires. This increase was observed to decline rapidly when the wires were annealed at the recrystallization temperature. The authors attributed the increase in catalytic activity to surface dislocations and vacancies, which were produced by the cold working. Keating, Rozner and Youngblood (*2*) showed that the rate of catalytic decomposition of hydrogen peroxide on the surface of platinum foil was related to the degree of cold working. X-Ray examination of the cold worked metal indicated that considerable line broadening occurred; however, the authors made no attempt to analyze the broadened X-ray lines. High catalytic activities have also been induced into metal surfaces by ion bombardment (*3, 4*), which has been shown to produce large concentrations of crystal defects.

On the other hand, carefully conducted experiments by Jaeger (*5*) failed to establish any relationship between the density of surface defects and catalytic activity for decomposition of formic acid on the surface of silver. In support of this work, Willhoft (*6*) has shown that on clean nickel surfaces, the catalytic activity for formic acid decomposition was independent of degree of cold working.

Thus, although there is evidence to suggest that crystal defects may provide active sites in catalysts, the exact nature and function of the sites in many practical catalysts is unknown. One of the reasons for this is that it is difficult quantitatively to assess the defect structures of technically useful catalysts, since these are generally obtained in powder form.

X-Ray diffraction line broadening analysis has been extensively used quantitatively to evaluate defect structures in cold worked polycrystalline powders. This technique permits measurement of

a. crystallite size, D_{hkl}, which is the mean diameter of the coherently scattering domains in the crystallographic direction ⟨*hkl*⟩;

b. microstrains, ϵ_{hkl}, which are nonuniform variations of the interplanar spacings, resulting from the presence of dislocations;

c. stacking faults, which are faults in the packing sequence producing localized changes in structure. Stacking fault probability is given as α, where $1/\alpha$ is the average number of layers between the faults. At the present time, the X-ray diffraction method is the only known means of measuring defect concentrations in crystalline powders. The object of our present experiments was to study the influence of defects on the properties of highly active powder catalysts.

It is known that Raney nickel and Raney copper catalysts of different activities and stabilities may be prepared, and that variation in the preparation and pretreatment can produce specimens with different specific surface areas and defect structure. Specimens of these materials were therefore prepared by different standard methods, and X-ray examination was carried out to determine crystallite sizes, microstrains and stacking fault probabilities. X-Ray examination was also made of ball-milled copper and nickel powders, in order to compare the structures of the catalyst powders with the well-established structures of the cold worked metals, which could then act as reference standards.

A study has been made to show how variation of the time and temperature of digestion of the Raney alloys affects the defect structures of the resulting catalysts. In addition, the aging process was investigated for a highly active Raney nickel, stored under ethanol at room temperature.

EXPERIMENTAL METHODS

Preparation of Ball-Milled Powders

Samples of copper powder (1 g each) were ball-milled for various periods of time in a copper milling pot with a copper plated steel ball. Nickel samples were similarly treated in an inconel pot with a nickel plated steel ball.

Preparation of Catalysts

a. Raney copper. Specimens were prepared from Devarda's alloy following procedures used by Stanfield and Robbins (*7*). Since the alloy produced a diffraction line very close to the 111 reflection of Raney copper, it was necessary to use longer digestion periods than those used in Stanfield's procedure. Five specimens of Raney copper were prepared by digesting the alloy for the following times and temperatures: 5 hr at 128°C, 5 hr at 95°C, 5 hr at 70°C, 15 hr at 45°C and 24 hr at 25°C. After washing well with water and ethanol, the resulting catalyst powders were kept under absolute ethanol.

b. Raney nickel. Catalyst W8 was prepared by digestion of nickel–aluminium alloy (supplied by B.D.H.) in sodium hydroxide solution at 100–105°C for 4 hr, following the procedure of Khan (*8*). Catalyst W1 was prepared by digesting alloy at 115–120°C for 4 hr after the method of Covert and Adkins (*9*).

Two specimens of the W2 type were prepared following the method of Mozingo (*10*). The specimens were prepared by digestion of the alloy at 75°C on a steam bath for 6 and 20 hr, respectively.

