The Sub-Structure in Single Crystals of Nickel

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A Prismatic structure has been found in the rodlike single crystals of nickel grown from the melt in the [001] direction. This structure, running along the growth direction, shows the difference of orientation between neighbouring lineages, which consists of a pure rotation about an axis parallel to the [001] direction, and simultaneously, has the segregation of impurities at its boundaries. It is also found that a diameter, l, of the cell which is a manifestation of the prismatic structure on the top free surface is not affected by any kind and any quantity of impurities but has a relation to the lowering speed, R, as follows: $l = C \cdot R^{-1/2}$. The explanation of these observations is given by the growing of the corrugations whose boundaries coincide with the network of sub-boundaries suggested by F.C. Frank.

INTRODUCTION

Buerger[1] suggested that crystals consist of "lineage structure" developed in the course of growth and his suggestion was soon confirmed by his finding, in the crystal of zinc, the prismatic structure which was formed in the direction approximately parallel to the one of growth. Nowadays the similar structure has been found by many workers in several kinds of metal grown from the melt and the mechanism of its formation has been studied.

Pond and Kessler[2] thought that the structure is a manifestation of the dendritic form of growth and that the sole reason for its occurrence is heat transfer in the plane of the growing solid-liquid interface. In contrast to them, on the basis of the broad experiments, Chalmers and his co-workers[3,4] reported that the structure is classified into two types according to its feature, namely "corrugations" and "striations", and they gave the following explanation for the origins of the both structures respectively: The corrugations arise from the particular distribution of impurities occurring in the liquid adjacent to the growing solid-liquid interface during the non-eqilibrium solidification. While, in the solid just after solidification, the boundaries of the striations are formed by the arrangement of the dislocations which are generated, according to the suggestion of Seitz[5], by the condensation of vacancies into disks and by the subsequent collapse of these disks.

In this paper are presented the results of the observations on the sub-structre in nickel and a mechanism for its formation is discussed.

EXPERIMENTAL

The materials used were wires of 98.51% and 99.21% pure nickel but partic-

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ularly, powder of 98,82% for the experiments of autoradiography. These chemical compositions are tabulated in Table 1.

Table 1. Chemical composition of materials (%).

	Ni	Co	C	Fe	Cu	Mn	Mg	Si	Pb	S
in wire	98.51	0.85	0.02	0.02	0.01	0.22	0.18			
in wire	99.21	0.78	0.002	0.002	0.002	tr.	tr.			
in powder	98.82	0.84	0.04	0.70	0.01	tr.	0.05	0.08	0.03	0.06

Single crystals were grown in a vertical porcelain container from the melt using the Bridgeman method. The temperature gradient at the melting point was about 80°C/cm in the present experiment. The crystals thus obtained were the rods of about 3mm in diameter and their axes were parallel to the [001] direction, which had been oriented by the seed crystals.

The flat surfaces parallel to the (001) and (100) plane were made by abrading from the rodlike crystals and were subsequently electropolished in a mixed solution of 10gr. chromic acid anhydride with 90gr. phosphoric acid; the current density was approximately 3amp./cm² with the solution temperature maintained near 90°C. Sub-structures were optically examined on such surfaces after etching in nitric acid or a solution of 5gr. ferric chloride, 2cc chloric acid and 99cc ethanol.

In order to determine the distribution of small amounts of impurity which was induced during the growth of crystal, the radioactive tracer technique was used. Radioactive sulphur 35 was chosen as the impurity, which was a beta emitter with a 87-day half life. To disperse uniformly small amounts of the tracer in the parent metal and to prevent vaporization of the tracer, which may happen in the vacuum furnace before melting, the following technique was employed. Nickel powder with 200 mesh was pressed in the shape of the thin porous plate under pressure of 350kg/cm². After reducing the plates for 10hrs. at 800°C in a hydrogen atomosphere, the plates of 10gr. were made to absorb 5ml of benzen in which radioactive sulphur of 100μc was dissolved. Using these plates, the specimens having the flat surfaces parallel to the (001) and (100) plane were produced by the above mentioned procedure. Photographs were taken by such a way that the Fuji autoradiography plate (strip type) was mounted on the flat surface of the specimen and was exposed for several days in a desiccator.

