Light-Figure Phenomena Revealed and Crystal Faces Developed by Chemically Etched Nickel-Copper Alloy Crystals

Light-Figure Phenomena Revealed and Crystal Faces Developed by Chemically Etched Nickel-Copper Alloy Crystals*

Mikio YAMAMOTO and Jirô WATANABÉ

The Research Institute for Iron, Steel and Other Metals

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Synopsis

The light-figure phenomena have been observed with single crystals of nickel-copper alloys containing 5~95 percent copper, etched with various chemical reagents, in order to obtain information regarding crystal faces developed by etching and to examine the suitability of the observed light figures to the orientation determination. The etching with boiling saturated aqueous solution of ferric chloride produces distinct light figures, suitable for the orientation determination, for all of alloy crystals, while any other reagent reveals only indistinct or no light figure. The main crystal faces developed by etching with ferric chloride solution are the $\{hk0\}$, $\{110\}$ and $\{111\}$-vicinal faces, $hk0$ varying from 910 for nickel crystals over 610 for 20%Cu alloy crystals to 210 for 95%Cu alloy crystals.

I. Introduction

The light-figure phenomenon is caused by the reflection of an incident light beam from crystal facets developed by etching on the surface of a crystal and so the light figure revealed shows the same symmetry as that of the arrangement of such facets. Accordingly, the light figures can not only be applied for the determination of crystal orientations[1] but also provide information concerning crystal faces developed by etching[2]. We have now studied on the light-figure phenomena revealed by chemically etched nickel-copper alloy crystals and obtained some interesting information concerning crystal faces developed by etching.

II. Procedures

The crystal specimens employed are circular rods of single crystals of nickel-copper alloys containing 5, 10, 15, 20, 30, 40, 60, 70, 80, 90, and 95 percent copper, about 3 mm in diameter and several cm in length, which were prepared by the Bridgman

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(1) M. Yamamoto, Nippon Kinzoku Gakkai-shi, **5** (1941), 214; Sci. Rep. Tôhoku Univ., **31** (1943), 121; Buturigaku Kôenshyû, **3** (1943), 193. M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **17** (1953) 5 and 9; Sci. Rep. RITU, **A7** (1955), 173; Oyô-Buturi, **24** (1955), 427 (cubic crystals). M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **13** (1949), No. 4; Sci. Rep. RITU, **A2** (1950), 270 (hexagonal crystals). M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **B15** (1951), 572; Sci. Rep. RITU, **A5** (1953), 135 (trigonal crystals). M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **17** (1953), 113; Sci. Rep. RITU, **A7** (1955), 161 (tetragonal crystals).

(2) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **17** (1953), 68; Sci. Rep. RITU, **A7** (1955), 145(Sn); Nippon Kinzoku Gakkai-shi, **17** (1953), 628; Sci. Rep. RITU, **A7**(1955), 329 (Zn); to be published (Bi).

method. Etching reagents tested were selected, taking into consideration of the results of previous studies by the senior of the present writers[3] on the light figures of nickel and copper single crystals, as follows:— (1) mixture of nitric acid and ferric chloride (6 : 4 in weight), (2) saturated aqueous solution of ferric chloride (at room and at the boiling temperatures), (3) mixture of hydrochloric acid and ferric chloride (1 : 1 in weight), (4) saturated aqueous solution of ammonium persulphate (at room and at the boiling temperatures), and (5) 20 percent aqueous solution of ammonium persulphate. The specimen crystals, etched preliminarily with the 6 : 4 mixture of nitric acid and ferric chloride for 30 seconds in order to maintain their initial conditions the same, were dipped into an etching solution to be tested, and picked up after an elapse of proper time. They were mounted on the apparatus described previously[1] and the light figures revealed were observed by naked eyes, sketched, and printed on contact photographic papers (medium contrast). At the same time angles between the symmetric centers and light spots of various light figures were measured by means of the procedure described previously[4], and the indicse of the crystal faces developed were determined by contrasting the measured angles with the calculated angles between various crystal planes.

