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Studies on the β-ε Transformation in Cobalt-Nickel Alloys. I
Propagation Process of the Transformation*

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Synopsis

The propagation of the diffusionless transformation of the f. c. c. structure (β) into the h. c. p. structure (ε) in cobalt-nickel alloys was microscopically investigated. As the transformation proceeds, many narrow relief markings such as slip lines appeared in parallel to the $\{111\}_\beta$ in flat free surface of the alloy. The cross section of each marking was a ridge or a valley with almost definite slopes on both sides but not symmetrical, and their inclinations were always less than 20°; its width was about $1\sim2\mu$. In pure cobalt, however, no marking was observable. The rate of growth of an ε crystal was less than ten-thousandth of that of a "Umklapp" martensite in steel, and these transformation processes are very resemble, when viewed from the growth rate, habit plane and structure of relief marking, to the "Schiebung" type of martensite in steel.

I. Introduction

It is known that the phase change of the β phase (face-centred cubic) into the ε (close-packed hexagonal) in cobalt and its alloys on rapid cooling takes place by one of the diffusionless transformations. Such a transformation of the face-centred cubic into the close-packed hexagonal is more suitable for the study of the propagation process of martensitic transformation due to the extremely simple correspondence of these two lattice types with each other. In the present study the propagation processes of this transformation, that is the process of growth of relief marking and its growth rate, the structure of cross section of marking and the relation of marking to the inner structure of transfromed phase were examined mainly with optical microscopic observation

II. Experimental methods and measurements of transformation temperature

1. Preparation of specimens and their heat-treatments

For the direct microscopic observation of the propagation process of transformation, it is most convenient that the transformation temperature is near room temperture. To investigate the influences of Ni concentration and of temperature on the propagation process, however, observation were carried out also on the several kinds of alloys shown in Table 1. The specimens were prepared by fusing electrolytic cobalt and electrolytic nickel in a high frequency furnace, annealing

* The 893rd report of the Research Institute for Iron, Steel and Other Metals. Reported in the Nippon Kinzoku Gakkai-Si, **19** (1955), 427.

Table 1. Analysed contents of nickel and carbon for various specimens.

Notation of specimens	Analysed content	
	Ni (wt %)	C (wt %)
CN- 0	0.35	0.076
CN- 5	5.45	0.071
CN-10	10.80	0.076
CN-20	20.42	0.073
CN-22	21.66	0.073
CN-25	24.61	0.075
CN-30	30.24	0.11

in vacuo at 1,000°C for 2 hrs, and forging into cylindrical rods, 6 mm in diameter. From these rods were prepared the specimens for microscopic examination, 5 mm in diameter and 10 mm in length, with a hole of 2 mm in diameter and 6 mm in depth in their bottom for insertion of the thermocouple, and also another rod, 5 mm in diameter and 70 mm in length, for thermal dilatation test. The contents of impurities not given in Table 1 were in the CN-20 specimens N: 0.028, Fe: 0.09, Si: 0.19, P: 0.001 and S: 0.009 per cent. Contents of C and N were further reduced by the heat-treatment mentioned below.* For examining the process of propagation of transformation along the surface of the specimens, the crystal grains are desirable to be very large, smooth and free of such specific surface structure as Beilby layer, and the grain boundaries and the twin boundaries are required distinctly to be visible For this purpose, the specimens were subjected to a preliminary heat-treatment as follows: All the specimens, polished electrolytically at room temperature, were heated at about 1,400°C just below the melting point for 2~3 hrs in a current of hydrogen containing a minute quantity of water vapor. Such a method of heating, besides causing the growth of the crystal grains to 1~3 mm in size, is superior to the ordinary vacuum heating on the following points: (1) By heating in vacuo, the grains in the interior of the specimens grow to a sufficient size, but on the surface some fine granules are left unassimilated, while in heating under hydrogen, such an undesirable result can be avoided. (2) The carbon content in the specimen that is the impurity most strongly affecting the transformation can be eliminated. (3) By decomposition of the water vapor in hydrogen gas under high temperature, a slight etching effect is brought out, so that the grain boundaries and, in particular, the twin boundaries are made clear, and the observation of the growth process is made easier. In this course of heating, care should be taken to avoid the temperature rise by steps, so as to assure the grain

* The analysed contnet of C after the heat treatment was 0.015 per cent.

boundaries or the twin boundaries at the highest temperature. The etching can be adjusted to an appropriate degree by controlling the rate of flow and the dehydration of the hydrogen gas and by regulating the exposure of the specimen to the hydrogen current.

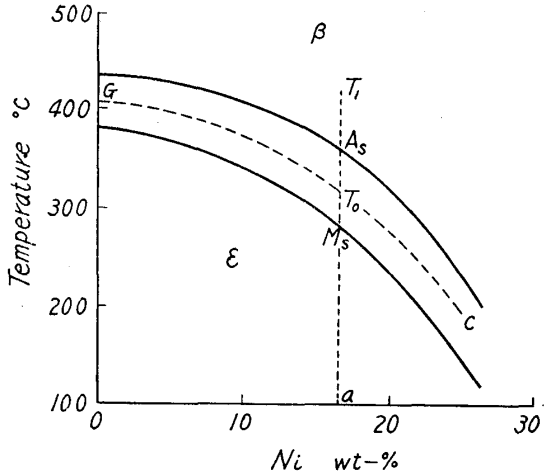


Fig. 1. As-Ms diagram of Cobalt-Nickel system. (full lines)

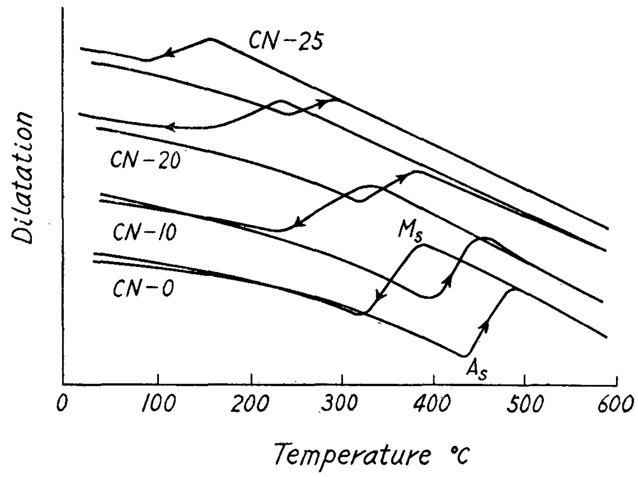


Fig. 2. Dilatation curves for specimens having various concentration of Ni.

