[Journal of the Faculty of Science, Hokkaidô University, Japan, Ser. II, Vol. V, No. 4, 1959]

On the Magnetic Annealing Effect in 2% Cobalt-Copper Alloy

*II. Precipitation Kinetics and Microscopic Examination

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(Received Sept. 25, 1959)

In order to obtain informations about the behavior of the precipitates during magnetic annealing and the origin of the induced magnetic anisotropy in precipitation alloys, the kinetics of isothermal precipitation of Co-rich phase from a supersaturated solid solution of 2 wt. % Co-Cu alloy in the temperature range 550 to 750°C has been studied by the measurements of the electric resistance, saturation magnetization and micro-Vickers hardness. The X-ary diffraction studies have indicated that f.c.c. Co-rich phase precipitates from the matrix during aging. The precipitation process during aging with or without magnetic field has been examined metallurgically by light and electron microscopes. It has been shown that the shape of the precipitates is highly anisotropic plate-like or lamella-like except a few round precipitates and a little directional distribution of elongated precipitates depends on the direction of magnetic field applied during aging. The effect of particle alignment on the micro-Vickers hardness has also been examined for the specimen aged variously with or without magnetic field and the directional anisotropy of hardness depending on the direction of magnetic field applied during aging has been found.

§ 1. Introduction

In the previous paper,[1] it was shown that the uniaxial ferromagnetic anisotropy induced by magnetic annealing in 2% Co–Cu alloys could be explained by the shape anisotropy and an anisotropic distribution of precipitated particles. It is the purpose of this paper to develop the physical picture of magnetic annealing of this alloy through metallurgical survey. For the study of the mechanism of magnetic annealing during precipitation process, it is required, in general, to perform many types of measurements to get sufficient informations concerning the precipitation process. In this note, we investigated the kinetics of precipitation process by the measurements of hardness, electric resistance and saturation magnetization in the

* Part I of this paper, "Induced Ferromagnetic Anisotropy" was published on J. Phys. Soc. Japan 13 (1958) p. 549.

same conditions as that the measurements of magnetic anisotropy were made.

The precipitation of Co-rich phase from Cu-rich solid solutions was studied extensively in past. M. G. CORSON[2] studied the hardness and electric resistance changes for certain Cu–Co alloys. G. TAMMANN and W. OELSEN[3] determined the solubility of cobalt in copper by measuring the specific magnetization and also measured the magnetic properties and hardness of aged alloys. In 1940, R. B. GORDON and M. COHEN[4] studied in detail the isothermal precipitation process for a series of aged alloys by magnetic, mechanical and electrical methods. Recently, R. NAGASAKI and K. KÔDA[5] studied the age-hardening of copper alloys containing 1.4 and 1.7 percent of cobalt. On the other hand, the magnetic properties of precipitates in this alloy were studied by J. J. BECKER,[6] L. WEIL *et al.*,[7] SUCKSMITH *et al.*[8] and our laboratories.[9]

§ 2. Preparations of the Specimens and Apparatus

The specimens used in this study were Cu–Co alloys containing ca. 2 wt. % Co, which were used in the measurements of the magnetic anisotropy in the previous study.[1] The specimens used in the electric resistance and magnetic measurements were cold-swaged into wires, 1.0 mm in diameter and 20.0cm long. The specimens for the hardness test were the same that were used in the torque measurements.
Electric resistance measurement was made by means of a potentiometer, its accuracy being ± 0.3 per cent at $15^\circ \pm 0.3^\circ$C. Hardness measurement was made by micro-Vickers hardness tester of the Akashi type with a diamond cone and a 500 gram load. Intensities of magnetization in magnetic field of up to ca. 8000 Oe were determined by using a Sucksmith ring balance and the determination of magnetic saturation was extrapolated to $H=\infty$ against $1/H$.

The specimens were solution-heat-treated in vacuum at ca. 1000°C for 2 hrs., rapidly quenched into water. The precipitation treatments were conducted in vacuum at 750, 600 and 550°C for a suitable time and repeated by quenching in the accumulating aging.