III. Results

The 6 : 4 mixture of concentrated nitric acid and ferric chloride attacked vigorously all of nickel-copper alloy crystals. But, no light figure was observed since the surface of crystals became bright. Thus, this reagent results the blank etching for nickel-copper alloy crystals including nickel and copper. Next, boiling saturated aqueous solution of ferric chloride was tested. Only etching with this reagent produced distinct light figures, of which the experimental results will be described later. In order to avoid the trouble of boiling, we tested, then, saturated aqueous solution of ferric chloride at room temperature and found indistinct light figures unexpectedly. The 1 : 1 mixture of concentrated hydrochloric acid and ferric chloride produced only indistinct light figures with 20 and 30 percent copper alloy crystals and very unclear ones with other alloy crystals. Finally, saturated aqueous solutions of ammonium persulphate at boiling and room temperatures and 20 percent aqueous solution of this reagent at room temperature revealed very indistinct light figures with alloy crystals, though they produce distinct light figures suitable for the orientation determination with nickel and copper crystals[3].

Experimental results obtained in the case of etching by boiling saturated aqueous solution of ferric chloride are as follows:—

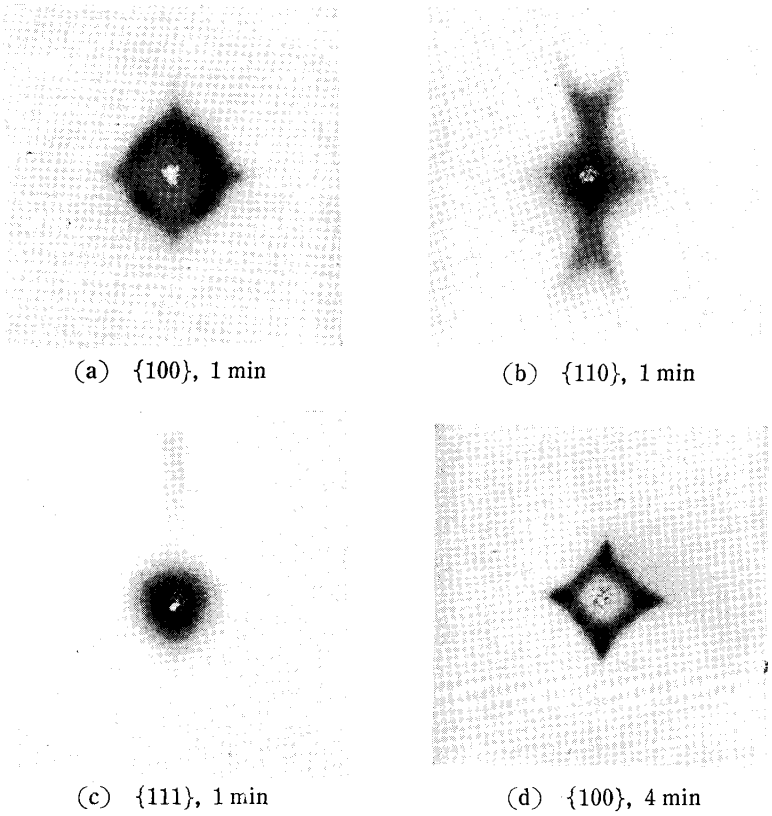
According to our previous study[5], nickel crystals etched with this reagent exhibit distinct light figures suitable to the orientation determination. The light

(3) M. Yamamoto, Nippon Kinzoku Gakkai-shi, **4** (1940), 368; Sci. Rep. Tôhoku Univ., **21** (1941), 113; Oyô-Buturi, 10 (1941), 199; Nippon Kinzoku Gakkai-shi, **6** (1942), 535.

(4) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **B15** (1951), 514; Sci. Rep. RITU, **A4** (1952), 127.

(5) M. Yamamoto and J. Watanabé, not yet published.

figures observed by etching for a minute are as follows:— The {100} light figure (Photo. 1(a); Fig. 1(a)) is of a square form with light spots on middle points of its sides. Lines connecting its symmetric center with the light spots extend to the {111} light figures (Photo. 1(c); Fig. 1(c)), and the measurment of angles between the symmetric center and the light spots indicates that the light spots are



(a) {100}, 1 min (b) {110}, 1 min

(c) {111}, 1 min (d) {100}, 4 min

Photo. 1. Light figures of Ni crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$.