Specimens W4, W5, W6 and W7 were all prepared by digestion of alloy at 50°C for 50 min, following the procedures of Adkins, Pavlic and Billica (*11–13*). In addition, further specimens of Raney nickel were made, following the procedure for the W4 catalyst, but using digestion times of 1, 2, 5 and 24 hr.

After careful washing, all Raney nickel specimens were stored under absolute ethanol.

Investigation of the Aging of Raney Nickel

Raney nickel W4 was stored under absolute ethanol at room temperature. X-Ray examinations were carried out over a period of 6 months.

X-Ray Examination and Analysis

X-Ray diffraction profiles were chart-recorded on a Philips diffractometer, using nickel filtered copper $K\alpha$ radiation. Raney nickel specimens were scanned at ½°/min in 2θ, and Raney copper at ¼°/min; ball-milled specimens were scanned at ⅛°/min.

In order to prevent the pyrophoric catalyst powders reacting with air, while on the diffractometer, the following procedure was adopted. A slurry of catalyst was pipetted from the ethanol mixture into ether. When the slurry had settled, excess ether was decanted and a 10% solution of paraffin oil in *n*-hexane was added. On evaporation of the hexane, the catalyst did not react with air. The specimens could then be spread on the diffractometer holder in the normal manner. Extremely flat specimens could be prepared, which enabled accurate positioning of the specimens in the X-ray beam.

The X-ray line broadening was analyzed by the integral breadth method of Williamson and Hall (*14*). For the less broadened peaks the integral breadths were evaluated after resolution of the $K\alpha_1$ component by Rachinger's method (*15*). With the very broadened reflections, where adjacent peak overlapping occurred, the total area under the overlapping peaks was divided up in the ratio of the intensities of the two peaks as indicated on the ASTM powder index. These ratios had previously been confirmed by examination of specimens in which adjacent peaks did not overlap. With the extremely broadened peaks, it was not necessary to resolve the measured peak into the $K\alpha_1$ and $K\alpha_2$ doublet, since the angular separation of the doublet was negligible when compared with the broadening of the peak. As a result, the $K\alpha_1$ and $K\alpha_2$ peaks could be regarded as coincident without causing serious error in the measurement of peak height.

Values of integral breadth (β_M) were obtained for each reflection by dividing the peak area by the peak height.

Correction for instrumental broadening was made using the equation

$$\beta_c^* = \beta_M^* - \frac{(\beta_I^*)^2}{\beta_M^*},$$

where $\beta^* = \beta \cos \theta_0/\lambda$;

β_c^* = total broadening after subtraction of the instrumental broadening;

β_I^* = the value of β^* obtained from an annealed sample, which was assumed to give instrumental broadening only.

The strain and crystallite size components of β_c^* were then separated using the equation of Williamson and Hall (*14*)

$$\beta_c^* = \frac{1}{D} + \frac{4\epsilon \sin \theta_0}{\lambda},$$

where D = crystallite size due to domain size and faulting;

ϵ = microstrain.

A plot of β_c^* against d^* ($=2 \sin \theta_0/\lambda$) yields $1/D$ as intercept at $d^* = 0$, the slope being equal to 2ϵ where $2\epsilon = \Delta d/d$.

With milled powders and Raney copper specimens, the multiple order reflections 111 and 222 were used to evaluate mean crystallite size D_{111}, and microstrain ϵ_{111}, in the ⟨111⟩ direction, perpendicular to the {111} planes. Similarly, the 200 and 400 reflections were used to obtain D_{100} and ϵ_{100}, in the direction perpendicular to the {100} planes.

With the Raney nickel specimens, only the 111 and 222 multiple order reflections could be measured and therefore only D_{111} and ϵ_{111} were evaluated.

Stacking fault probabilities were calculated from the angular separation of the 111 and 200 reflections, following the procedure indicated by Warren (*16*). Due to the considerable overlapping of reflections, it was not possible to measure twin fault probabilities.

