1. On a Method of Producing Single Crystal and the Discrimination of Crystal Grains of Silver Chloride

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I. Introduction

Single crystals of ionic compounds have hitherto been prepared by the crystallization from the solution or by the solidification from molten state. Since some ionic crystals, *e.g.* silver chloride, silver bromide, thallium chloride, *etc.*, have so remarkable plasticity(1) that they can be rolled, it is expected that a single crystal can be prepared by the so-called stress-annealing *i. e.* the recrystallization method which has been used mostly when metallic rods or plates composed of fine crystals are to be converted into single ones. In the present experiment, single crystals of silver chloride, whose diameters are about 2 cm., were obtained by applying this method on the rolled plate.

Macroscopic and microscopic discriminations of crystal grains are one of the most important and widely employed methods for studying metals and ionic crystals. The size, the shape and the orientation of crystals in a given specimen have been studied by means of microscope. The action of etching reagent is to dissolve the thin layer of worked metal produced by grinding or polishing and then to attack the underformed crystal beneath and, in this case, etching depends on the different orientations of the crystals. Etching reagents used for metals and alloys have often been reported, but for the discrimination of silver chloride crystal grains sodium thiosulphate solution alone has been generally used. In this experiment, another discrimination method was investigated for the purpose of microscopic and macroscopic examination.

Epitaxy growth of lithium chloride, sodium chloride, sodium iodide, potassium chloride, potassium bromide, potassium iodide and ammonium chloride showed a remarkable epitaxy growth, and it was found that the epitaxy prowth could also be applied for the discrimination of matrix silver chloride crystal grains.

II. Method and results of producing single crystals of silver chloride

In the previous paper[1], it was reported that some ionic crystals, silver

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chloride, for example, had remarkable plasticity and could be rolled to thin plate which has fibre structure and recrystallization phenomenon by annealing under the proper temperature, as in the case of metals and alloys. Therefore it is expected that besides the methods of crystallization from the solution or the solidification from the molten state, the method of the so-called stress-annealing *i. e.* recrystallization method can be applied to prepare the single crystals of silver chloride.

As the silver chloride which was prepared from silver nitrate and hydrochloric acid has more remarkable plasticity than those from silver nitrate and alkali chloride, original silver chloride specimen was prepared from silver nitrate and hydrochloric acid. The white powder of silver chloride thus obtained, was melted in the porcelain crucible at 510°C and was cast into another crucible and then it was rolled by the hand-driving two step roller (roll diameter being about 30 mm.) to the plate whose thickness is about 1.5 mm. corresponding to 60% reduction. From this plate, specimens whose dimensions are about 15 × 50 × 1.5 mm., were cut off and annealed about 2 hours at 350°C. Annealing in the above condition is thought to be enough for recrystallization to remove the stress which is caused during the rolling, since it has been already confirmed from the X-ray investigation[1] that silver chloride was recrystallized by the annealing at 100°C for 240 min. or at 150°C for 3 min.

To give the proper strain for the recrystallization, specimens were again rolled to 1.5, 3.2 and 8.3 reduction percentage, and then annealed for 2 hours at 250°, 300° and 380°C.

The increase in grain size with annealing temperature and with the decrease of reduction percentage can be seen qualitatively in microscope and results obtained are shown in Table 1, in which the value of numbers of grain per cm. shows the mean value of grain numbers counted in two directions which are vertical each other.

Table 1.

Annealing Temp. (°C)	250°		300°		380°	
Reduction %	Maximum Diameter of Grain (mm.)	Numbers of Grains per cm.	Maximum Diameter of Grain (mm.)	Numbers of Grains per cm.	Maximum Diameter of Grain (mm.)	Numbers of Grains per cm.
1.5	5	6.1	5.6	5.3	7.0	4.2
3.2	2.1	7.1	2.8	7.1	2.5	7.5
8.3	1.8	15.3	2.5	12.5	2.1	13.8

Since the fact that the smaller the reduction percentage, the larger the grain size becomes, it is desirable that the reduction percentage is as small as possible and the annealing temperature is as high as possible below the melting point, as in the case of metals and alloys.