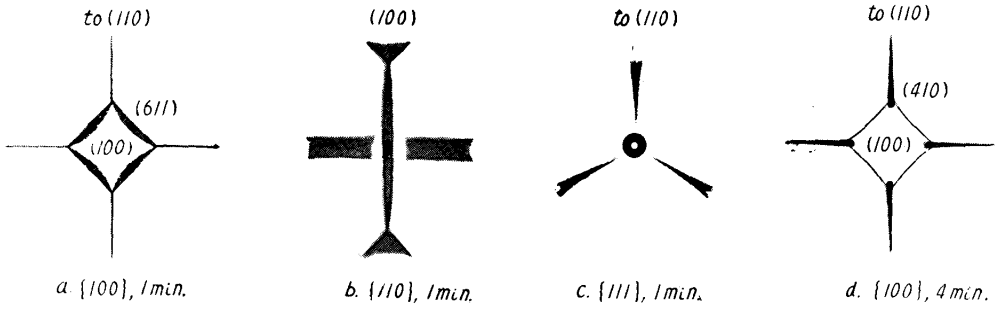
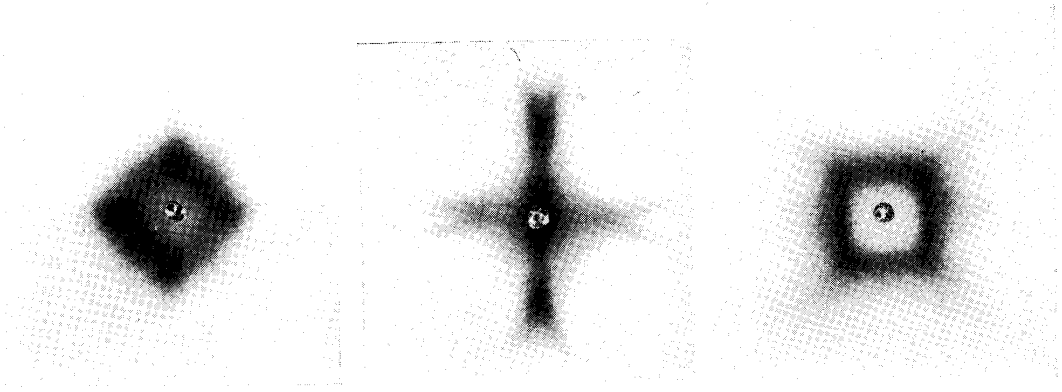


Fig. 1. Light figures of Ni crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$.

caused by the development of {611} faces. The {110} light figure (Photo. 1(b); Fig. 1(b)) has a light spot at its symmetric center which is due to the development of {110} faces; arrows at its top and bottom are corners of the {100} light figures and arcs at its both sides are parts of the {111} light figures. The {111} light figure is composed of a small ring radiating three arrows which point to the {110} light figures. The small ring of this light figure indicates the development of

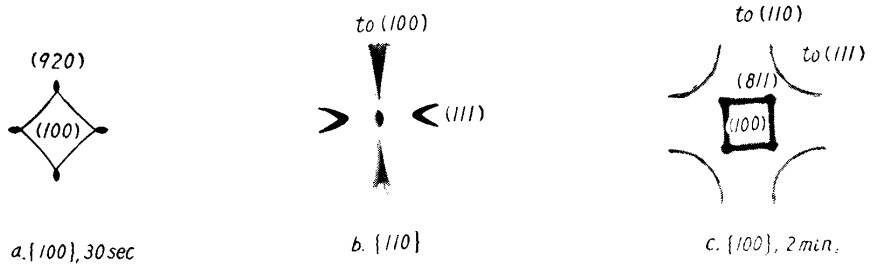
vicinal faces adjacent to {111} faces. Etching over 4 minutes changes the {100} light figure into another square form whose apexes have light spots revealed by the development of {410} faces (Photo. 1(d); Fig. 1(d)).

5 and 10% Cu alloy crystals etched for a half minute revealed distinct light figures, suitable to the orientation determination, (Photos. 2(a), 2(b) and 1(c); Figs. 2(a), 2(b) and 1(c)), which are roughly similar to light figures observed with nickel crystals etched over 4 minutes. The measured value of an angle between the symmetric center and light spots in the {100} light figures is 12.6°, corresponding to the development of {920} faces. Thus, these light figures indicate the development of the {920}, {110} and {111} vicinal faces. Etching over 2 minutes changed the {100} light figure of 5% Cu alloy crystals into another square form whose apexes had light spots (Photo. 2(c); Fig. 2(c)). The measured angle between these light spots and the symmentric center is 9.7°, showing the development of {811} faces.