2. Transformation temperature

The transformation temperature of this alloy is markedly influenced by the grain size and the content of carbon as impurity, i.e., the transformation point shifts toward lower temperature, the smaller the grain size or the larger the carbon content. Thus, for proceeding the study on the transformation of Co-Ni alloy, it is indispensable to make a precise measurement of the beginning temperature of the transformation during cooling (point Ms). The full lines in Fig. 1 show the transformation temperature obtained by measurement of differential thermodilatation versus the Ni concentration as shown in Fig. 2, which are approximately in agreement with those obtained by Masumoto[1]. The broken line GC shows the temperature at which the free energy of two phases β and ε becomes equal; it was deduced from the data obtained by Hess and Barrett[2]. When the temperature, though higher than Ms, is lower than this point, a slightly mechanical shock initiates $\beta \rightarrow \varepsilon$ transformation, and so a minute care must be taken to avoid it.

3. Method of observation

Upon completion of the foregoing heat-treatment, the specimens were cooled down to about GC temperature in the furnace in hydrogen current to prevent them from oxidation, and then were placed in a furnace of small-size kept at the same temperature. Then the propagation figures of the transformation appearing on the surface of the specimens during cooling were examined with a microscope, the temperature being measured with copper-constantan thermocouple.

(1) H. Masumoto, Kinzoku no Kenkyu, **2** (1925), 1023.
(2) J. B. Hess and C. S. Barrett, J. Metals, **4** (1952), 645.

III. Results of observation

1. propagation process of the transformation relief markings

When the temperature came down to Ms point, relief marking closely resembling slip lines, as shown in Photo. 1, appeared. As will be explained below, these lines are made of layers of close-packed hexagonal crystals formed in the interior of the specimen due to the transformation and grown to the surface. For simplicity such a line may be called "marking".

Such a marking first arose from a point on or near a grain boundary of the mother phase and grew in a straight line till it came into contact another marking. No line was observed deviating from the straight course or stopping on the midway. The directions of the growth of markings in one crystal grain were four at most, and as these are always parallel to the annealing twin of a face-centred mother crystal, it is assured that the lines grow along the $\{111\}_\beta$ plane, so that in this transformation the habit plane is $\{111\}_\beta$ plane.

It was found that a strong tendency of formation of a series of parallel markings was a characteristic of growth that is, an appearance of one marking on one of $\{111\}_\beta$ planes is accompanied by another marking on the adjacent $\{111\}_\beta$ planes side by side; thus in a short time a group of markings running in the same direction was formed as shown in Photo. 2.

Consequently, the group of the markings appearing first in a certain direction contiuned to grow ahead to form a broad zone through the crystal grain, while the other markings that grew on the other $\{111\}_\beta$ planes inclined to the preceding $\{111\}_\beta$ by the angle of 70.5° appeared in the interspaces of the first markings as the temperature was lowered. This process was repeated and the mother phase was subdivided into a number of small areas by straight lines. In the special cases in which the surface of specimen was parallel to the $\{100\}_\beta$ or to the $\{111\}_\beta$ plane, marking appeared only in 2 or 3 directions. Photo. 3 shows the markings on a crystal with surface almost parallel to the $\{111\}_\beta$ plane. Photo. 4 shows the markings on the surface nearly parallel to the $\{100\}_\beta$*, wherein markings will be seen running in two directions perpendicular to each other. The follow-up observation of the growth of these lines revealed that, first the group of markings in the horizontal direction in the picture started from the left-hand side and crooked at the twin boundary (a. b) but not stopped to grow beyond it untill they reached the grain boundary in 1∼2 seconds. When the temperature was lowered by 5∼6°C, the markings in the vertical direction appeared between the above mentioned horizontal markins, and upon further drop of the temperature, horizontal markings appeared between the virtical ones. In this manner the transformation goes on, that is, the transformation is not proceeded continuosly, but it goes on intermittently as mentioned above. This transformation process is very similar to the one of the "Schiebung" type of martensite transformation in iron-nickel alloys.[3]

(3) S. Takeuchi, T. Honma and H. Suzuki, Nippon Kinzoku Gakkai-Si, **21** (1957), 51.

* The triangle pattern in Photo 3 and the square pattern in Photo 4 show respectively the etched figure of the $\{111\}_\beta$ and the $\{100\}_\beta$ planes appearing during the heating process in hydrogen current.

2. Relation of the markings to the inner structure of ε crystal

When a transformed specimen is polished by 0.05 mm in depth electrolytically in a mixed medium of phosphoric acid and glycerin, the surface markings fade and twin-like shaped ε-crystals bounded by straight lines appear in the place of the markings

Photo. 5 shows such a etched structure of ε crystals in Co-25 per cent Ni alloy. Photo. 6 (a) shows an unetched surface of transformed specimen containing 20 per cent nickel, in which many parallel markings are seen running from the left hand side to the right over two crystal grains. Photo. 6 (b) shows the same area as Photo. 1 (a) after polishing by 0.01 mm in depth and Photo 6 (c) the same area after polishing by 0.05 mm. From these photographs it becomes clear that many parallel markings in Photo. 6 (a) corresponds to one single ε-crystal in Photo. 6 (c).

Photo. 7 is the enlarged microphotograph of one part of Photo- 6 (b), and shows that the traces of markings are still observable after polishing by 0.01 mm in depth.

In Photo. 8 is shown the structure of the same place as that in Photo 4, but polished and slightly etched. The ε-crystal seems to correspond exactly to the markings in Photo 4.

Thus a single ε crystal is found to be composed of many parallel lamellas extending along the $\{111\}_\beta$ plane.