RESULTS

Residual Microstrain and Crystallite Size in Ball-Milled Copper and Nickel

Figure 1 shows the effect of ball-milling time, at room temperature, upon the integral breadth plots of β_c^* vs d^* for multiple order reflections from copper powder. Similar results were obtained with milled nickel powder. Values of crystallite sizes and microstrains resulting from plastic deformation are shown in Tables 1 and 2. Although there are differences in detail, it was observed with both metals that the microstrain increased as crystallite size was reduced. As shown, the values are markedly anisotropic. This is generally found with plastically deformed crystals,

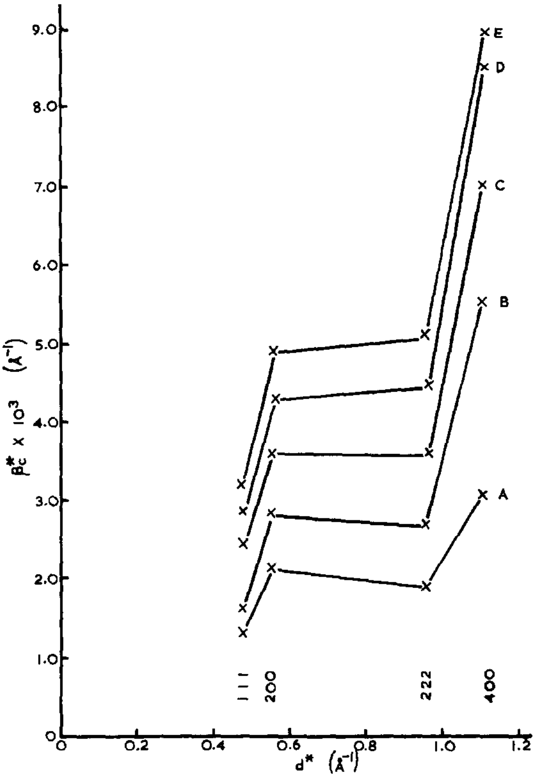

FIG. 1. Integral breadth plots for ball-milled copper powder for various milling times. Milled: (A) 1 min; (B) 10 min; (C) 30 min; (D) 1 hr; (E) 2 hr.

since the moduli of elasticity vary with crystallographic direction.

The Effect of Digestion Conditions on the Defect Structures of Raney Copper and Nickel

a. Raney copper. Figure 2 shows plots of β_c^* vs d^* for specimens prepared by digestion of Devarda's alloy at different temperatures and times. An estimate of the error of the integral breadths is included in the plots. All X-ray peaks could be measured except the very broadened 400 peaks from the specimens prepared at the two lowest temperatures. Values of crystallite size, microstrain and stacking fault probability (α) of the different specimens are shown in Table 3.

TABLE 1
MICROSTRAIN AND CRYSTALLITE SIZE IN BALL-MILLED COPPER POWDER

Milling time (min)	D_{100} (Å)	ϵ_{100} ($\times 10^{-3}$)	D_{111} (Å)	ϵ_{111} ($\times 10^{-3}$)
1	>1000	1.35	>1000	0.65
10		2.45	>1000	1.08
30		3.22	800	1.20
60		3.88	800	1.70
120		3.80	770	2.00

TABLE 2
MICROSTRAIN AND CRYSTALLITE SIZE IN BALL-MILLED NICKEL POWDER

Milling time (min)	D_{100} (Å)	ϵ_{100} ($\times 10^{-3}$)	D_{111} (Å)	ϵ_{111} ($\times 10^{-3}$)
1	>1000	1.00	>1000	0.92
10	510	1.00	≃1000	1.10
20	360	2.76	870	1.89
120	380	3.50	720	2.15
480	160	3.76	250	2.68

b. Raney nickel. With Raney nickel, excessive line broadening generally permitted measurements to be made of peaks up to the 222, the 400 reflections being too broadened for reliable measurement. Figure