(a) {100}, 30 sec (b) {110}, 30 sec (c) {100}, 2 min

Photo. 2. {100} and {110} light figures of 5%Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$.



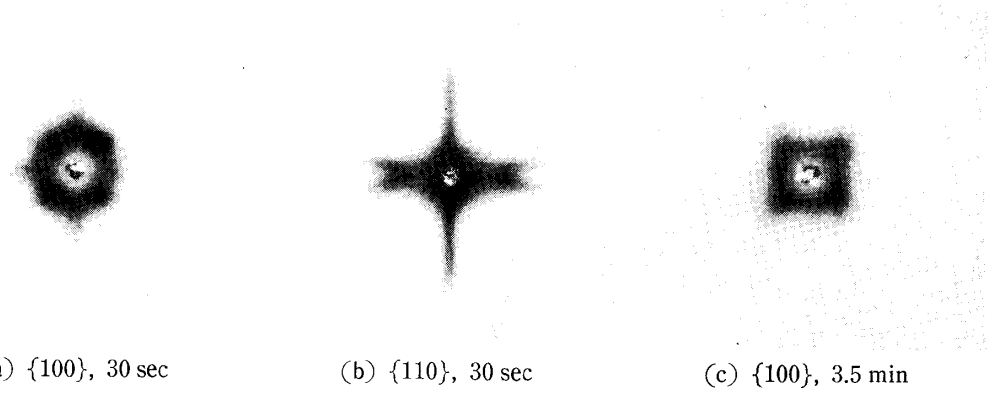
a. {100}, 30 sec b. {110} c. {100}, 2 min.

Fig. 2. {100} and {110} light figures of 5%Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$.

15% Cu alloy crystals etched for two minutes showed distinct light figures, suitable to the orientation determination, which are similar to those observed with 5%Cu alloy crystals etched over 2 minutes (Photos 2(c), 2(b) and 1(c); Figs. 2(c), 2(b), and 1(c)). The measured angle between the light spots and symmetric center of the {100} light figure is 12.2°, corresponding to the theoretical angle {711}/{100} = 11°25′. The {100} light figure changed into a form shown in Photo. 2(a) and Fig. 2(a) which was due to the development of {920} faces when the etching time

exceeded 5 minutes, and further into a form similar to Photo. 1(d) and Fig. 1(d), for which the measured angle between the light spots at apexes and symmetric center was 10.5°, being in an agreement with the theoretical angle $\{510\}/\{100\} = 11°19'$.

20% Cu alloy crystals etched for 30 seconds revealed distinct {100}, {110} and {111} light figures suitable for the orientation determination. The {100} light figure (Photo. 3(a); Fig. 3(a)) is of a square form having distinct light spots on its apexes and on middle points of its sides. The measured angles between the symmetric center and light spots at apexes and between the symmetric center and



(a) {100}, 30 sec (b) {110}, 30 sec (c) {100}, 3.5 min

Photo. 3. {100} and {110} light figures of 20% Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$.

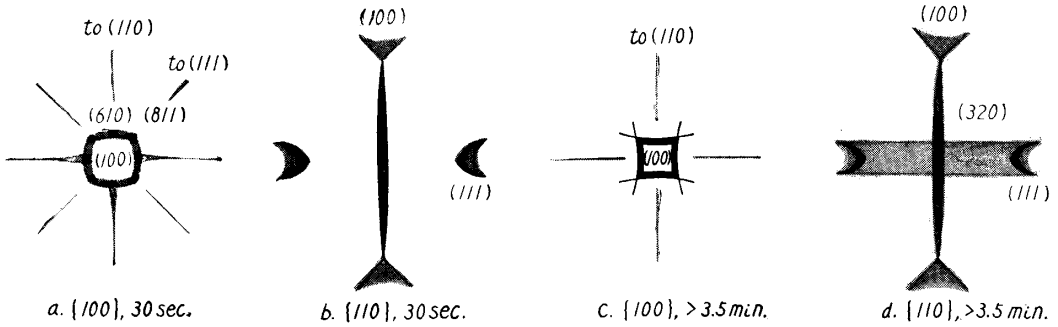


Fig. 3. Light figures of 20% Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$.

