

Electron Diffraction Study of Evaporated Films of Nickel and Cobalt

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Evaporated thin films of nickel and cobalt formed on amorphous bases were studied by the radial distribution method. Such thin films consist of crystallites with size of the order of 10\AA .

For nickel crystallites, the lattice constant and the amplitude of thermal vibration are the same as those of massive crystals but anomalous neighbours of h.c.p. type are found. These results are the same as those for silver which were studied in the previous work (J. Phys. Soc. Japan **13** (1958) 1015).

For cobalt crystallites at room temperature, the amplitude of thermal vibration turns out to be twice as large as that of massive cobalt crystals and the numbers of neighbours are found to be equal to those which are calculated for a mixture of h.c.p. and diamond structures. At high temperatures, no remarkable difference is found in either the number of neighbours or the amplitude of thermal vibration as compared with massive crystals.

Introduction

Very thin evaporated films of mean thickness of the order of 10\AA are not continuous and consist of small crystallites. Such films of face-centered cubic metals, such as silver and gold, produce electron diffraction patterns with anomalous intensities, although films of aluminum show no anomaly^{1) 2) 3)}. In order to study this anomaly, the radial distribution method was applied to silver films by the present author³⁾. The analysis revealed that the lattice constant and the thermal vibration are the same as those of massive silver crystals but the anomalous neighbours of h.c.p. type exist in small crystallites. In the present work, the structures of very thin nickel and cobalt films are studied by the same method.

Experiment and analysis

Thin films of the order of 10\AA were prepared by the vacuum evaporation on bases of amorphous carbon or Formvar films which were kept at temperatures $20^\circ\text{C}\sim 500^\circ\text{C}$. Some of the specimens deposited on 20°C bases were heated up to 500°C , and some of the specimens deposited on high-temperature bases were cooled down to a room temperature. In order to avoid the oxidation, the evaporation and heat treatment were carried out in the diffraction camera.

The specimens were examined by electron diffraction at various stages of heat treatments. Similarly to the diffraction study of gas molecules⁴⁾, the diffraction intensities were measured by the sector-microphotometer

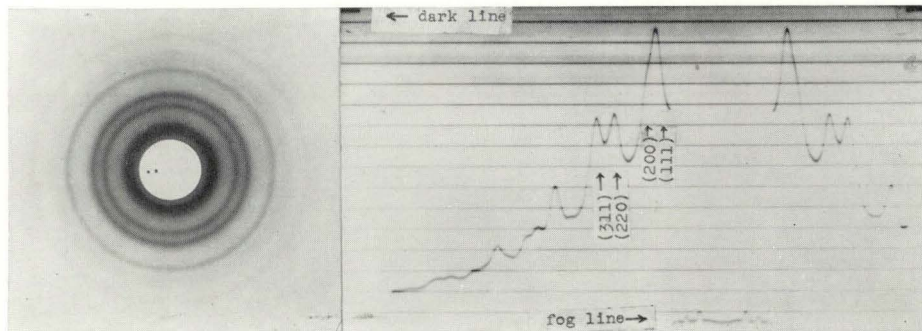


Fig. 1. Diffraction photograph and microphotometer record of nickel film (specimen No. 3; thickness 15\AA , deposited on 20°C base).

method and then the radial distribution functions were calculated. The sector was of the type of s^1 . The specimen-to-plate distance of the camera was about 24 cm and the accelerating voltage was about 40 kV. An example of diffraction photographs with its photometer record is reproduced in Fig. 1.

To obtain the radial distribution function, sine-transformation was carried out according to

$$D(r) = \int s \frac{I_{obs} - I_i - I_b}{f^2} \exp(-0.2s^2/\pi^2) \sin sr ds, \quad (1)$$

where f is the atomic scattering factor of metal and I_{obs} , I_i and I_b are respectively the observed total intensity, the inelastic scattering from the evaporated metal film and the scattering from the base film. The exponential term is the so-called artificial temperature factor. The integrating region was always $6.0 \leq 10s/\pi \leq 48.4$, and the interval of the numerical integration $(10/\pi)\Delta s = 0.2$ or 0.4 . The calculation was carried out by the use of the electronic computer PC-1 in University of Tokyo.

Results for nickel

All radial distribution functions of nickel specimens consisted mainly of the peaks corresponding to the normal neighbours of f.c.c. type. An example of them is reproduced in Fig. 2a. Solid lines in Fig. 2b show the

distances of normal neighbours of f.c.c. type which are given by

$$r_i = d_0 \sqrt{i}, \quad (2)$$

where d_0 and r_i are the distances of the nearest and the i th neighbours. Dotted lines in Fig. 2b show the distances of anomalous neighbours of h.c.p. type which are given by $i = 2\frac{2}{3}, 3\frac{2}{3}, \dots$ in Eq. (2). When the normal peaks were subtracted from the radial distribution function, a residual part was obtained at the position of anomalous neighbours (Fig. 2c). This residual proved that the anomalous neighbours of h.c.p. type exist in the nickel crystallites in the same order as for silver crystallites³⁾. Therefore, the stacking fault energy of nickel may be the same order as that of silver. The number of anomalous neighbours decreased with the increase of thickness of film and also with the increase of temperature.

From the half breadth of normal peaks, the amplitude of thermal vibration turned out to be $0.10 \pm 0.03 \text{ \AA}$ at 20°C and 0.13 \AA at 300°C . These values agree well with those for massive nickel crystals.