§ 3. Experimental Results and Discussions

A. Precipitation kinetics.

Changes of the electric resistance, saturation magnetization and hardness during the isothermal aging in the temperature range 550° to 750°C are shown in Figs. 1 and 2. The results of the electric resistance and hardness show the same tendency as that reported by R. NAGASAKI and N. KÔDA.[5] The results of aging at various temperatures indicate two stages of the precipitation process. For the aging at 550°C, the nucleation stage predominates rather than the growth stage during the measured time-interval of aging. Hardness shows a marked increase and the electric resistance a pronounced decrease at the first one hour aging, and then the hardness shows a gradual decrease and the electric resistance a slight decrease. And, for 750°C-aging a predominant growth stage takes place; the electric resistance decreases rapidly at the first stage of ca. one hour aging and then becomes almost constant for longer aging time, and on the other hand the hardness becomes the maximum value with the shortest aging time of ca. 0.5 hour after an abrupt increase. Moreover, the result of the magnetic saturation measurement shows also that the nucleation stage predominates at 550°C and the growth stage at 750°C, since the magnetic saturation corresponds to the total amount of ferromagnetic phase present, independent of its particle size.

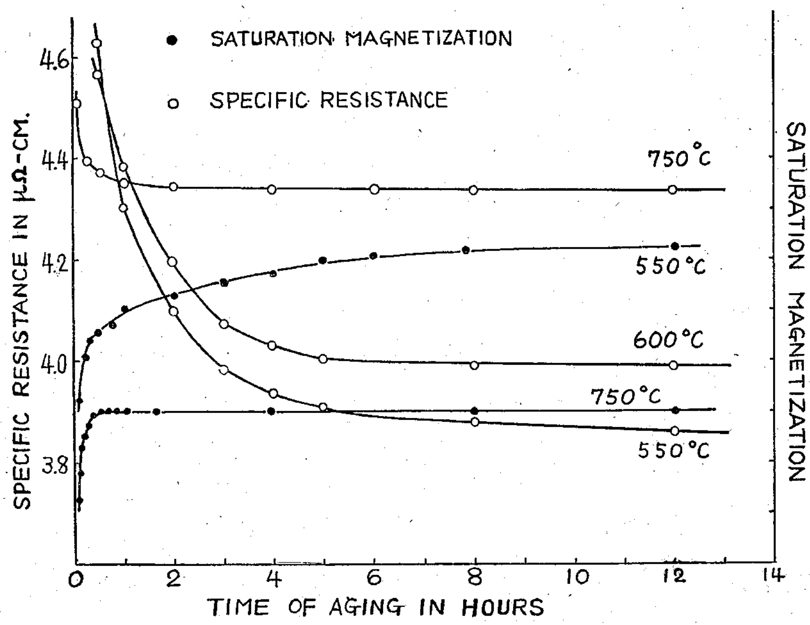

Fig. 1. Variations of electric resistance and saturation magnetization with aging time at various temperatures.

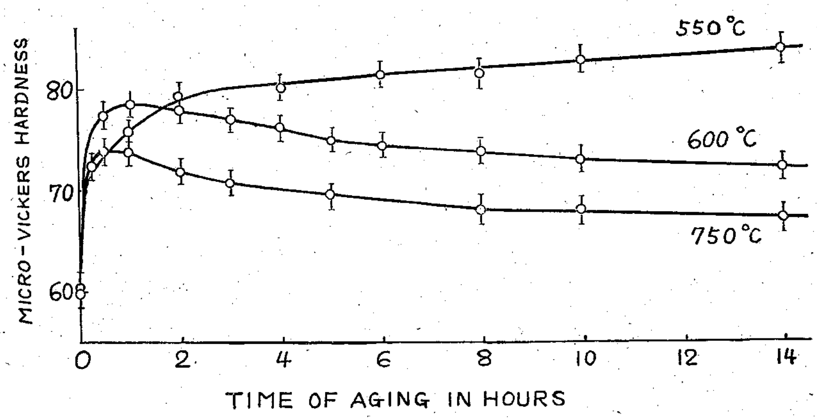

Fig. 2. Variation of micro-Vickers hardness with aging time at various temperatures.