middle points of sides in the {100} light figure are, respectively, 9.8° and 9.4°, which coincide well with the theoretical angles $\{811\}/\{100\} = 10°01'$ and $\{610\}/\{100\} = 9°28'$. The {110} light figure (Photo. 3(b); Fig. 3(b)) has a straight-line form with small arcs on its both sides which indicates the development of $\{lm0\}$ faces. The {111} light figure (Photo. 1(c); Fig. 1(c)) is regarded as caused by the development of {111}-vicinal faces. With a continuation of etching, the {610} spots situated on middle points of the sides of the {100} light figure disappeared first, and then the {811} spots located on its apexes vanished, and after 3.5 minutes' etching the {100} light figure took a square form as shown in Photo. 3(c) and Fig. 3(c), indicating the develoment of vicinal faces belonging to the $[80\bar{1}]$ zones and adjacent to {100} planes. In the {110} light figure, the central parts of the straight line became more distinct with an increasing of etching time (Fig. 3(d)). The measured angle between the symmetric center of the {110} light figure and ends of a straight-line

is 12.0° and coincides with the theoretical angle {320}/{110} = 11°19′, indicating that the {lm0} faces with $l/m < 1.5$ are more stable. While, three arrows in the {111} light fiigure disappeared by prolonged etching.

30% Cu alloy crystals etched for about 30 seconds produced the same distinct light figures, suitable for the orientation determination, as those of 20% Cu alloy crystals etched for the same periods. It is to be noted, however, that the {100} light figure with such a square form as shown in Photo. 4 and Fig. 4 was also observed locally on the crystal surface. The measured angle between the light spots at its apexes and symmetric center is 11.9°, which agrees with the theoretical angle {510}/{100} = 11°19′. With an increase of etching time the distinctness of the former {100} light figure faded gradually and over 7 minutes' etching only the second one remained. The changes in forms of the {110} and {111} light figures were quite similar to those of 20% Cu alloy crystals. From these observations, it may be concluded that at first {811} and {610} faces and then more stable {510} faces, {lm0} faces with $l/m < 1.5$, and {111}-vicinal faces are developed.

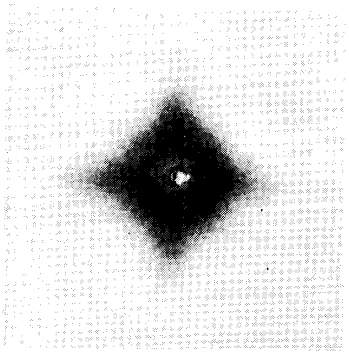


Photo. 4. {100} light figure of 30% Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 30 sec.

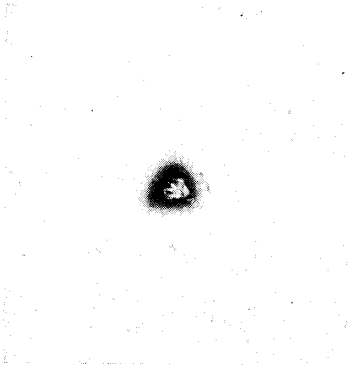


Photo. 5. {111} light figure of 40% Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 3.5 min.

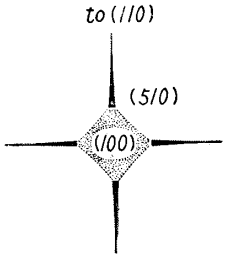


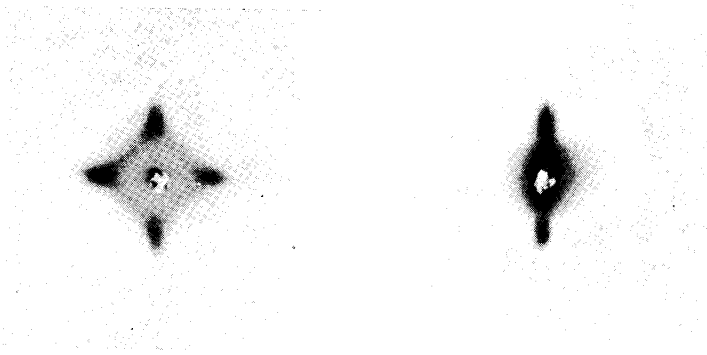
Fig. 4. {100} light figure of 30% Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 30 sec.