In addition to the radioactive tracer technique, the X-ray back reflection Laue method modified by the micro-beam technique[6] was employed for the investigation of the difference of orientation between sub-structures. The incident X-rays were collimated by passing through the capillary slit made from a long glass thermometer tube. On the surface of specimen, this fine beam had a comparable width to the sub-structure which will be shown in the following section. The analysis of a Laue spot was, therefore, easily made in comparision with the optical observation.

RESULTS

When the specimens is grown within the intermediate renge of lowering

speed (1mm/min to 10mm/min), the polygonal cells divided by ditches is observed on the top surface of the specimen where solidification took place out of contact with the container (Fig. 1). As the lowering speed increases, the cell tends to take the shape of square whose diagonals are parallel to the [100] and [010] directions. A sub-structure is also found by etching as the cell on the cross-sectional surface apart from the top of the specimen and as the lineage parallel to the axis of specimen on the side surface. These sub-structures are found by the more detailed observations to be the different manifestations of the sub-structure which has been formed prismatically along the axis of the specimen during the growth.

The examinations by means of the autoradiography were carried out not only on the top free surface but also on the side surface of the specimens (Figs. 2 and 3). These photographs show that the concentration of tracer increases abruptly at the part of the ditches dividing the cells on the top free surface, and it increases at the narrow strip regions along the boundaries of lineage on the side surface, though these regions vary in width along the direction of growth.

After the specimen was annealed for 100 hrs. at 1350°C in vacuum, an autoradiograph was made from its side surface. Although the strip region is not always continuous, it does occupy the same position as before annealing and becomes more distinctive in the shape (Fig. 4).

For the investigation of the difference of orientation between the lineages, a series of Laue patterns was taken on the side surface of the specimen at the intervals equal to the diameter of the X-ray spot across the width of the specimen. A typical example is shown in Fig. 5 which shows apparently the splitting of spots due to the difference of orientation between the lattices of neighbouring lineages, consisting of a pure rotation about an axis parallel to the [001] direction. The same results are also obtained from other patterns. Through all the patterns, it is found that the difference of orientation between neighbouring lineages lies in the wide range such as from 1′ to 1°, and the direction of rotation is kept at random but the sum of all the rotations in one direction is very nearly equal to the one in the opposite direction.

Furthermore, the Laue patterns were taken from a series of specimens grown by various lowering speeds. These results show that each of specimens gives the same results as descrived above and that the neighbouring lineages between which a large difference of orientation exists, increase in number with increasing the lowering speed.

As the lowering speed decreases below the intermediate range, the polygonal cell tends to take the irregular shape. In this stage, an autoradiograph was made from the sectional surface of the specimen as shown in Fig. 6, which shows a noteworthy fact that the boundary of the cell breaks off, then both of the broken points are shaped like the ball and tend to separate each other as indicated by the arrows. Here, it is interesting that there exists the sub-boundary which terminates inside of the crystal.

The specimens grown by the far slower lowering speed than the intermediate range are examined through a microscope, but neither the lineages nor the cells are observed by any etching procedure. Moreover, the autoradiograph obtained on
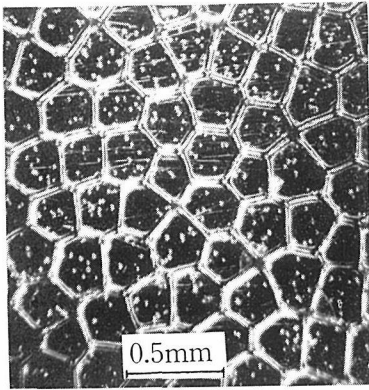
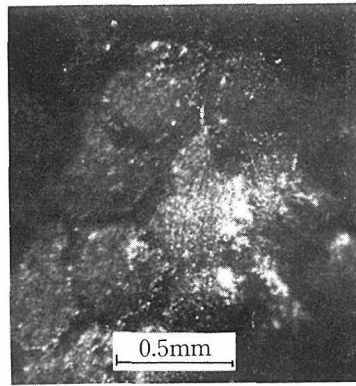Fig. 1.   Microstructure on the top free surface. Lowering speed, 1mm/min.

