1. On the Orientation of Growth Texture of Metals deposited by Electrolytical Solutional Tension

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I. Introduction

When metals and alloys grow or plastically deformed, (under the stress of drawing, rolling, forging, compression, tension, *etc.*), they often have fibre structure which microcrystal grains orient to special direction.

The cases which fibre textures are brought out by growing are as follows:

(A) Growth texture from solid to solid, *i.e.* recrystallizatton structure.

(B) Growth texture from liquid to solid, *i.e.* cast structure.

(C) Growth texture from gas to solid, *i.e.* evaporating and spattering structures.

(D) Growth texture from solution to solid:

(a) Deposited by electrolysis.

(b) Desosited by chemical reaction.

(c) Deposited by electrolytical solutional tension.

Among the above cases (A), (B), (C) and (D)-(a) have been reported by H. Hirata,[1] O. Rüdiger[2], G. Finch[3], W. Burgers[4], *etc.*, (D)-(b) have been reported by one of the authors that silver deposited from ammoniacal silver nitrate solution on mica cleavage (001) plane have fibre structure whose axis was <110>, but silver from the same solution as above deposited on calcite and Iceland spar cleavage $(01\bar{1}1)$, rock crystal surface m $(10\bar{1}0)$ r $(10\bar{1}\bar{1})$ z $(01\bar{1}\bar{1})$ and glass surface had not preferred orientation and was consisted of random congregations of micro crystals, and also copper deposited from Fehling's solution on mica, calcite, Iceland spar, rock crystal and glass surface had not oriented structure.

But on (D)-(c), that is, growth texture of metals deposited by the difference of electrolytical solutional tension have not yet been reported except for silver[6], copper and lead[7].

In this investigation copper, lead, iron, nickel, cobalt, zinc, cadmium, thallium, arsenic, bismuth and tin have been studied by X-ray Laue method.

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II. Experiment

When these grown crystals deposited from the solution by electrolytical solutional tension are used as specimens, perpendicular to primary X-ray beam which emitted from copper or cobalt anti-cathode, the diffraction rings of some speimens are consisted of concentric uniformly intensive rings which suggest no preferred orientation, but the diffraction rings of the other specimens are very intensive in localized parts as though crystal grains are contributing for reflexion effects in certain directions, and it can be realized that these texture have preferred orientaion.

The analyis of these orientation can be performed by using Yoshida's crystallographic globe and by comparing the X-ray photograph with theoretical figures which are obtained by calculation with the formula

$$\cos\delta=(\cos\alpha-\cos\beta\cdot\sin\theta)/\sin\beta\cdot\cos\theta,$$

where θ is the angle of incidence, α is the angle between the normal to the set of reflecting planes and the fibre axis, δ is the angle measured on the film between radius drawn through a particular intensity maximum and the vertical line, and β is the angle between the fibre axis and the direction of primary X-ray beam.

Copper: Metallic copper deposited from 0.5 N and saturated cupric sulphate solution by introducing a small piece of zinc grows in the form of warty process and crust-like copper.

When distilled water was employed as solvent, crust-like copper is apt to grow, but cupric sulphate solution prepared by water containing a small quantity of sodium sulphate or zinc sulphate have a tendency to deposit warty process copper.

As illustrated in Fig. 1, X-ray photograph of these warty processes shows that specimen has fibre structure, from the fact that localized intensive maxima exist in Debye rings diffracted by the characteristic X-ray of copper anti-cathode.

Comparing the above photograph with theoretical figure, and using Yoshida's crystallographic globe, fibre axis is determined to be <110>.

Regarding to copper deposited from electrolytical solutional tension, it was reported that the growth structure had not preferred orientation and was consisted of as random congregation of micro crystal grains as to the crystal direction.

In this investigation warty process copper has fibre structure as described above, but the X-ray photograph of crust-like copper deposited on zinc is consisted of uniformly intensive Debye rings which indicate that these

specimens are consisted of an irregular congregation of micro crystals of $10^{-2}\sim10^{-3}$ cm. in diameter.

Certain reddish-black colour materials which were deposited on the surface of zinc together with metallic copper, were determined to be Cu_2S by means of the powder method.

Lead: Metallic lead deposited from saturated solution of sugar of lead by introducing a small piece of zinc grow in the form of scale-like crystal, and X-ray photographs, as illustrated in Fig. 2, of these specimens show the localized intensive diffraction rings which indicated that these specimens have fibre structure whose axis is <110>.

It was reported that the growth texture deposited from lead nitrate solution also had fibre structure whose axis was <110>[7], and the fibre axis was the same <110>[1], in the case of lead deposited by electrolysis from the solution of lead nitrate or sugar of lead.

Gold: Metallic gold film deposits on the surface of zinc introduced in the solution which is prepared by dissolving 0.3 g. chlorauric acid in 100 cc. water and contains tri-valent auric ion.