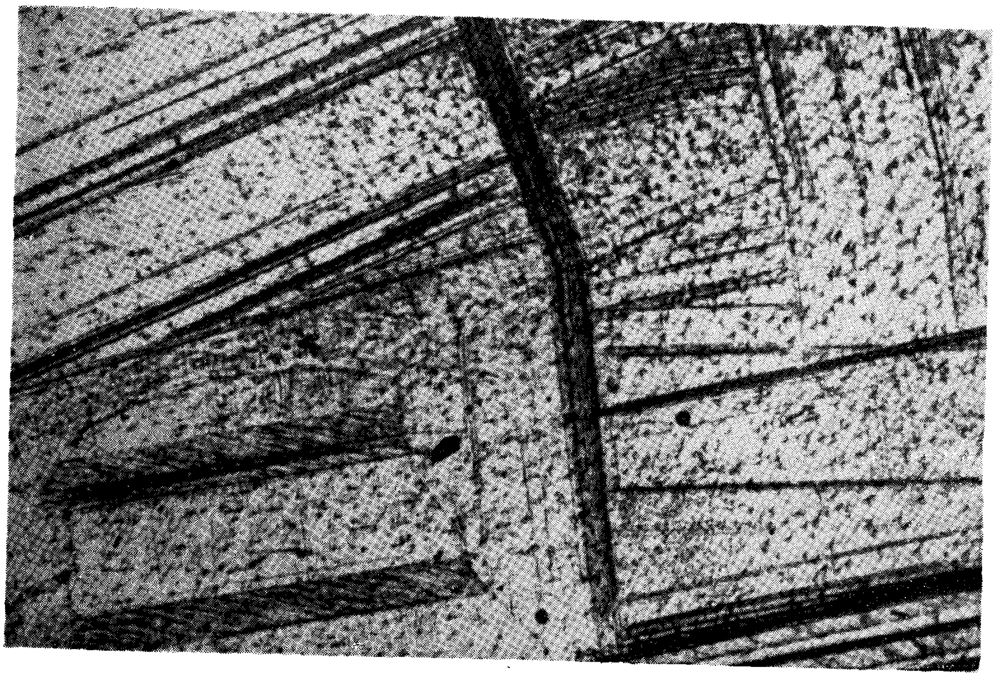
3. Behaviour of markings at grain boundaries and twin boundaries

The growth of martensite plate terminates generally at grain boundaries or twin boundaries, but as the habit plane in this transformation is in accord with the slip plane of mother crystal, markings can pass through or refract at a grain boundary or a twin boundary, if the angle between any set of $\{111\}_\beta$ planes of two neighbouring crystal grains is small. After etching the protion of boundary at which the passing or refraction of markings took place become very indistinct as the orientations of the ε crystals in the two grains resemble each other. But an ε crystal near the grain boundary where a group of markings stop shows a wedge-shaped structure as seen in Photo. 9 and a considerable amount of β phase is retained between the wedge-shaped ε crystals and so, when the grain size of mother phase is smaller, the amount of the retained β phase will be larger.

4. Velocity of propagation of transformation

The abnormally high velocity of propagation has been cited as one of the outstanding chracteristics of martensitic transformation(4) (ca. 1/3 of the velocity of sound in Fe-Ni alloys), but in the above-mentioned transformation, the growth of markings was observable under a microscope with sufficient composure. If the speed at which a marking grows in a straight line is presumed as the definition of the propagation velocity of transformation, its magnitude will be of the order of 1~100 mm/sec and below 1/10,000 of that of umklapp's type martensite in steels.

(4) R. F. Bunshah and R. F. Mehl, J. Metals, **5** (1953), 1251.



×150

Photo 1. Relief markings on the unetched surface. (specimen CN-25)

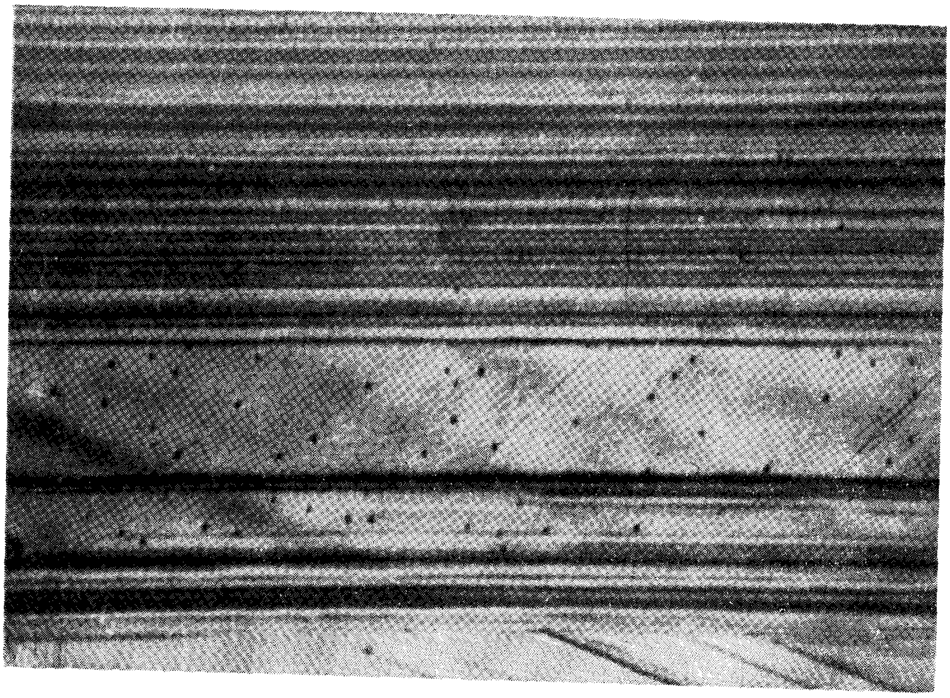


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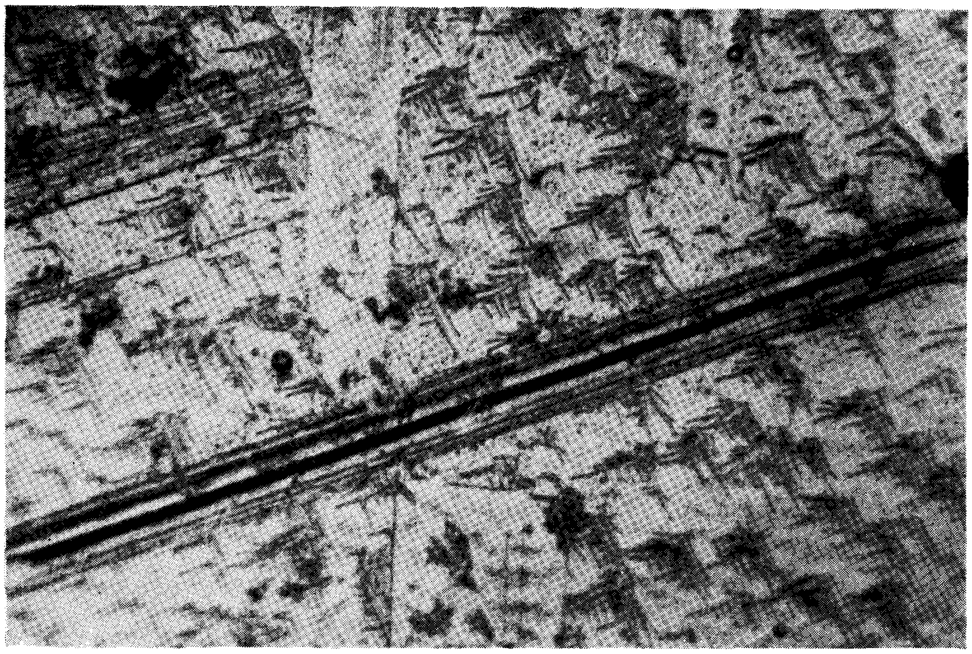
Photo 2. A group of many parallel markings. (specimen CN-25)