Fig. 2.   Autoradiograph made from the top free surface. Lowering speed, 0.5mm/min.
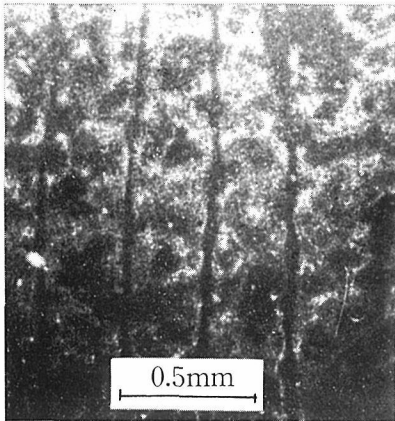
Fig. 3.   Autoradiograph made from the side surface. Lowering speed, 0.5mm/min.
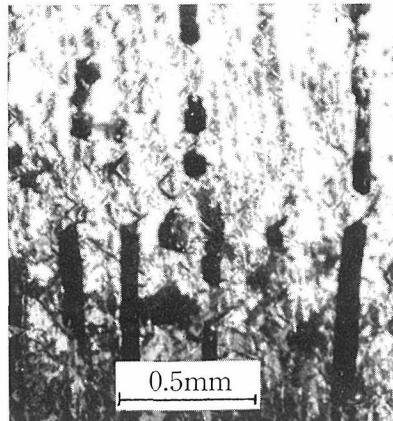
Fig. 4.   Autoradiograph made from the side surface after annealing for 100 hrs. at 1350°C. Lowering speed, 1.4mm/min.

Fig. 5.   X-ray back reflection Laue pattern taken from the side surface. Note apparent split of the spots.
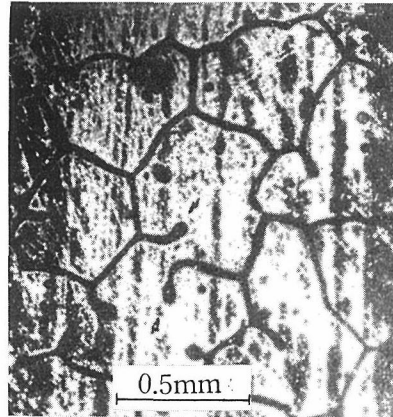
Fig. 6.   Autoradiograph made from the cross-sectional surface. Lowering speed, 0.35 mm/min.

the side surface is shown in Fig. 7, in which there is no particular segregation of the tracer corresponding to the lineages but exists the distinctive regions of the irregular shape with high concentration of the tracer.

The phenomena described above are in common with the three kinds of specimen tabulated in the Table 1. On the other hand, when the the specimen with 98.51% purity is grown at so fast lowering speed over 10mm/min, the appearance of the sub-structure changes suddenly, that is, the sub-structure which consists of islands of irregular shape is observed by etching both on the side surface and the sectional one (Fig. 8). This structure bears some resemblance to the polycrystalline structure, but it is ascertained by means of X-ray microscopy that the difference of orientation between the islands is not more than 3°. The same substructure is observed on the specimen made from powder nickel with 98.91% purity. The side surface is also observed by the autoradiography. The photograph obtained shows that there are in rows parallel to the axis of specimen the oval regions in the interior of which the concentration of tracer is low in comparison with its outer area (Fig. 9).
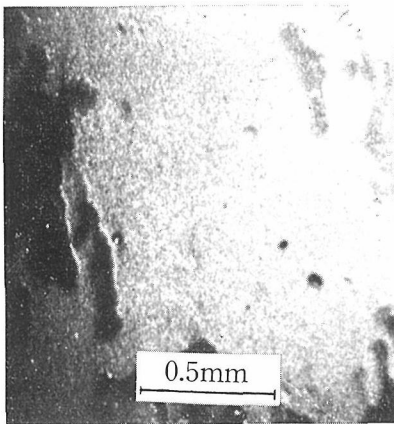

Fig. 7. Autoradiograph made from the side surface. Lowering speed, 0.27mm/min.
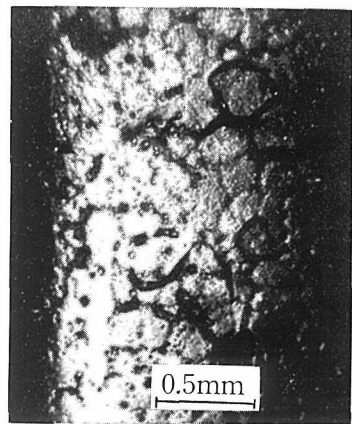