Thus, precipitation is completed even before the shortest aging times at 750°C. For the longer aging times the nucleation comes to an end and the total volume of precipitates becomes constant, since the electric resistance and saturation magnetization are practically constant for longer aging times.

From the results of these measurements and the magnetic anisotropy measurements in Part I, therefore, it is concluded that the nucleation stage of precipitation is completed before the rise of the magnetic anisotropy to its maximum and the changes of the induced magnetic anisotropy during magnetic annealing for all aging times and temperatures are not related to a change of the total amount of precipitates, but of the particle size at the growth stage of precipitates. Moreover, it was shown that the induced anisotropy goes to maximum and then falls with the increasing time of magnetic annealing as shown in Part I. The aging stage corresponding to the decrease of anisotropy is considered to be an over-growth stage of precipitates from the consideration above mentioned. Accordingly, it is confirmed that the precipitates respond to magnetic annealing at the nucleation stage and at the earlier growth stage but not at the over-growth stage.

B. Crystal Structures of the Precipitates and Matrix.

The crystallographic structures of the precipitates and the parent lattice were determined by using Norelco X-ray diffractometer. To determine the crystal structure of the precipitates, the specimen was aged at 700°C for ca. 20 hours and quenched into water. It was found that the lattice parameter for the precipitate of f.c.c. structure is 3.61±0.05 A and for the parent lattice of f.c.c. structure is 3.55 ± 0.05 A. This result coincides with the result of magnetocrystalline anisotropy obtained by torque measurements of single crystals.[10] The same result was also obtained by D. S. RODBELL.[11] Consequently, it seems that the contribution to magnetocrystalline anisotropy is negligible since the magnetocrystalline anisotropy of f.c.c. structure of Co-rich precipitates is cubic and the induced anisotropy is uniaxial.

C. Metallographic Examination by Light and Electron Microscopes.

In order to observe the shape anisotropy of precipitates, the metallographic examination of some of the specimens was carried out by using light and electron microscopes. The specimens used were the same polycrystals as used for the measurement of the magnetic anisotropy. Electron and light micrographs were obtained from the prepared surface of the disk-shaped specimens which were heat-treated for the suitable aging at various temperatures. In the polishing process one must be careful to prevent eventual deformation resulting from the mechanical polishing. For this purpose the following procedure described by GORDON and COHEN[4] is suitable; the surface of the specimen was abraded on the fine carborundum polishing papers. The distorted surface layer was removed by electropolishing for ca. $6\sim8$ amp./dm^2 at ca. $3\sim4$ volt in electrolytic solution of orthophosphoric acid with the specific gravity of 13.5 and the specimens were electroetched for ca. $2\sim5$ minutes at 1.2 volt with the same solution. The volume of electrolyte is about 500 cc and the cathode is made of pure copper with about 30 times of the area of the specimen. The specimen was washed with distilled water and dried rapidly.

The preparation of replicas for electron microscopy was made with the carbon replica method of double stages. The electron micrograph was taken with the JEM. T-4 type using 50-KV electrons.

Some examples of the micrographs, thus obtained, with the interpretation of their photographs may be summarized as follows:

1) The over-aged specimen to which the light micrograph was obtained exhibits a great deal of precipitate phase. Photo 1 a was obtained to the specimen aged without magnetic field for 20 hrs. at 550°C. Photo 1 b is a light micrograph of the specimen aged without magnetic field for 15 hrs. at 750°C. The shape of precipitates at this stage of aging shows predominately the lamella or plate having the major diameter of ca. 30 μ, the minor diameter of ca. 7 μ, and the thickness of ca. $1\sim3$ μ. The plate-like

precipitates form on the copper parent lattice of the {111} planes as a Widmannstätten pattern except the very small fraction of spherical shaped precipitates.