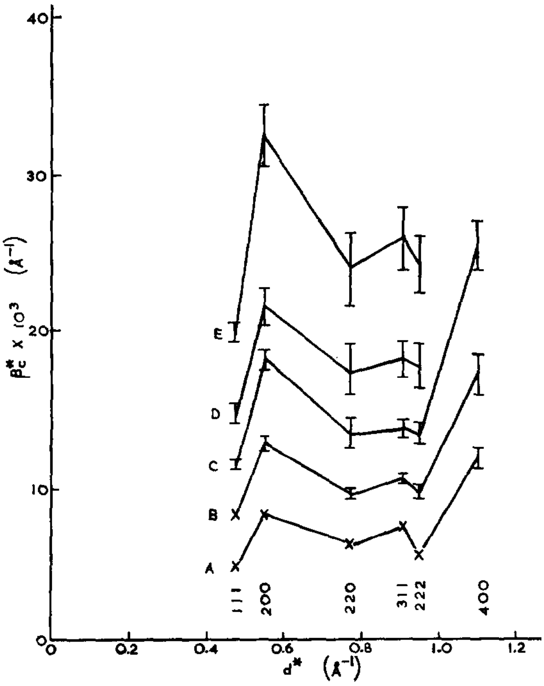

FIG. 2. The effect of digestion temperature and time on the integral breadths of Raney copper. (A) 5 hr at 128°C; (B) 5 hr at 95°C; (C) 5 hr at 70°C; (D) 15 hr at 45°C; (E) 24 hr at 25°C.

TABLE 3

EFFECT OF DIGESTION CONDITIONS UPON MICROSTRAIN, CRYSTALLITE SIZE AND STACKING FAULT PROBABILITY OF RANEY COPPER

Sample treatment (digestion time and temp)						
(hr)	(°C)	D_{100} (Å)	ϵ_{100} (×10^{-3})	D_{111} (Å)	ϵ_{111} (×10^{-3})	Stacking fault probability (α)
5	128	208	2.75	239	0.75	—
5	95	104	3.75	147	1.55	—
5	70	88	6.25	105	2.05	0.0056
15	45	73[a]	—	88	3.30	0.0075
24	25	54[a]	—	65	4.60	0.0093

[a] Estimated value.

3 shows plots of β_c^* vs d^* for Raney nickel specimens W1–W8. It was observed that the results paralleled those obtained with Raney copper. However, the reflections were far more broadened, which led to increasing error in evaluation of the integral breadths. The values of β_c^* obtained for specimens W4–W7 were very similar and a representative plot has been made. Crystallite sizes and microstrains were deter-

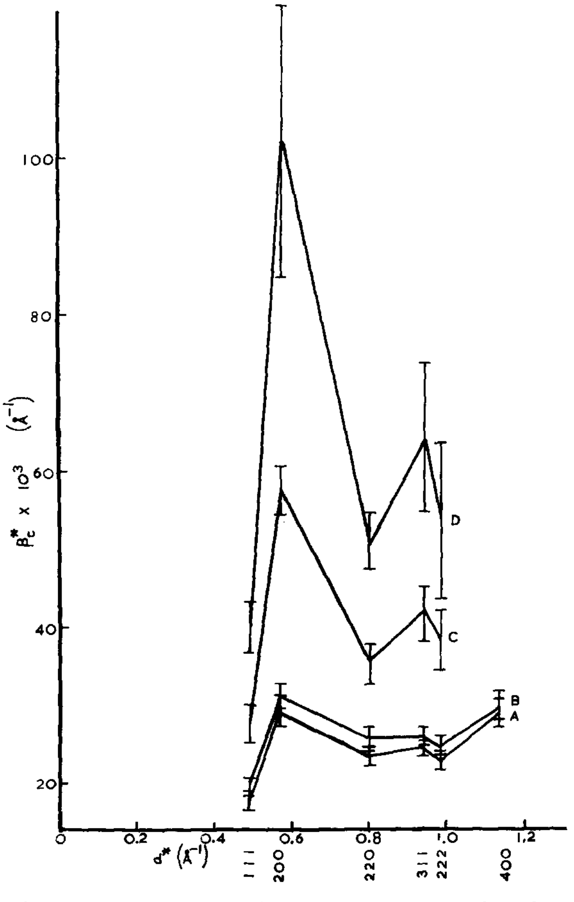

FIG. 3. Effect of digestion temperature and time on the integral breadth plots of Raney nickel. (A) W1 catalyst; (B) W8; (C) W2; (D) W4–W7.