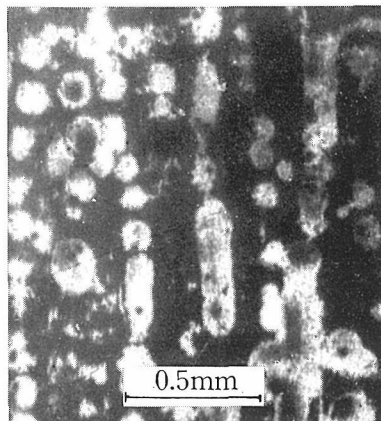Fig. 8. Microstructure on the etched side surface. Lowering speed, 10mm/min.

Fig. 9. Autoradiograph made from the side surface. Lowering speed, 10mm/min.

However, in case of the specimen prepared from the material with 99.21% purity, even when the lowering speed is over 10mm/min, the cells on the top free surface and the lineages on the etched side surface are still observed.

The relation between the cell size, l, and the lowering speed, R, was studied on the specimens with 98.51% and 99.21% purity grown in a definite temperature gradient. The average cell size was measured on the microphotograph taken from the top free surface. The results obtained have been plotted in Fig. 10 as l vs. $1/R^{1/2}$; these indicate a noticeable evidence that the both kinds of specimen used here contain different impurity as tabulated in the Table 1. Nevertheless, the cell size is independent of any kind of specimens and varies with the lowering speed according to the relation defined as follows:

$$l = C/R^{1/2}$$

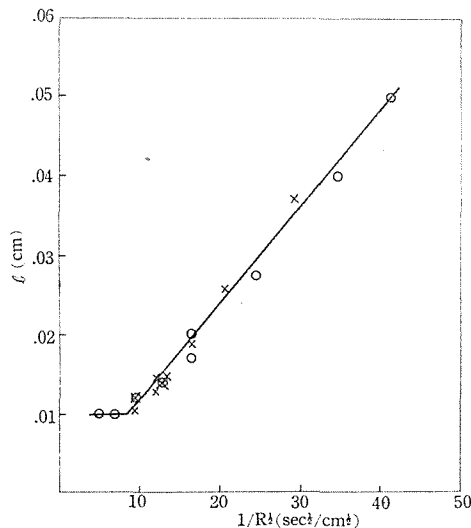where C is the constant which is evaluated from the experiments as $1.2 \times 10^{-3} cm^{3/2}/sec^{1/2}$.

Fig. 10. Variation of cell diameter, l, as a function of lowering speed.
$\times$······98.51% pure Ni ; $\bigcirc$······99.21% pure Ni.

DISCUSSION

In the present work, it is confirmed that the prismatic structure developed in the course of growth from the melt exists in the crystals of nickel as well as in a number of other metals. On the one hand, the appearance of the sub-structure is the same as the corrugations, that is, the sub-struture develops only in a certain range of the lowering speed and manifests itself as polygonal cells on the top free surface, which are surrounded by the ditches and segregate impurities at their boundaries. On the other hand, this sub-structure has the alternative features which could not be regarded as those of the corrugations; the impurities segregated into the boundaries of lineages are stable under the thermal treatment; there is the orientation differnce between neighbouring lineages, consisting of the pure rotation about the [001] direction; the diameter of the cell increases linearly with

$R^{-1/2}$ regardless of any kind or any quantity of impurities. Thus, it seems that this sub-structure may not be developed by the mechanism for the formation of corrugations only, but by the more complicated one.

In order to explain a feature of the striation, Frank[7] suggested that the arrangement of edge dislocations created by the disk of vacancies might form a sub-structure which grows nearly parallel to the direction of growth with a shape of network in a plane perpendicular to it, and causes the difference of orientation consisting of a uniaxial rotation between the sub-structures. It is, therefor, considered that the sub-structures in nickel are the corrugations whose boundaries coincide with the network of sub-boundaries suggested by Frank. This consideration may also be supported by the fact[8] that although a sub-structure distinguished by a difference of orientation was examined in detail by means of the X-ray microscopy on the side and the sectional surface of the present specimens, the striations could not be found separately except the boundaries of lineages or cells observed here.