2) Photos 1 c and d show the precipitates of the specimen which is aged at 750°C for 15.0 hours with magnetic field of 1000 Oe. The precipitates lie to four systems of (111) plane in spite of the presence of magnetic field. That the platelets of such precipitates lie on the {111} planes of the matrix was determined by plotting a stereographic projection and by marking slip bands on the {111} planes of deformed specimen. Thus, it is found that the shape and the orientation of the over-grown precipitates do not respond markably to magnetic field applied during aging.

3) Photo 2 shows the electron-microscopic micrograph of the specimen corresponded to the maximum uniaxial anisotropy. This specimen was aged with magnetic field of ca. 8000 Oe at 750°C for 2 hours. In this microphotograph, it could not discussed unfortunately the change of precipite shape because the electron microstructure of the precipitates is less clear than the light microstructure, though a small directional distribution of precipitates appears along the direction of magnetic field.

4) Measurements of precipitate diameter, length and thickness on the many shape of precipitates were made from many micrographs. As shown in the above illustrated photographs, the distribution of precipitate shapes lies in very wide range as well as the size distribution. From data obtained by measuring each of 200∼300 particles which could be resolved in these photographs, we estimated the average value of 0.7 for the demagnetizing factor N, which depends on the ratio of length to diameter of precipitates, as assumed the types of a prolate ellipsoid, a ellipsoidal disk and a sphere for the measured precipitates. Using the average value of $N=0.7$, we obtained the estimated value of 5×10^4 ergs/cc for the induced anisotropy, being approximately in agreement with the observed maximum value of $10^4\sim8\times10^3$ ergs/cc as was shown in Part I.

The conclusion derived from this micrographs about the precipitate shape is that the coarsened precipitates, indicating over-growth stage, predominately take the form of plate-like shapes on the {111} planes of the matrix. This is in contradiction to the results reported by BECKER[6] and RODBELL.[11] RODBELL concluded that the precipitate particles when initial formed have shapes possessing cubic symmetry and are probably spheres and that with growth the particles change and become general ellipsoids whose two larger semiaxes define planes that are parallel to {100} crystal planes. However, there is not yet a definitive answer to the question though it becomes of sifinificance to ask under what conditions the precipitate shape and habit plane for precipitate formation would be different in this alloy.

§ 4. Effect of the Directional Distribution of the Precipitates on the Micro-Hardness

Since the aggregate of precipitates in the alloy annealed with magnetic field have a directional distribution, it is to be expected that the anisotropy of the hardness is also found. Micro-Vickers hardness has been measured on the surface of the same specimen, which was used in the magnetic anisotropy measurement, after various aging treatments with or without magnetic field.

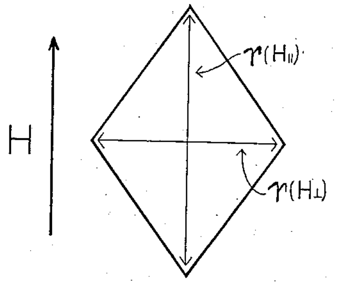

Fig. 3.
A pair of diagonal lengths $r(H_{/\!/})$ and $r(H_{\perp})$ of a mark on the specimen.

The method of the measurement is as follows: A pair of diagonal length $\boldsymbol{r}(\boldsymbol{H}_{/\!/})$ and $\boldsymbol{r}(\boldsymbol{H}_{\perp})$ with a mark of test cone was measured, where one of the diagonals is parallel and the other is perpendicular to the direction of magnetic field applied during aging, as shown in Fig. 3.