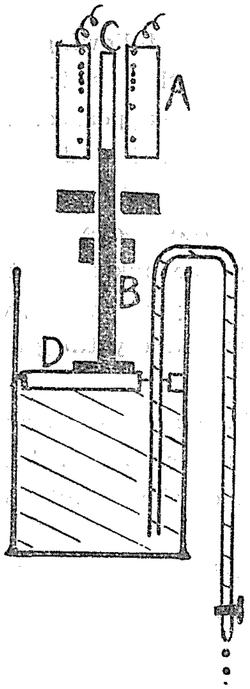

Fig. 1.

Further, annealing on a descending specimen was attempted. The apparatus, as shown diagrammatically in Fig. 1, was designed for the purpose of producing a long single crystal plate. In Fig. 1, A, which is fixed vertically, is the electric furnace consisting of a porcelain tube (20 cm. long and 4 cm. in diameter) and around it nichrome wire is wound in different density to keep proper temperature gradient. B is the supporter on which the specimen is fixed and this is attached to the cork plate D which is floating on the water in a water-vessel. Descending velocity of the specimen through the electric furnace is controlled by the cock of syphon which is connected with a water-vessel.

Among the several experients, the largest single crystal, whose diameter was about 2 cm., was obtained under the following condition: the highest temperature in the furnace 400°C, reduction percentage of rolling 1.5%, and descending velocity of specimens 1 cm. per hour, respectively.

III. Discrimination of crystal grains

Crystal grains thus obtained were examined by the Laue method using the heterogeneous X-rays emitted from copper-target. By the inspection with crystallographic globe and the stereographic analysis of X-ray Laue photograph (Fig. 2), obtained from each crytal grain, these crystal grains were confirmed to be a single crystal.

In order to discriminate the crystal grains macroscopically, several discrimination methods were tried and the results obtained were as follows:

(a) Macroscopical discrimination

When the specimen contains crystal grains which are large enough to be seen by the naked eye and are suitably etched, the grain size and shape are readily observed. Sodium thiosulphate solution has hitherto been used as a etching reagent of silver chloride, but this method is not always successful to discriminate grain and moreover by this method, the etching must be deep enough to form the difference of each etched grain surface to make visible to the naked eye. But silver depositing method on silver chloride specimen from ammoniacal silver nitrate solution by the so-called silver-mirror reactions is very suitable and simple for the macroscopical examinations of crystal grains.

Ammoniacal silver nitrate solution was prepared by the following way: 8 g. of silver nitrate was dissolved in 100 cc. water, and then added concentrated ammonium hydroxide solution until precipitation disappeared. After silver chloride specimen was dipped into the solution, a few drops of formaldehyde were added, and then a silver was deposited on the specimen within few minutes. By taking out the specimen from the above solution and by washing with water, it was observed clearly by the naked eye that the lustre of silver deposited on the surface of different crystal grains, wer distinguished apparently, and thus we could discriminate the crystal grains, as shown in Fig. 3.

As lustre of silver deposited on uneven surface of the same crystal grain could not be distinguished, it was supposed that the differences of lustre did not depend on the uneveness of crystal surface, but on the so-called epitaxy of silver on matrix silver chloride.

Another strong point of this silver depositing method is that the deposited silver can be easily removed by dissolving in nitric acid without damaging the specimen.

(b) Microscopical discrimination

One of the other ways to discriminate the grain more precisely is to produce the etching figure on the grain surface. This method is very convenient for the determination of crystal plane indices and for the detection of slip band as well as the deformation band. In this investigation, among many etching reagents which were attempted for the microscopical discrimination of silver chloride, the following method was most suitable for this purpose: after dipping the specimen in sodium thiosulphate solution (200 g. sodium thiosuldhate/l.H_2O), and washing with distilled water, the specimens were treated with saturated sodium chloride solution at about 70°C for 10 minutes. As illustrated in Figs. 4, 5 and 6, the etching figure can be observed clearly.

In this case hydrochloric acid (12 *N*) can be used instead of saturated sodium chloride solution, but the results obtained are inferior to the former.