Fig. 5. {111} light figure of 40% Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 3.5 min.

Distinct light figures suitable for the orientation determination were observed with 40 and 60% Cu alloy crystals etched for 3.5 minutes and with 70% Cu alloy crystals etched for 5 minutes. The {100} and {110} light figures revealed are the same as those observed with 30% Cu alloy crystals etched for a long time (Photo. 4; Fig. 4 and Photo. 3(b); Fig. 3(b)), while the {111} light figure (Photo. 5; Fig. 5) is a small halo triangular spot around which three small arcs corresponding to the line parts of the {110} light figure located. Thus, it may be seen that the

{510}, {*lm*0} with $l/m < 1.5$, and {111}-vicinal faces are developed.

80% Cu alloy crystals revealed distinct light figures suitable for the orientation determination by etching for 1 minute. The {100} light figure (Photo. 6(a); Fig. 6(a)) has a square form at apexes of which light spots locate. The measured angle between the light spots and symmetric center is 18.1°, corresponding with the theoretical angle {310}/{100} = 18°26′. The {110} light figure shows such a form as shown in Photo. 6(b) and Fig. 6(b). Light spots located at both ends of a



(a) {100}, (b) {110}

Photo. 6. {100} and {110} light figures of 80%Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 1 min.

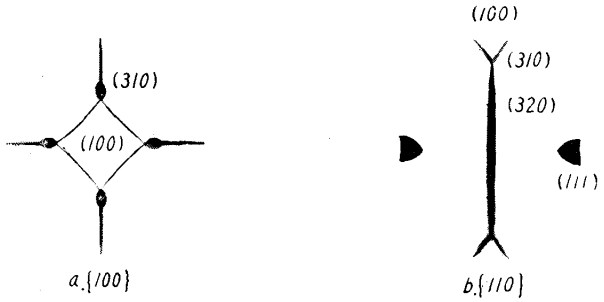
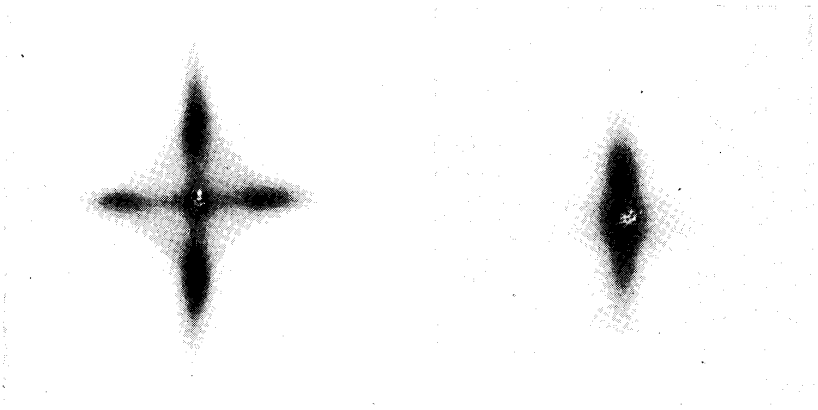


Fig. 6. {100} and {110} light figures of 80%Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 1 min.

straight line are the {310} spots in the {100} light figure and those situated on its both sides are parts of the {111} light figures. The central, espececially distinct, portion of a straight line corresponds with the {110}−{320} faces. On the other hand, the {111} light figure is quite the same as that observed with 40~70 percent copper alloy crystals (Photo. 5 and Fig. 5). These observations indicate that the {310}, {*lm*0}($l/m < 1.5$) and {111}-vicinal faces are developed.