The discrimination of anisotropy of micro-hardness, $\bar{\boldsymbol{X}}$, due to the anisotropic distribution of precipitates is given by

$$\bar{\boldsymbol{X}}=\Big[\sum_{i=1}^{N}\boldsymbol{X}_i\Big]\Big/\boldsymbol{N} \tag{1}$$

and the dispersion of $\boldsymbol{X}_i$, σ^2 is given by

$$\sigma^2=\Big[\sum_{i=1}^{N}(\boldsymbol{X}_i-\bar{\boldsymbol{X}})^2\Big]\Big/\boldsymbol{N}\,, \tag{2}$$

where

$$\boldsymbol{X}_i=\Big[\boldsymbol{r}_i(\boldsymbol{H}_{/\!/})-\boldsymbol{r}_i(\boldsymbol{H}_{\perp})\Big]\Big/\boldsymbol{r}_i(\boldsymbol{H}_{/\!/})\,, \tag{3}$$

N, total number of the measurement is ca. 100 and $\boldsymbol{r}_i(\boldsymbol{H}_{/\!/})$ and $\boldsymbol{r}_i(\boldsymbol{H}_{\perp})$ are i-th measured values. Thus, from the measurement of $\boldsymbol{r}_i(\boldsymbol{H}_{/\!/})$ and $\boldsymbol{r}_i(\boldsymbol{H}_{\perp})$, the value $\bar{\boldsymbol{X}}$ and σ^2 are calculated by eqs. (1) and (2). The results obtained from the specimen which was aged at 750°C in the various treatments are shown in Table 1.

TABLE I.

Aging time	Strength of magnetic field at heat treatment	$\bar{X}$	σ^2
5.0 hr.	1000 Oe.	0.0072	0.0002
5.0 hr.	without field	0.0008	0.0001
15.0 hr.	1000 Oe.	0.0006	0.0002
15.0 hr.	without field	0.0005	0.0002
5.0 hr.	7000 Oe.	0.0306	0.0019

The results show that the specimen exhibits the anisotropy on the micro-Vickers hardness, which depends upon the direction of applied field, and the decrease of the anisotropy of hardness coincides with the disappearence of a uniaxial magnetic anisotropy for the aging time of ca. 15 hours as was shown in Part I. This result suggests that the aggregates of procipitates have a small directional distribution at the earlier stage of the precipitation process.

Moreover, the stress-strain relation in the rod-shaped specimens annealed with magnetic field was studied. They were aged for two hours at 750°C with field of 3000 Oe applied along the specimen axis and other specimens in the same condition of aging treatments without field. However, there was no significant difference between their stress-strain curves. Recently, J. D. LIVINGTON[12] independently examinated to detect the same effect of magnetic annealing in the stress-strain relation and also found the effect was negative. It is expected that any effect might be found by the experiment under very strong magnetic field of 10^4 Oe, and using single crystal specimen, which has no grain boundary and has considerably less slip systems than polycrystal specimen. If the very strong magnetic field could control distributions of precipitates sufficiently, we can investigate the effect of precipitates to the plastic slip of the materials in the controlled manner.

§ 5. Conclusion and Summary

From the results mentioned above, it should be pointed out that the behavior of ferromagnetic precipitates of 2% Co–Cu alloy may be interpreted by the shape effect of fine particles and the origin of the uniaxial ferromagnetic anisotropy induced by magnetic annealing in this alloy may be due to the shape anisotropy of preferentially precipitated particles, as expected from the discussion of Part I. It is also found that the over-grown precipitates during aging do not respond to magnetic field. Accordingly, magnetic field has a influence on the nucleation or earlier precipitation and growth of the precipitates rather than over-growth stage of precipitates.

In the present study the crystal structure and shape of the precipitates and their relations to the matrix lattice in the earlier precipitation which is influenced by magnetic field were not examined.

In addition to this, the results of the precipitate shape in this alloy, obtained by us, is somewhat different from that reported by BECKER.[6] This difference may be due to the situation that different treatments of the sample preparation and the quenching procedure give the remarkable influence on the precipitation as studied by us[13] recently.