×250

Photo 3. Relief marking structure and thermal etch figures on the nearly $\{111\}_\beta$ plane. (specimen CN-20)

×250

Photo 4. Relief marking structure on the nearly $\{100\}_\beta$ plane. (specimen CN-20)

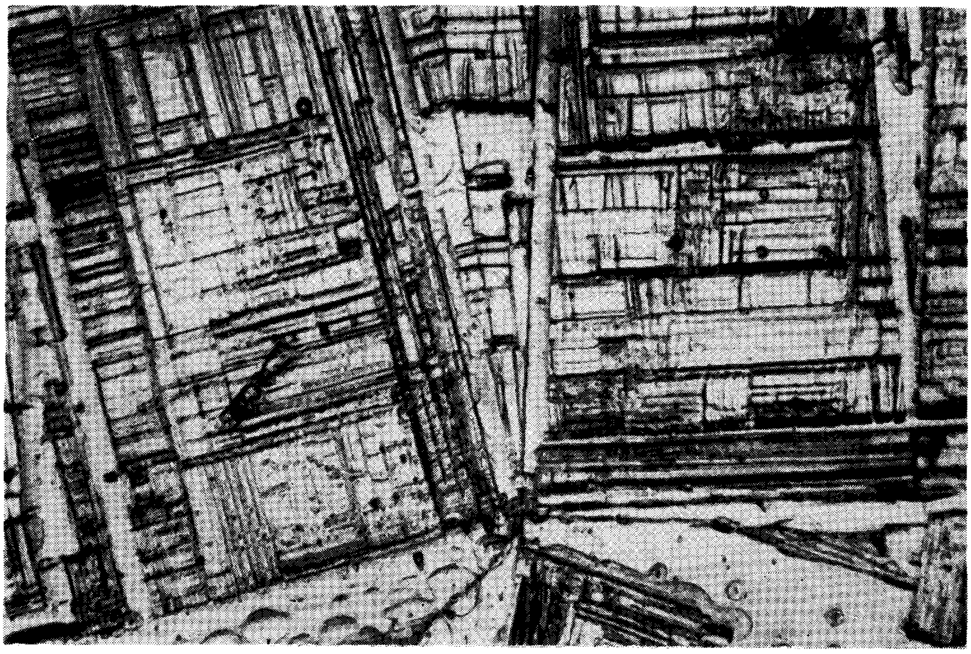


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Photo 5. Etched structure of ε crystals. (specimen CN-25)