Results for cobalt

Cobalt films thinner than about 50 \AA deposited on 20°C bases showed diffuse-halo patterns. The radial distribution analysis revealed that the numbers of neighbours,

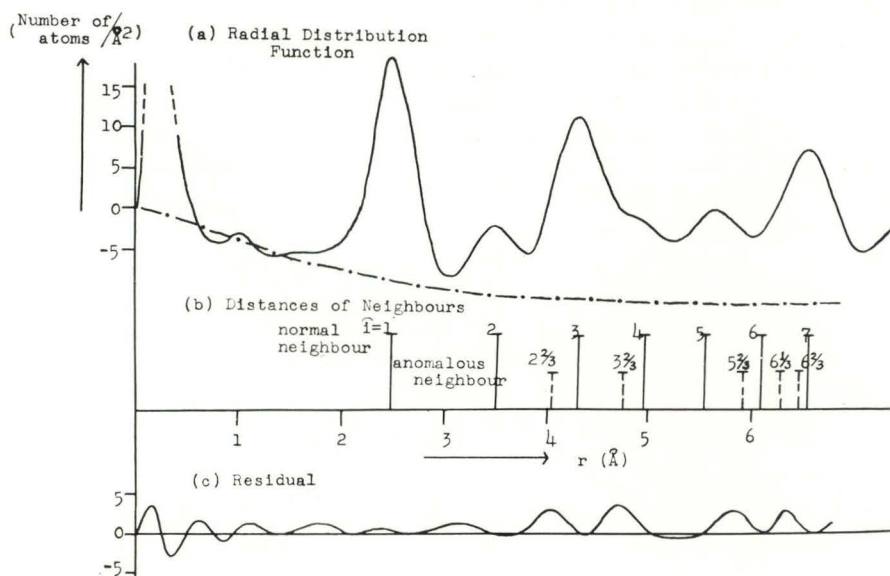


Fig. 2. Radial distribution function and residual of nickel specimen No. 3.

N_i 's, differ far from those in both the close packed structures, hexagonal and face-centered, and are nearly equal to the average of N_i 's for h.c.p. and N_i 's for diamond structure (Table 1). Therefore, it is supposed that one half or more of crystallites have diamond structure. The amplitude of thermal vibration turned out to be 0.20 Å at 20°C, twice as large as that of massive cobalt crystals. The existence of diamond structure in cobalt crystallites may be due to the less metallic

property of cobalt and the large amplitude may be caused by the less close packing of the diamond structure.

For cobalt films thicker than about 50 Å or for thin films at temperatures higher than about 200°C, no remarkable difference is found in either the crystal structure or the amplitude of thermal vibration compared with massive cobalt crystals. The structure is h.c.p. below 400°C and gradually transforms to f.c.c. above 400°C.

The full report of this work will be published in J. Phys. Soc. Japan **17** (1962) 136.

Table I. Number of Neighbours.

i	Co specimen No.1 (thickness 10 Å)	f.c.c.	h.c.p.	diamond
1	8.2	12	12	4
2	1.4	6	6	0
$2\frac{2}{3}$	7.1	0	2	12
3	4.4	24	18	0
$3\frac{2}{3}$	8.0	0	12	12
4	2.8	12	6	0
5	3.2	24	12	0

References

- 1 L. H. Germer and A. H. White: Phys. Rev. **60** (1941) 447.
- 2 K. Kimoto: J. Phys. Soc. Japan **8** (1953) 762.
- 3 H. Morimoto: J. Phys. Soc. Japan **13** (1958) 1015.
- 4 I. L. Karle and J. Karle: J. Chem. Phys. **17** (1949) 1052; J. Karle and I. L. Karle: J. Chem. Phys. **18** (1950) 957.

DISCUSSION

S.H. BAUER: In view of the small crystallite size you worked with, it is not clear how you separated (in the analysis of your intensities to give R.D. curves) the effect of small crystal size from temperature motion.

H. MORIMOTO: The amplitude of thermal vibration was estimated from the breadth of peaks in the radial distribution curve. The size of crystallites was estimated from the slope of $N_i/N_{i\infty}$, where N_i is the number of the i -th neighbour in the analyzed specimen and $N_{i\infty}$ is that in the infinite-size crystal. The detail of my results has been reported in J. Phys. Soc. Japan **13** (1958) 1027.

A.J.C. WILSON: I should like to ask two related questions. First, has it been possible to form a physical picture of how the atoms giving rise to the anomalous interatomic distances are arranged? Are there perhaps amorphous regions, or 'mistake,' or is the metal two-phase? Secondly, on the two-phase picture, is the quantity of the second phase (hexagonal in Ni, diamond-type in Co) great enough so that one would expect to see additional reflections in the electron diffraction patterns, and if so have they been observed?

H. MORIMOTO: We could not propose the physical pictures for the atomic arrangement, because the analysis was one-dimensional and the experimental error was not very small. However, it is supposed that the h.c.p. type neighbours in nickel may be due to the stacking faults and the diamond-type neighbours in cobalt may involve amorphous region.

For nickel, as for silver, electron diffraction patterns showed only anomaly of broad (200) reflection. For cobalt, diffraction patterns consisted of diffuse halos and were of diamond type rather than h.c.p. type.