On the other hand, unfortunately, the nature of the precipitation reactions influenced by the sample preparation and quenching method has not yet definitely established, nor is there even a knowledge on the crystal force due to the favored coherency of the matrix and precipitates, though such problems are the more important one in order to clarify the mechanism of this magnetic annealing in detail. It is hoped that a further study will clarify these points and explain more precisely the behavior of precipitates in each stage of nucleation and earlier precipitation.

More recently, to clarify the correlation between the behavior of the precipitates and their magnetic properties such as the uniaxial anisotropy and magnetocrystalline anisotropy, a refinement of these studies on single crystal specimens was carried out by us.[10] Moreover, the author studied[14] the effect of the magnetic annealing and the relation between the phase transformation of the precipitates and induced anisotropy for 2% Fe–Cu alloy.

The author wishes to express his sincere thanks to Prof. S. MIYAHARA for his encouragement and to members of our research group for many valuable discussions. He also wishes to thank Prof. N. KÔDA and members of Department of Metallurgy for valuable helps and advices in metallographical matters and for the preparation of the specimens, and Mr. T. TAKEYAMA for his guidance and Messrs. K. MATSUURA, S. IZUMI and G. TOMITA for their assistances on the techniques of the light and electron microscopic study. Moreover, the author expresses his sincere thanks to Mr. Y. HAMAGUCHI for his valuable information on this problem. A part of the finance of the present study was supported by the Scientific Research Fund of the ministry of Education.

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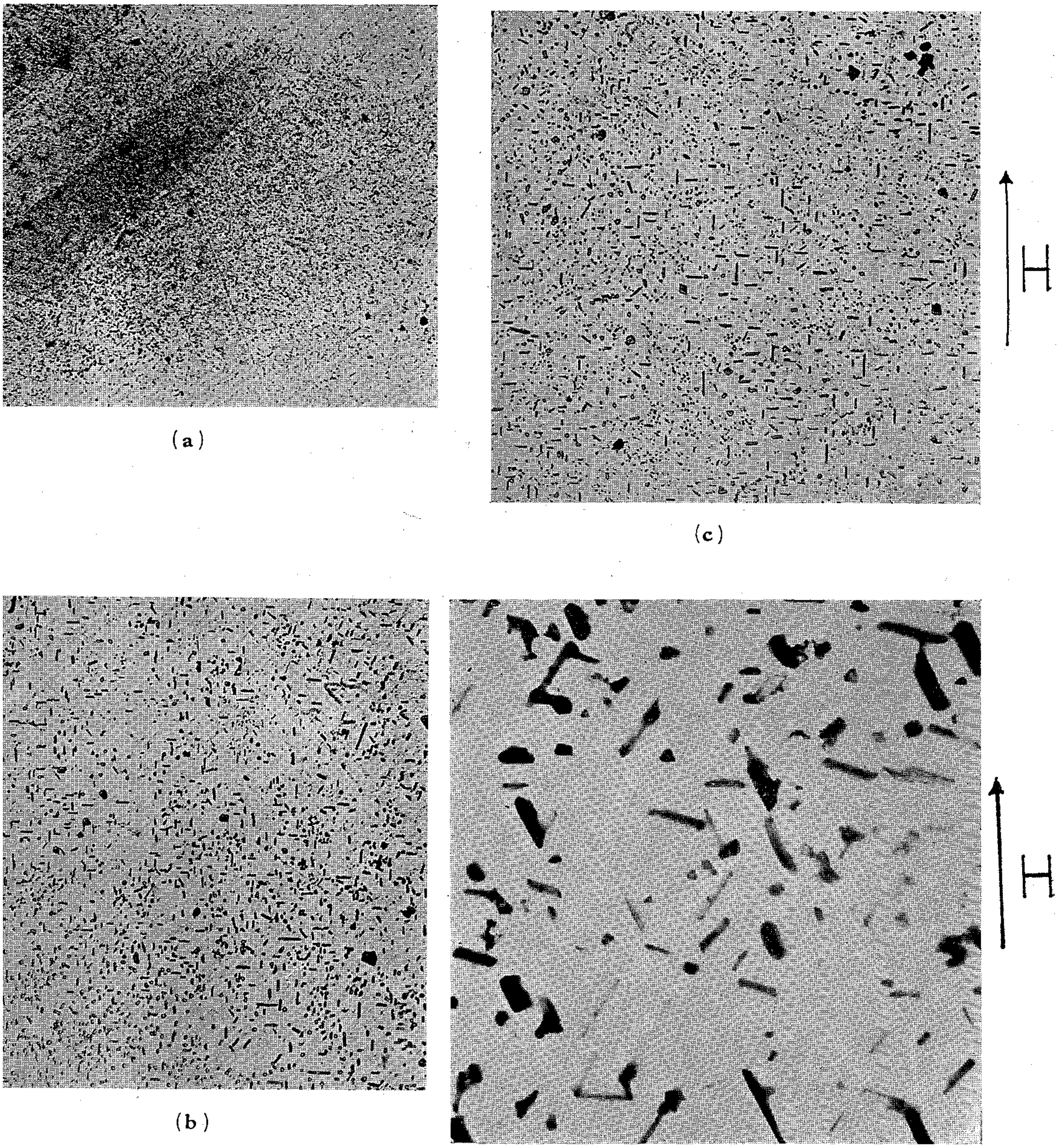