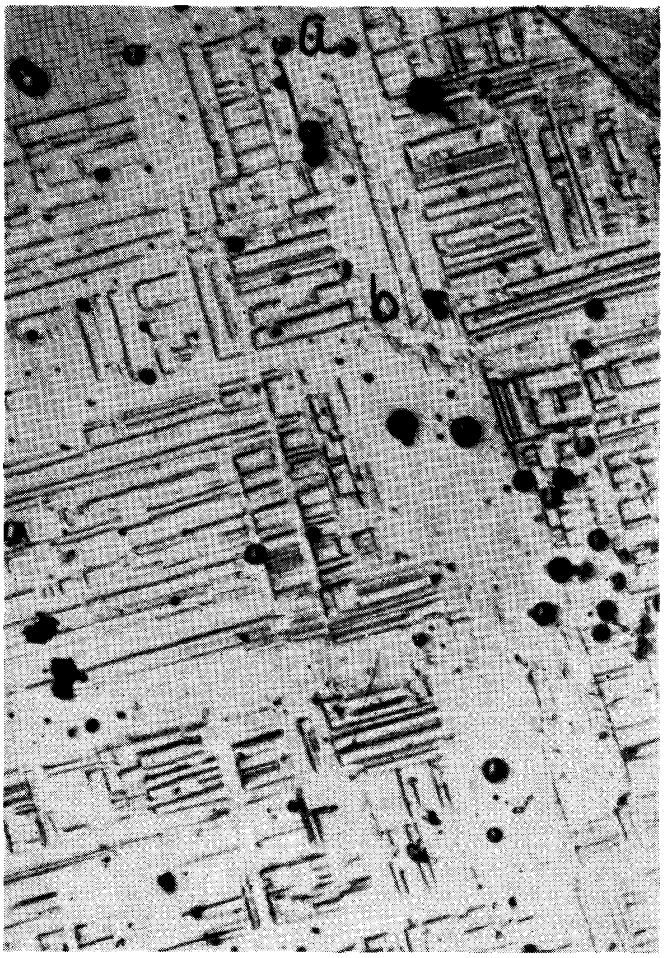

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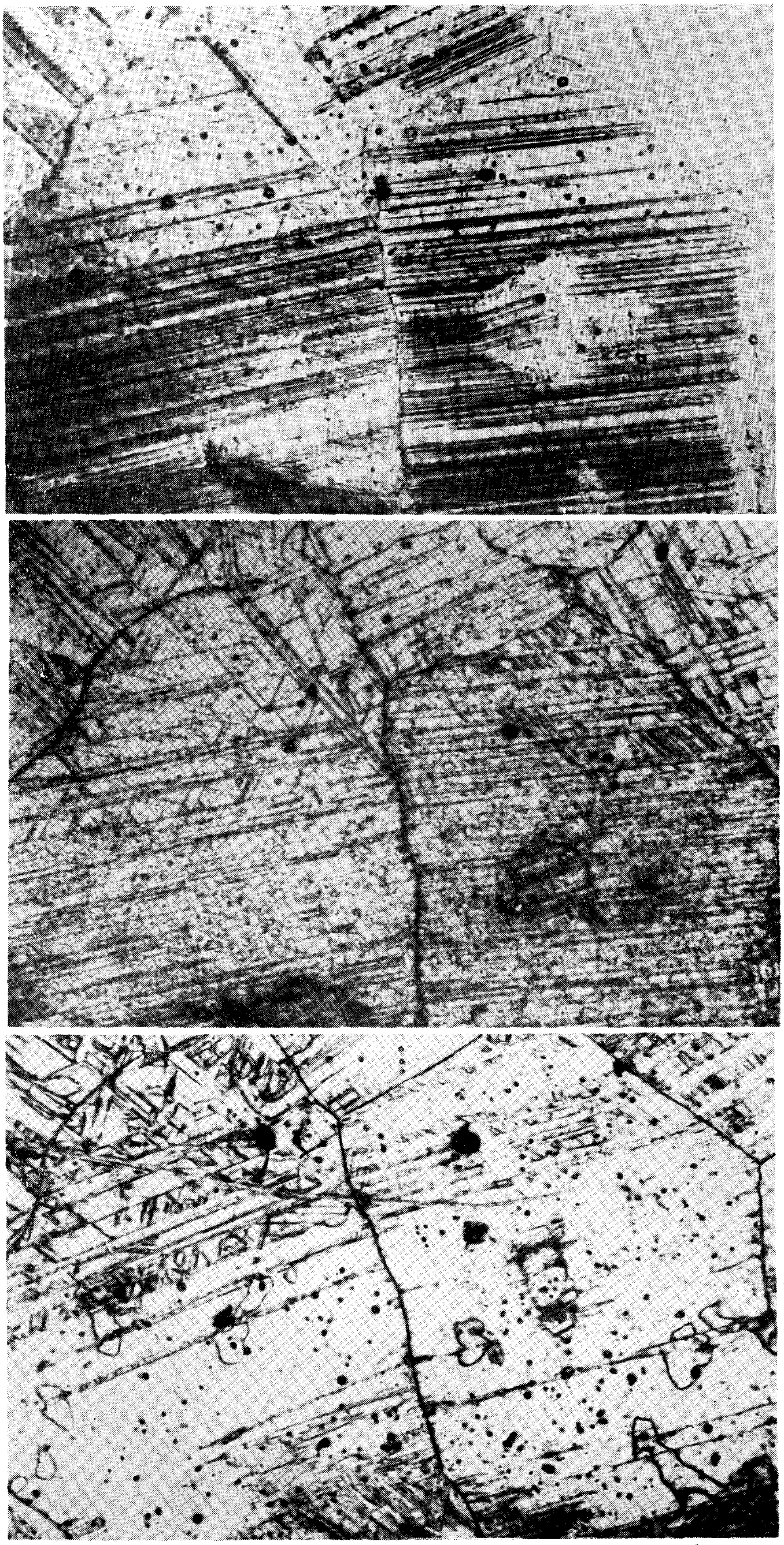
Photo 8. Etched structure of the same position as photo 4.



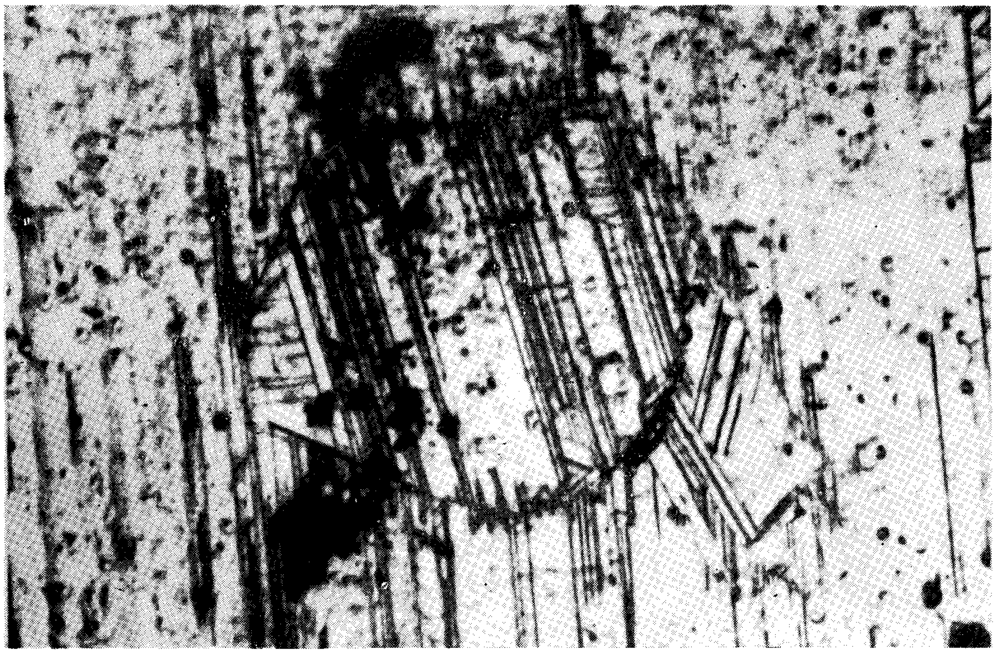
(a) Unetched surface

(b) Polished 0.01 mm

(c) Polished 0.05 mm

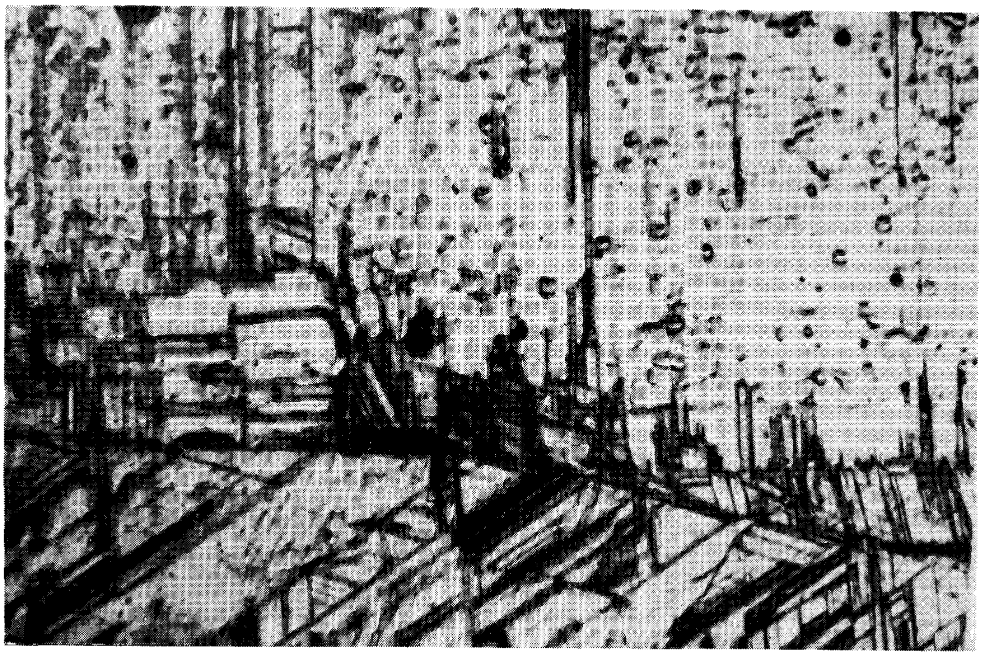
×100

Photo 6. Correspondence of relief markings with etched ε crystals.