In this case, warty process or scale-like gold does not deposit on the surface of zinc.

X-ray diffraction rings (111) and (200) of this gold film are uniformly intensive and indicate that the specimen has not preferred orientation.

As to gold deposited by electrolysis, it was reported by H. Hirata[1] that growth structure had not preferred orientation, while axis of growth structure was <110> by G. Finch[3].

Iron: (1) Metallic iron deposited from the solution which contains ferrous ion.

Both metallic iron deposited from 0.5 *N* solution of ferrous sulphate and from 0.3 *N* solution of Mohr's salt by introducing a small piece of magnesium, grow in the form of film-like crysal. By investigating these specimens by X-ray Laue method using cobalt anti-cathode, it is indicated that growth texture of these iron films has not fibre structure.

As it had been reported that the growth structure of iron by electrolysis deposited from the solution of Mohr's salt had fibre structure whose axis was <111>[10] and iron from 50 percent ferrous chloride solution to which a small quantity of calcium chloride was added, had fibre structure whose axis was <112>[8], invetigation has been carried out with the same solution as above introducing a small piece of magnesium, but deposited iron film has not preferred orientation, and is consisted of an irregular congregation of micro crystal grains of $10^{-3}\sim10^{-4}$ cm. in diameter.

(2) Metallic iron deposits from the solution which contain ferric

ion.

Metallic iron deposited from ferric chloride solution has not also preferred orientation.

Cobalt: Metallic cobalt deposits from 0.5 *N* solution of cobaltous chloride on the surface of magnesium immersed into the solution. This cobalt film has not fibre structure as in the case of iron. Its diffraction rings by the chracteristic X-ray emitted by cobalt anti-cathode are uniformly intensive, while the deposited structure of cobalt by electrolysis was determined to be <110> by G. Finch[3].

Nickel: Metallic nickel deposits from 0.5 *N* solution of nickel sulphate on the surface of magnesium. Its diffraction rings (111), (200) are uniformly intensive and the specimens have no preferred orientation as is in the case of iron.

Arsenic: Arsenic deposits on the surface of tin immerged in arsenious chloride solution which is prepared by dissolving arsenious anhydride in hydrochloric acid.

X-ray diffraction rings of this deposited arsenic are uniformly intensive and the specimen is consisted of random congregates of micro crystal grains of the diameter about 10^{-4} cm.

Bismuth: Metallic bismuth deposited on the surface of tin immerged into 0.5 *N* bismuth nitrate solution have not preferred orientation and is consisted of random aggregates of micro crystal grains as in the case of arsnic.

On the other hand it was reported that the deposited bismuth had fibre structure: its axis was <211> by H. Hirata[1] or <100> by G. Finch[3].

Cadium: Cadium deposited from 0.5 *N* cadmium nitrate solution on the surface of magnesium or zinc also have not fibre structure. A. Rubio[11] determined that the axis of growth texture of cadmium deposited by electrolysis is $<11\bar{2}>$.

Zinc: Metallic zinc deposited after about a week from 0.5 *N* zinc chloride solution by introducing a small piece of magnesium grow in the form of scale-like crystal. When this scale-crystal is used as a specimen perpendicular to primery X-ray beam, the intensive maxima take part in the appropriating diffraction rings reflected by characteristic X-ray as illustrated in Figs. 3~4.

Diffraction pattern of tilting specimen at angle 45 degree to primary X-ray beam, as illustrated in Fig. 5, also is consisted of localized intensity maxima.

By comparing these diffraction patterns with each theoretical figure and by inspection using crystallographic globe, it can be determined that these

scale-like zinc have fibre structure whose axis is <100>.

It has been reported that the fibre axis of zinc deposited by electrolysis was also <100>.[1),3)]

Thallium: metallic thallium deposited from 0.3 *N* solution of thallium nitrate by introducing a small piece of zinc or manganese grows in the form of needle-like crystal.

X-ray photograph indicates that these needle-like crystals have fibre structure whose axis is <001>. Diffraction pattern of tilting specimens at anlge 45 and 50 degree to primary X-ray beam, as illustrated in Figs. 6~7, fit each theoretical figure of <001> axis and also fit <001> orientation using crystallographic globe.

Thallium deposited from 0.03 *N* thallium nitrate is needle-like crystal, but as the Laue spots of this specimen are arranged on the ellipses, this needle-like crystal may be thought to be a single crystal.

Growth texture of thallium by electrolysis has not yet been determined.

Tin: (1) metallic tin deposited from stannous ion.

Metallic tin deposited from solution containing 0.5 *N* stannous chloride grows in the form of needle-like crystals which have fibre structure whose axis is <101>, as illustrated in Fig. 8. As to the growth structure of tin by electrolysis, H. Hirata reported that growth structure had also <101> fibre axis.