IV. Discrimination of grain by the epitaxy growth

In relation to the phenomenon from the crystallization of solid, *i.e.*

solidification after melting, to the remarkable efficiency of silver iodide in promoting the nucleation of snow, numerous examples of epitaxy growth of one crystal have been reported.

In searching for epitaxy growth, Solat and Menzins[2] observed that such growth occurred only when the lattice dimensions were commensurate within about a few percent. Royer[3] considered that similarity of interatomic binding of partners favoured such growth. That this view requires modification concerning the interatomic binding and misfit of lattice dimensions between both crystals, has been indicated in recent works: G. W. Johnson[4] found the epitaxy growth of ionic crystal on metals and the author[5] found this phemenon of silver on mica.

As it is expected that epitaxy growth can be applied for the discrimination of grain, alkali halides and ammonium chloride which have also ionic binding, were attempted in relation to the matrix silver chloride specimen. All observations of the orientation of crystal were made with an optical microscope. The solution of the above compound was applied by the dropper to the surface of specimen which was placed on the glass plate and was heated by the gas-burner under the glass plate. In this procedure, it is important that the heating must be made slowly and be stopped before the perfect drying so as to prevent epitaxy crystal from bursting.

When iodide solution was applied, yellow film which was supposed to be silver iodide produced on the matrix, and when lithium chloride was applied, as this crystal was somewhat deliquescency, to observe with optical microscope was very difficult.

Among the results obtained, shown in Table 2, the epitaxy growth of potassium chloride and bromide occuried easily as illustrated in Fig. 7 and 8. and each grown crystals lie arranged in their corresponding direction in parallel each other.

Table 2.

	Epitaxy Crystal					Matrix Crystal
	NH_4Cl	KBr	KCl	LiCl	NaCl	AgCl
Type of Crystal Lattice	CsCl	NaCl	NaCl	NaCl	NaCl	NaCl
Difference of Ion Distance (Å)	0.57	0.52	0.37	0.20	0.04	~
Ratio of Ion Radius	1.22	1.46	1.36	3.02	1.90	1.44
Epitaxy Growth	easy	easy	easy	difficult	difficult	~

Ammonium chloride has phase transition and belongs to sodium chloride type above 184°C, and to cesium chloride type at room temperature, but in either case it belongs to cubic system and also showed the epitaxy growth as illustrated in Fig. 9.

By comparing the difference of ion distance which is equal to a half of lattice constant and the ratio of ion radius which are calculated from the value by L. Pauling, it is confirmed that the ratio of ion radius is an important factor as well as the difference of ion distance.

As described above, epitaxy growth can also be applied to discriminate the silver chloride crystal grains, but it is inferior to the method with sodium thiosulphate and sodium chloride solution.

V. Conclusion

From the present investigation, the author concludes as follows:

(1) The single crystals of silver chloride of ionic binding can be prepared by the so-called stess-annealing method which has been applid to the metals and alloys.

(2) Sodium thiosulphate solution has been generally used for the discrimination of silver chloride crystal grains. The silver-depositing method by the silver-mirror reaction is more suitable for macroscopical examination, and the treatment with sodium thiosulphate and sodium chloride solution is also suitable for the microscopical discrimination.

(3) Epitaxy growth can also be applied to the discrimination of grains and potassium chloride and bromide are desirable for this purpose and from the above facts the ratio of ion radius is thought to be an important factor for the epitaxy growth.

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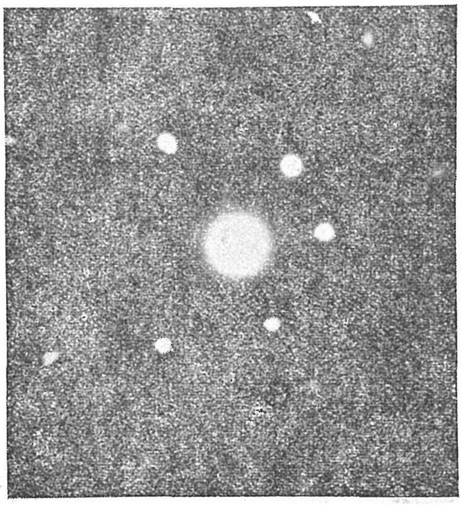

Fig. 2. Laue photograph of AgCl crystal.