90 and 95% Cu alloy crystals etched for 30 seconds to 2 minutes revealed similar and distinct light figures, suitable for the orientation determination. The {100} light figure (Photo. 7(a); Fig. 7(a)) has a square form with a cross, at apexes of which light spots locate. The measured angle between the light spots and symmetric center in the {100} light figure observed with 90%Cu alloy crystals is 24.2°, corresponding to the theoretical angle {940}/{100} = 23°58′, while that with

95% Cu alloy crystals is 25.8° corresponding to the theoretical angle {210}/{110} = 26°34′. The {110} light figure (Photo. 7(b); Fig. 7(b)) has a light spot at its symmetric center, arrows at its top and bottom, and acrs at its both sides; arrows



(a) {100}, (b) {110}

Photo. 7. {100} and {110} light figures of 90%Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 30 sec.

Fig. 7. {100} and {110} light figures of 90%Cu alloy crystals etched with boiling sat. aq. sol. of $FeCl_3 \cdot 6H_2O$ for 30 sec.

are corners of the {100} light figures and arcs are parts of the {111} ones. The {111} light figure is similar to that shown in Photo. 1(c) and Fig. 1(c). Prolonged etching resulted a slight decrease in sharpness of the light figures. The crystal faces developed are found to be the {940}, {110} and {111}-vicinal faces for 90% Cu alloy crystals and {210}, {110} and {111}-vicinal faces for 95% Cu alloy crystals.

Finally, according to our previous study[5] the etching of copper crystals with the same etchant produced distinct {100} light figure of single light spot caused by the development of the {100} faces and none of {110} and {111} light figures.

In conclusion, the etching with boiling saturated aqueous solution of ferric chloride for several minutes produces distinct light figures, suitable for orientation determination, for all of nickel-copper alloy crystals. The etching time required for revealing distinct light figures varies with the composition of alloy crystals, being longer in alloy crystals containing more nickel and more copper, respectively, and shorter in alloy crystals of medium compositions. The colour of light figures is yellow for alloy crystals containing less copper and become reddish bitter orange with increasing copper content. The crystal faces developed by etching are

summarized as follows :-

Composition of alloy crystal wt.-% Cu	Developed crystal faces
0	{410}, {611}, {111}–vicinal
5	{920}, {811}, {110}, {111}–vicinal
10	{920}, {110}, {111}–vicinal
15	{920}, {711}, {510} (more stable), {110}, {111}–vicinal
20	{610}, {811}, {*lm*0} (l/m <1.5), {111}–vicinal
30	{610}, {811}, {510} (more stable), {*lm* 0} (l/m < 1.5), {111}–vicinal
40~70	{510}, {*lm*0} (l/m<1.5), {111}–vicinal
80	{310}, {*lm*0} (l/m<1.5), {111}–vicinal
90	{940}, {110}, {111}–vicinal
95	{210}, {110}, {111}–vicinal
100	{100}

It may be seen that the crystal faces developed by etching change systematically with composition of alloy crystals and that, except for the commonly developed {110} and {111}-vicinal faces, the crystal faces developed are further distant from the {100} faces in alloy crystals containing more nickel and more copper, respectively, and close to the {100} faces in alloy crystals of medium compositions.

Summary

The light-figure phenomena have been observed with chemically etched single crystals of nickel-copper alloys containing 5~95 percent copper and information regarding the crystal faces developed by etching and suitability of the light figures observed for the orientation determination have been obtained. Reagents tested are the 6:4 (in weight) mixture of nitric acid and ferric chloride, saturated aqueous solution of ferric chloride (at room temperature and at the boiling temperature), 1:1 (in weight) mixture of hydrochloric acid and ferric chloride, saturated aqueous solution of ammonium persulphate (at room temperature and at the boiling temperature) and 20 percent aqueous solution of ammonium persulphate. It has been found that the etching with boiling saturated aqueous solution of ferric chloride produces distinct light figures, suitable to the orientation determination, for all alloy crystals, while any other reagent reveals indistinct or no light figure. Crystal faces developed by etching with boiling saturated aqueous solution of ferric chloride are {100}, {111}-vicinal, and {*hk*0} faces, *hk*0 varying systematically from 410 for nickel crystals over 610 for 20%Cu alloy crystals to 210 for 95%Cu alloy crystals, although {*lm*0} faces with $l/m > 1.5$ are developed on alloy crystals containing 20 to 80 percent copper and (u11) faces with $u = 6\sim8$ are developed in an early stage of etching on alloy crystals containing less than 30 percent copper.