×500

Photo 7. One part of photo 6 (b) polished by 0.01mm in depth (specimen CN-25)



×500

Photo 9. Etched structure near the grain boundaries.

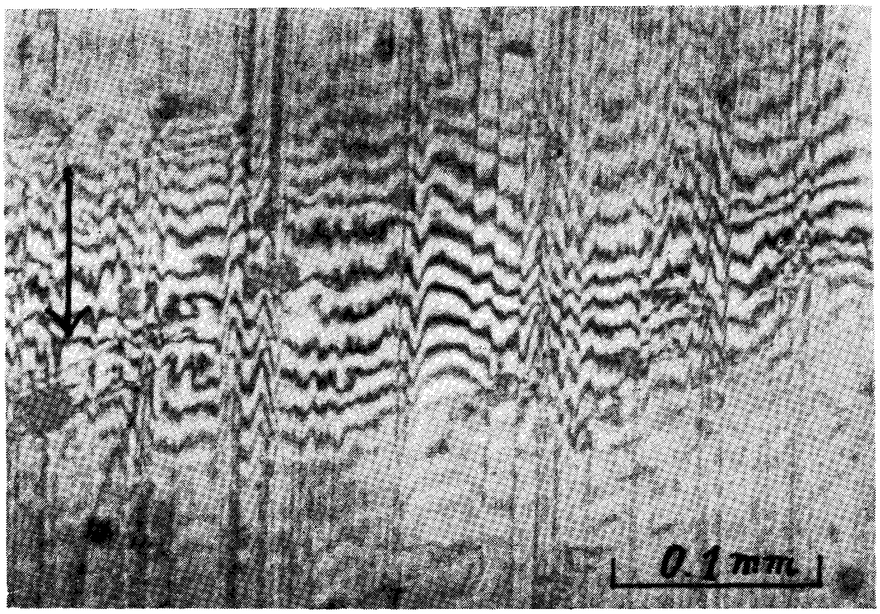
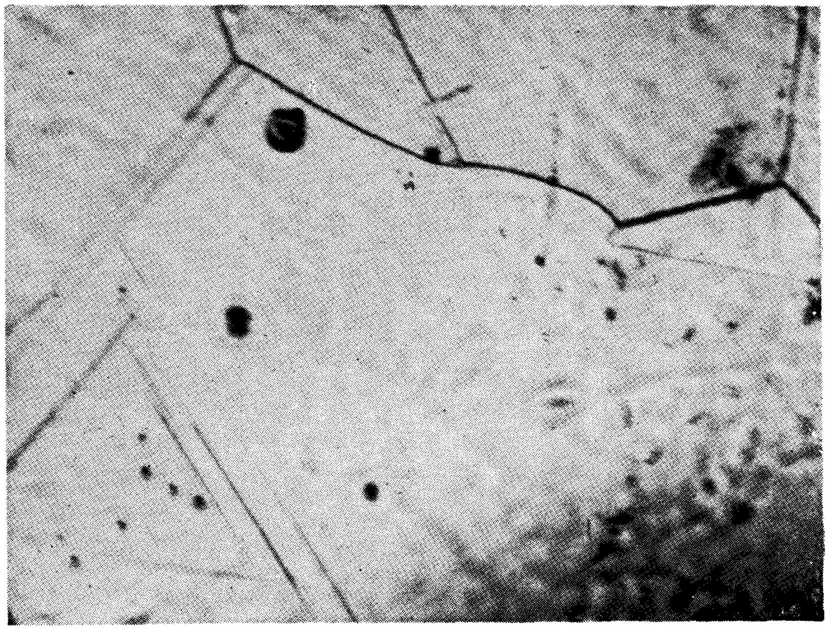
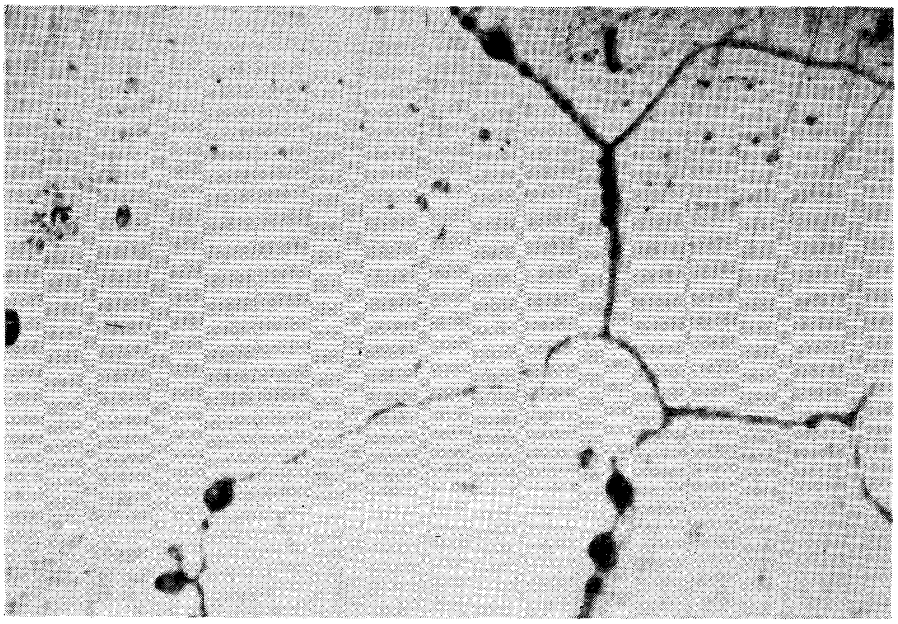


Photo 10. Interferogram of relief-markings. (CN-20)
the arrow represents the direction of upheaval.