(2) Metallic tin deposited from stannic ion.

Metallic tin deposited from the 0.5~0.1 *N* stannic chloride solution grows in the form of comparatively thick plate-like crystal.

As illustrated in Figs. 9~12, the higher the concentration of thallium nitrate solution becomes, the more the Laue spots of specimen extend, and show the asterisms, but the more dilute the solution becomes, the more corresponing Laue spots converge, and asterisms disappear. This fact probably indicates that, as deposition from the solution of high concentration quickly proceeds, the lattice planes become somewhat irregular, but deposition from dilute solution slowly proceeds and then lattice planes become regular.

III. Conclusion

From the present investigation, the authors have obtained the following results:

(1) The growth textures of iron, nickel, cobalt, cadmium, arsenic and bisumuth are consisted of random congregation of micro crystal grains and have not preferred orientaion.

(2) Growth texture of some metals have some fibre structurs whose axis

is <110> for copper and lead, <101> for tin, <001> for thallium and <100> for zinc.

(3) In regards to valency, both iron deposited from ferrous ion and from ferric ion have not preferred orientation.

Tin deposited from stannous ion has fibre structure but tin deposited from stannic ion has a tendendency to grow to be a single crystal.

(4) In the case of growing to a single crystal, it is desirable that the concentration of solution is dilute.

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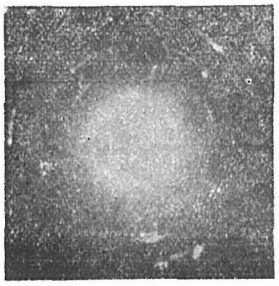


Fig. 1.

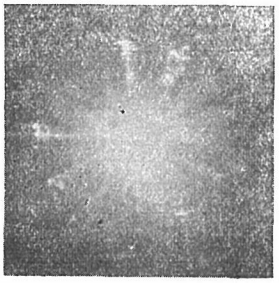


Fig. 2.

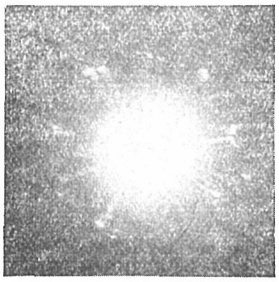
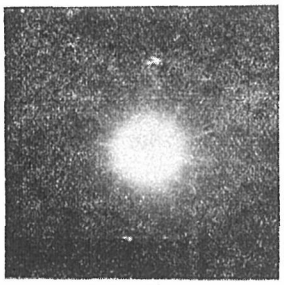


Fig. 3.



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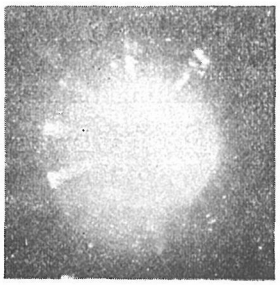

Fig. 5.

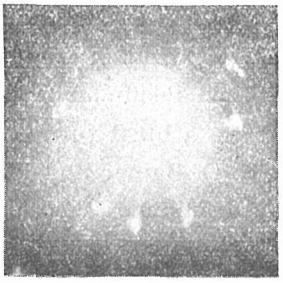

Fig. 6.

Fig. 7.

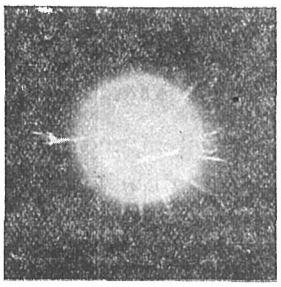

Fig. 8.

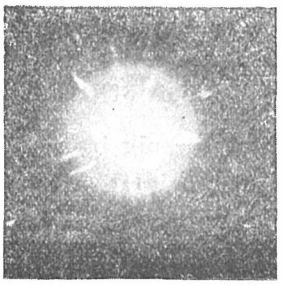

Fig. 9.

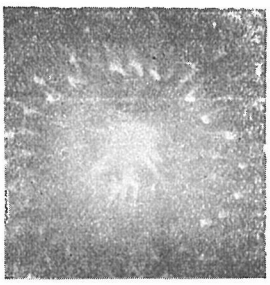

Fig. 10.

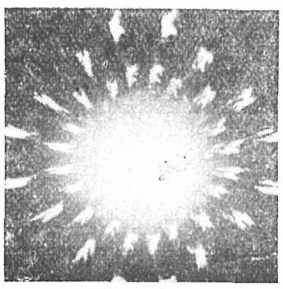

Fig. 11.

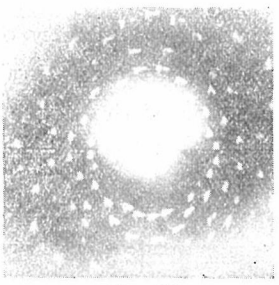

Fig. 12.