Fig. 3. Silver coated AgCl crystal grains (×10).

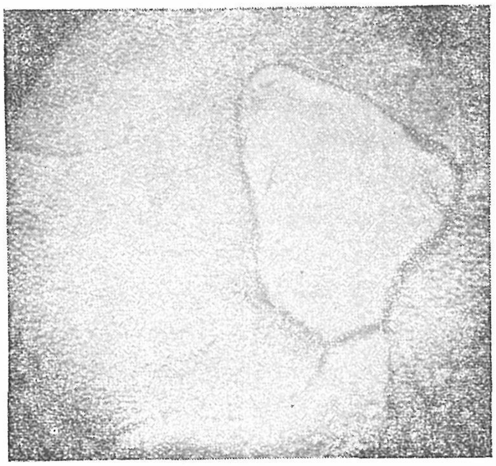

Fig. 4. Etching figure of AgCl crystal grains treated with sodium thiosulphate solution and NaCl solution (×50).

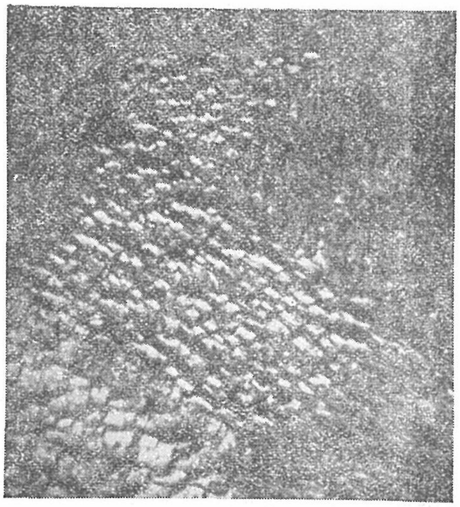

Fig. 5. Etching figure of AgCl crystal griains treated with sodium thiosulphate slution and NaCl (×150).

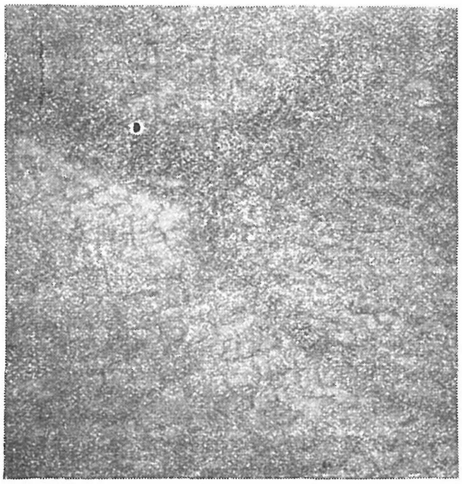

Fig. 6. Etching figure of AgCl crystal grains etched by sodium thiosulphate solution and NaCl solution (×150).

Fig. 7. Epitaxy growth of KCl on AgCl crystal grains (×7_).

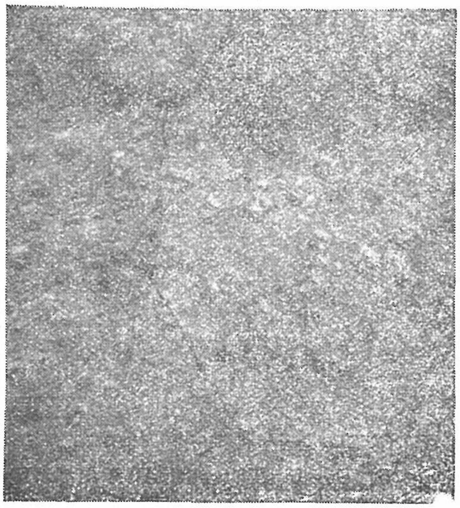

Fig. 8. Epitaxy growth of KBr on AgCl crystal grains (×70).

Fig. 9. Epitaxy growth of NH_4Cl on AgCl crystal grains (×70)