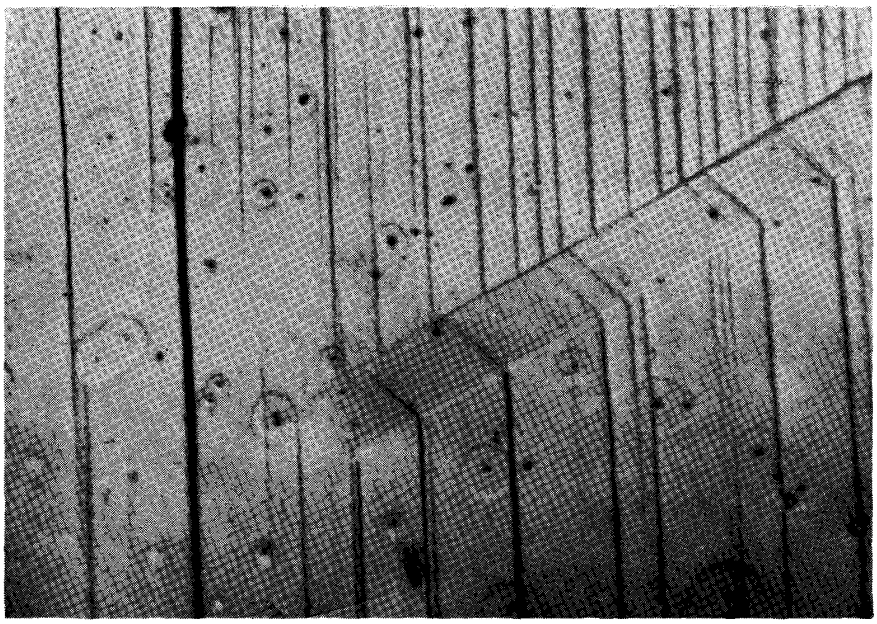
×250

Photo 11. Surface structure of unetched specimen CN-5.



×250

Photo 12. Surface structure of unetched specimen CN-O.



×350

Photo 13. Relief markings due to external stress.
(specimen CN-30)

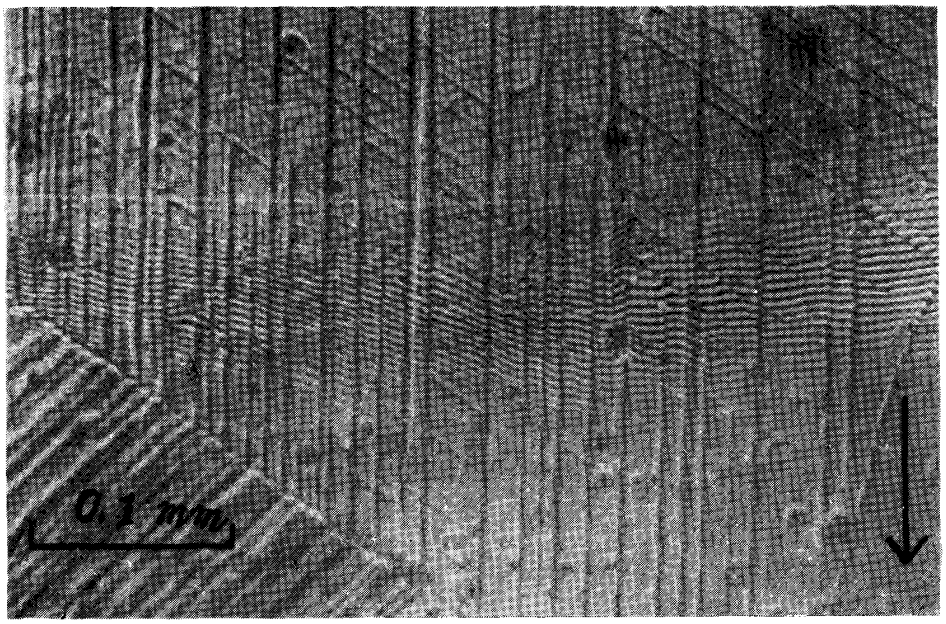
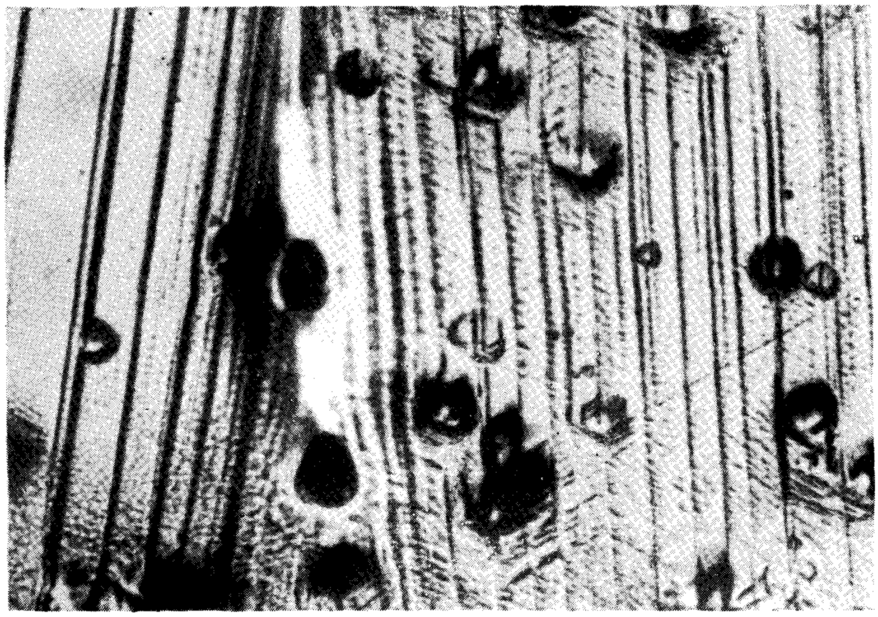


Photo 14. Interferogram of relief markings induced by external stress. (CN-30) the arrow represents the direction of upheaval.



×500

Photo 15. Etched structure of ε crystals due to external stress. (specimen CN-30)

If it is taken into account that a group of markings of the same direction forms one ε-crystal corresponding to one martensite plate, it can be seen that the time required for the growth will be of widely different order in these two cases, though both are instances of diffusionless transformation.

5. Interferogram of the markings

The structure of the cross-sections of the markings appearing on the surface of the specimens was considered to be characterized by the co-operative motion of atoms in the $\{111\}_\beta$ planes, and so the cross-section of markings was examined with a microinterferometer.