Photo. 1. Light micrographs.

(a) Aged at 550°C for ca. 20 hrs. without magnetic field. (× 150)

(b) Aged at 750°C for ca. 15 hrs. without magnetic field. (× 150)

(c) Aged at 750°C for ca. 15 hrs. with magnetic field. (× 150)

(d) Aged at 750°C for ca. 15 hrs. with magnetic field. (× 800)

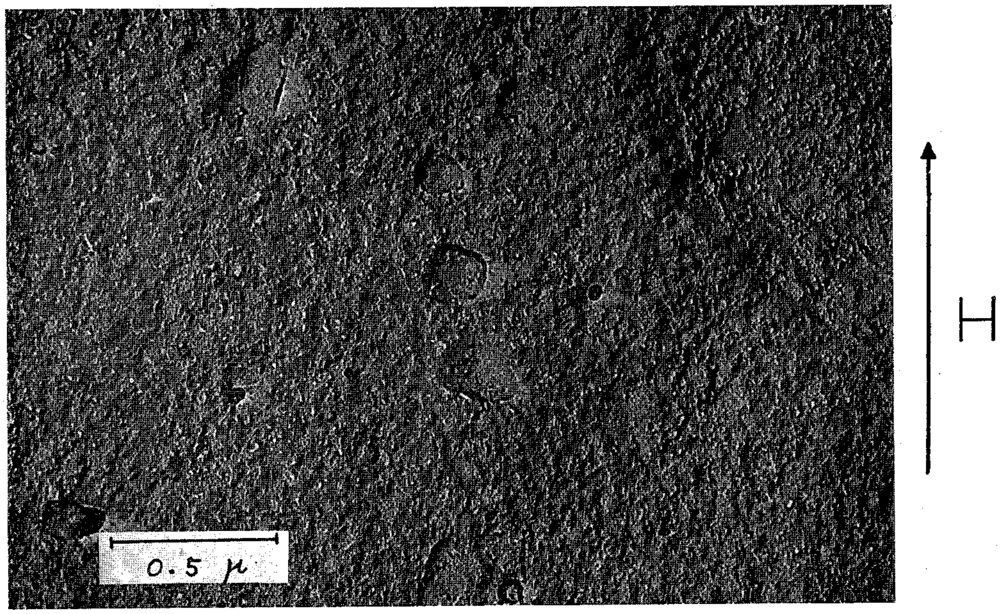

Photo. 2.

Electron micrograph showing the effect of aging with magnetic field. Aged 2.0 hrs. at 750°C with the field of 8000 Oe.