TABLE 4

EFFECT OF DIGESTION CONDITIONS ON MICROSTRAIN, CRYSTALLITE SIZE AND STACKING FAULT PROBABILITY OF RANEY NICKEL

Specimen type and digestion conditions	D_{111} (Å)	ϵ_{111} ($\times 10^{-3}$)	Stacking fault probability (α)
W1, 4 hr at 115–120°C	81	5.6	0.036
W8, 4 hr at 100–105°C	72	5.7	0.036
W2, 6 hr at 75°C	53	9.5	0.089
W4–W7, 50 min at 50°C	36	13.0	0.152

mined from the multiple order 111 and 222 reflections. Values of crystallite size, microstrain and stacking fault probability for various catalysts are shown in Table 4.

The Effect of Digestion Time on the Structure of Raney Nickel

Table 5 shows the changes of defect structure produced by varying the digestion time at two different temperatures. It was observed that little change in crystallite size D_{111} occurred during the time period considered, although there was a marked decrease in microstrain and stacking fault probability. The X-ray results showed that a relatively large change took place in the broadening of the 200 reflection, which indicated that the value of D_{100} and ϵ_{100} had altered.

The Effect of Digestion Temperature on the Structure of Raney Copper and Nickel

It was observed that change of digestion temperature had a marked effect on the crystallite sizes of both Raney copper and nickel. Corresponding changes were also observed in the microstrain and in the stacking fault probabilities. Tables 3 and 4 show that for both copper and nickel, microstrain and stacking fault probability are linearly related, whereas microstrain is inversely related to crystallite size.

TABLE 5

EFFECT OF DIGESTION TIME UPON CRYSTALLITE SIZE, MICROSTRAIN AND STACKING FAULT PROBABILITY OF RANEY NICKEL

Time of digestion (hr)	D_{111} (Å)	ϵ_{111} ($\times 10^{-3}$)	Stacking fault probability (α)
At 50°C			
1	48	16	0.188
2	47	15	0.143
5	45	13	0.143
24	46	10	0.133
At 75°C			
6	53	9.5	0.089
24	51	8.1	0.052

The Aging of Raney Nickel Under Ethanol at Room Temperature

X-Ray examination of aged Raney nickel W4 indicated that a fairly rapid change in ϵ_{111} occurred with time. After 1 month, ϵ_{111} had changed from 15×10^{-3} to 5×10^{-3}. Thereafter, the value remained constant over a 6 month period. Only a small increase took place in the value of D_{111}; however, there was a considerable increase in D_{100}. The actual value of D_{100} could not be determined exactly since multiple order peaks could not be measured; however, D_{100} increased by approximately 40% during the 6 month period. Stacking faults were also observed to disappear slowly on aging.

DISCUSSION AND CONCLUSIONS

There are close similarities between the $\beta_c{}^*$ vs d^* plots for both cold worked and catalyst powders and it is seen that the differences between the structures of the two types of material are mainly in the degree of defect concentrations. It is concluded that the integral breadth method of X-ray line broadening analysis provides detailed information on the defect structures of highly active Raney metal catalysts. Similar trends are observed for variation of microstrain with crystallite size in both catalyst and cold worked metals.

However, the magnitude of the microstrain for a given crystallite size is somewhat smaller for the catalysts.

The effect of digestion temperature on the crystallite size, microstrain and faulting is very marked, and of similar form for both Raney copper and nickel. The rates of crystallite growth and strain relief must be very fast initially, but as growth proceeds the rates rapidly decrease. Approximate values of the mean activation energy for the early stages of crystallite growth, based on the change of D_{111} with temperature change, are 2.2 kcal mole^{-1} for Raney copper and 2.9 kcal mole^{-1} for Raney nickel. The sensitivity of the structure to temperature change, exhibited by the catalysts, is not observed with cold worked copper and nickel. These do not begin to anneal rapidly until they attain the recrystallization temperature.