According to the above consideration, the boundary of lineage consists of impurities and an arrangement of edge dislocations. As pointed out by Cottrell[9], the impurity atoms reduce the strain energy of a edge dislocation in the vicinity of it, when they have different size from the atoms of the main constituent. For this reason, a large activation energy is required to diffuse the impurty atoms apart from the boundaries of lineage. This would be understood as a reason for the evidence that the impurities in the boundaries of lineage remain there without diffusing during a prolonged heat treatment at elevated temperature.

As for the above consideration, there remains a further question, that is, by what mechanism are formed the corrugations coincident with a network of sub-boundaries. This can be explained as follows: Though sub-boundaries are in general fairly mobile at a high tenperature near the melting point, their movement would be restricted when they are formed in a network. While, when the impurity atoms segregate at a region in the crystal, they cause a large increase of strain energy owing to the difference in size from the atoms of the main constituent. Besides, the impurity atoms are fairly diffusible at such a high temperature. Thus the impurity atoms would migrate into the more stable positions which are provided by a network of sub-boundaries, then would be trapped there. As a consequence, a network of sub-boundaries would become more immobile.

Although this consideration may seem to offer the explanation of the formation of the impurity sub-boundaries at the network of sub-boundaries in a crystal after solidification, the following explanation could be given to the assumption that the corrugations coincident with the network of sub-boundaries are already developed at the growing solid-liquid interface. On the basis of a thermodynamical calculation, Bolling and Tiller[10] pointed out that the solid-liquid interface is developed in the shape of a groove at the position meeting the sub-boundary, and the solid surface inside the groove is kept in equilibrium with the super-cooled liquid.

Suppose that there is the growing solid-liquid interface with the small projections at the base of which the boundary of corrugations is formed. When the network of sub-boundaries meets at this interface and then the grooves are further formed

there, the impurities in the liquid in the vicinity of the interface would be compelled to diffuse toward the depth of grooves in order to reduce super-cooling in the inside liquid of the grooves by increasing the impurities content. Consequently, the base of the projections would be transferred to the position of the network of sub-boundaries.

The above consideration predicts that the cell size coincides with the mesh size of the network of sub-boundaries. According to the suggestion by Frank, it is expected that the cell size is also determined by a distance over which vacancies can diffuse, but is independent of any kind or any quantity of impurities contained in the specimen.

Under a growing condition of a linear temperature gradient, dT/dx, and of a growth rate, R, the distance, lv, of vacancy migration in the solid near the growing interface was given by Elbaum[11] as follows:

$$lv = \left[\frac{DkTm^2}{RU(dT/dx)} \right]^{\frac{1}{2}}$$

where D is the diffusion coefficient, U the energy of formation of a vacancy in the crystal lattice, k the Boltzmann constant and Tm the melting point. Since the boundary of a cell is formed at the place where a vacancy can reach from the center of a cell, the diameter of a cell, l, is given by:

$$l = 2lv = 2 \left[\frac{DkTm^2}{U(dT/dx)} \right]^{\frac{1}{2}} \cdot R^{-\frac{1}{2}} \quad .$$

This equation represents the same result as the experimental one in the linear relation between the diameter of a cell and $R^{-1/2}$. Moreover, in order to investigate a quantitative validity, the coefficient of $R^{-1/2}$ is calculated by substituting in the above equation the following experimental values:

$$
\begin{aligned}
Tm &= 1728° K \\
dT/dx &= 75°C/cm \\
D &= 1.3 \times 10^{-9} cm/sec \\
U &= 2.2 \times 10^{-12} ergs
\end{aligned}
$$

where the value determined by Nakamura and Takamura[12] is used for the formation energy of a vacancy, while, the diffusion coefficient of a vacancy near the melting point is determined from it and the activation energy, Q, of diffusion of a vacancy at 1000°C reported by Burgess and Smoluchowsky[13] in accordance with the following equation:

$$D = D_{1000°C} \exp Q/k \ (1/1273 - 1/Tm)$$

The value of C obtained is tabulated with the experimental value as follows:

	Experimental	Theoretical
C cm$^{3/2}$/sec$^{1/2}$	1.2×10^{-3}	1.0×10^{-3}

radioactive tracer work. The author is greatly indebted to Professor Y. Nakamura and Dr. Y. Deguchi for their discussions.

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