Photo. 10 is a micro-interferogram of a group of markings grown in the same direction in specimen CN-20. As white ray was used, the interval between two neighboring interference fringes corresponded to the mean half wave length of 3,000 Å. The low magnification failed to reveal the microstructure of markings, but rough estimations of the angle of slope and of the direction were possible. As seen in photo. 10, the cross-section of markings shows a structure of ridges or valleys and is clearly dissimilar to that slip bands observed by Heidenreich et al.(5) The arrow mark in Photo. 10 shows the direction of the rising ridge. The fine markings are around 2μ in width and the extent of displacment of interference fringes are about $0.2\sim0.3\mu$ and so the inclinations of markings are $11\sim17°$. As an outstanding feature, the markings are generally unsymmetrical on both sides and have no tendency of gradual decrease in the inclination due to the occurrence of slip accompanied by the transformation as found in Ti.(6) In each crystal grain under observation and in markings of different orientation in the same crystal grain, the inclinations of the markings were naturally not equal to one another, but in no case the inclination larger than 20° was observed. A very stout mraking of heigh elevation (10μ in width and mean inclination 3°30′) was seen at the middle of the picture, but the small unevenness in the fringes suggests that it is composed of several small markings. This band contains parts of valley structure and of untransformed structure, which causes the mean inclination to be reduced further

6. Influence of nickel concentration

The width of the markings tended to decrease slightly with the decrease in Ni content, though it remained $1\sim2\mu$ in the range of $10\sim25$ per cent Ni. In alloys containing less than a few per cent of nickel, however, it decreased abruptly and as shown in Photo 11 a few fine markings can be barely observed in the surface of the Co-5 per cent Ni alloy. In pure Co (specimen CN-O), as shown in Photo. 12, such a marking was never observed even on the surface of the specimen in the completely transformed state.

7. markings induced by external stress

When an alloy specimen containing 30 per cent Ni (CN-30), in which no

(5) R. D. Heidenreich and W. Schockley, Rep. Bistol Conf. London, (1948), 57.
(6) A. J. Williams, R. W. Cahn and C. S. Barrett, Acta, Met., 2 (1954), 117.

spontaneous transformation took place at room temperature was compressed, the markings were induced on the surface of specimen as seen in Photo. 13.

Such a compressed specimen, after electrolytic polishing and etching in nital reagent (95 per cent C_2H_5OH + 5 per cent HNO_3), revealed the etched structure of transformed ε-crystal corresponding to each marking as shown in Photo. 15, and so this marking is not due to plastic slip but due to transformation.

As shown in Photo. 14, however, the interferogram of markings in this case gives a different figure of interference fringes as compared with Photo. 10 and accordingly, it is shown that the cross section of marking induced by external stress does not take a ridge but takes a precipice-shape extending in one direction as in the slip band.

IV. Discussion

It has been found from microscopic observations that the process of growth of marking and its growth rate, the structure of cross-section of a marking and the relation of makings to the inner structure of ε crystal in the β→ε transformation in Co–Ni alloys are remarkably differnet from those in the common martensite of "Umklapp" type in steels.

In the present study these differences were considered to be due to the difference in their propagation mechanisms of transformation.

For the mechanism of the f. c. c. → h. c. p. transformation, Nisiyama[(7)] has obtained the following lattice relation as shown in Fig. 3, that is, the transformation is accomplished by slipping of the pair of neighboring two atomic planes in the $(111)_\beta$ plane in the direction of $[11\bar{2}]_\beta$ by the distance of $a/\sqrt{6}$ (here a is the lattice parameter of β lattice). Though the reason why such motion of atoms is realizable in actual crystal will be discussed in the 2nd report,[(8)] if a marking due to transformation has been produced in such a manner, no inclination larger than 19°28′ should appear on the surface of specimens and this conclusion is in agreement with the present result.

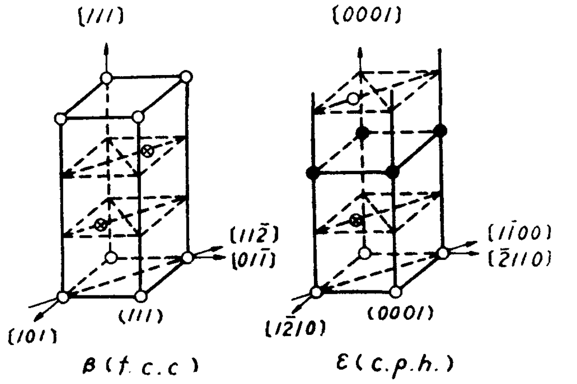


Fig. 3. Lattice relations between β (f. c. c.) and ε (c. p. h.).

Further, from considering the fact that cross section of a marking shows usually a ridge structure having unequal inclinations on both sides, the marking structure can be explained to be due at least to two kinds of shearing motions of atomic planes in different directions.

It can further be estimated that the markings appearing in the same $(111)_\beta$

(7) Z. Nisiyama, Sci. Rep. Tohoku. Univ., **26** (1936), 77.
(8) S. Takeuchi and T. Honma, to be published in Sci. RITU **A9**, No. 6. (1957).

plane are usually composed of three kinds of tilted plane as can be seen from Fig. 3.

If it is considered that the transformation developed by the above-mentioned three kinds of homogeneous shear, one group of numerous parallel markings must corresponed to a single crystal of transformed phase. Still more, if each of the three kinds of the homogeneous shear occurs in such a way in which the shear suitable for eliminating the strain due to the preceding one is successively enforced, it will be possible to elucidete reasonably the account for the observed facts that marking takes a ridge-shaped cross section, or takes a precipitate-shaped extending in one direction under external stress, or has a strong tendency of formation of a group of parallel markings.

This however, cannot be examined under an optical microscope and hence, more detailed studies are now in progress with an electron microscope.

Summary

Using specimens of Co-Ni alloys, the propagation process of face-centred cubic →close-packed hexagonal lattice transformation was studied from the relief markings appearing on the crystal surface and the following results were obtained.

(1) The markings show the cross-section of ridges (or valleys) formed by more than two different tilts, of which the inclination never exceeds 20°. The width of the markings is between $1\sim2\mu$ in alloys of $10\sim25$ per cent Ni, and decreases slightly with a reduction in the Ni concentration.

(2) No such marking is observable in pure Co specimen.

(3) The time required for the formation of one individual ε-crystal is more than 10,000 folds of that for growth of martensite of "Umklapp" type in steels.

Acknowledgments

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