Aging of Raney nickel under ethanol, and increasing the digestion time of the Raney alloy, gave rise to similar changes in the defect structure of the highly active W4 catalyst. The changes observed were (1) a large, initially rapid decrease in ϵ_{111} and also a decrease in α towards more stable values, (2) a considerable increase in D_{100} and presumably a corresponding decrease in ϵ_{100}. During digesting and aging, D_{111} was observed to undergo little change, within the periods of observation.

Schwab and Markenthall (*17*) showed that the BET surface area of a Raney nickel catalyst, similar to W5, decreased by 40% in 6 months when stored under ethanol at room temperature. Our observations on the W4 catalyst indicated that D_{100} increased by 40% over the corresponding period. Specific surface area and crystallite size are not strictly comparable; nevertheless, the observations are in general agreement with regard to the trend.

Although the highly active catalysts are much less stable than the cold worked metals, they sustain much smaller crystallite sizes and higher microstrains and faultings than can be achieved by cold working of powders. It is suggested that impurities may play a part in the observed behavior, since it is known that impurity atoms lock in dislocations. A possible explanation is that adsorbed hydrogen, which exists in Raney nickel in large quantities, may prevent easy motion of dislocations in the vicinity of the surface. This phenomenon has already been observed by Barrett (*18*) for thin oxide films on surfaces. Alternatively, aluminum might serve to stabilize the particles; however, similar annealing changes were observed to occur under ethanol, where the aluminum content remained constant. The annealing processes might be considered to be due to diffusion of matrix metal atoms, but it is difficult to conceive that D_{111} would remain constant if this were the case.

Herbstein and Smuts (*19*) used X-ray diffraction line broadening to measure defect structures in relatively inactive iron catalysts and cold worked iron. In this case, the Fourier method of Warren (*16*) was used to evaluate crystallite sizes, microstrains and faultings. The same method has also been used by Hofer and Hintermann (*20*) to evaluate the defect structure of Raney nickel catalysts. The Fourier method depends on accurate measurements of peak profiles in order to yield reliable measurements of crystallite size and microstrains. A disadvantage is that small crystallite size in highly active catalysts leads to excessive Cauchy broadening in the peak tails, and for reflections at high angles the peak profiles may be distorted due to overlapping of the tails of adjacent peaks. In the present work, it was observed that the 222 peak overlapped with the 311, and the 111 peak with the 200. Our view is that the best method of analysis for very active catalysts is the integral breadth method, since this is less sensitive to the effects of overlapping of the peak tails. The analytical method of Williamson and Hall (*14*) was chosen since this method assumes a Cauchy distribution of intensity in the peak profile. This is the most suitable technique to use when crystallite size is the major cause of broadening (*16*).

Our results correspond with those of Hofer and Hintermann (*20*), who examined annealed catalysts which were much less active. Similar trends are shown between the temperature of preparation and defect structure. Our results also agree with these authors, and with Herbstein and Smuts (*19*), in that crystallite size and microstrain are inversely related. The values of stacking fault probability in the present work are in good agreement with the values expected from the results of Hofer and Hintermann. Examination of the defect structures of the nickel catalysts in the present and previous work indicates that the more stable catalysts with smaller activities have larger crystallite sizes and smaller microstrains and stacking fault probabilities.

Inspection of the relative integrated intensities of the reflections from the cold worked metals and Raney copper specimens indicated that the accuracy of measurement was approximately ±10%. However, with the integral breadth method, errors in peak measurements tend to cancel, and the estimated accuracy of the integral breadths was generally better than ±5%.

With the very broadened reflections from Raney nickel, the integral breadths could only be measured with accuracies estimated between ±5 and ±20%, these values depending on both peak intensity and extent of broadening. Since greater error occurred in the measurement of integral breadths at high angles, the microstrain values are likely to be subject to greater error than the crystallite size. Nevertheless, the values of microstrain obtained in the present work compare well with values obtained with Raney nickel by the authors using a recently developed electron diffraction technique (*21*).

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