[CONTRIBUTION FROM THE DEVELOPMENT LABORATORIES OF THE HAWTHORNE WORKS, WESTERN ELECTRIC COMPANY, INCORPORATED]

GRAIN GROWTH IN LEAD CONTAINING ONE PER CENT. OF ANTIMONY

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Introduction

The importance of grain size and its influence on various physical properties of metals have long been recognized. The mechanism of grain growth in metals and methods of controlling it have been the subject of a great deal of investigation in recent years. In our study of the 99% lead–1% antimony alloy as used in the manufacture of cable sheath, we found it necessary to investigate, rather carefully, the relations of time, temperature and amount of deformation to grain size. This alloy lends itself admirably to a study of this kind, as it is a homogeneous solid solution,[1] grain growth proceeds at relatively low temperatures and the alloy exhibits no transformations in the temperature range studied.

A discussion of the mechanism of grain growth as indicated by these results is given.

Experimental Part

The alloy was made from Doe Run Super-refined metal containing 99.999% lead, and the highest grade of Chinese antimony, and cast into cylindrical slugs 9 mm. diam. × 25 mm. high. The slugs were deformed by compressing them longitudinally in a smooth-jawed vise to a definite length. While this method of straining takes no account of the amount of energy applied, it is one which can be easily and accurately duplicated on soft metals. The amount of deformation was expressed in the percentage reduction in length.

The slugs were immersed in a thermostatic bath for the required time, removed and quenched in carbon tetrachloride. The most suitable material for the annealing bath was found to be "Crisco," a partly hydrogenated vegetable oil sold by the Proctor and Gamble Company. This material can be heated to 250°, for a long time, with only slight decomposition. After annealing, the samples were polished, etched, photographed and the crystals measured.

The most satisfactory method of preparing the samples for photographing was found to be the following which had been developed in the laboratories of this Company. The samples were flattened with a coarse file, smoothed with a fine file and polished on a cloth-covered wheel using magnesia as a polishing agent. The best etching liquid found was a mixture of three parts of glacial acetic acid and one part of 9% hydrogen

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[1] R. S. Dean, THIS JOURNAL, 45, 1683 (1923).

peroxide. After etching, the samples were cleaned in concd. nitric acid. While this etching liquid requires from 10 to 30 minutes to develop a good structure, any number of samples can be treated at once, so that the time consumed is not excessive. This method gives uniformly good results.

The majority of the samples were photographed at 100 diameters, although in some cases the crystals were so large that it was necessary to use a lower magnification. The grain size was measured by the method described by Jeffries. A circle 76 mm. (3 inches) in diameter was drawn on the photograph. The number of grains entirely within this circle plus one-half the number of grains partly within, gave us the number of grains in the area of the circle. The area of the circle in square millimeters divided by the number of grains and by the square of the magnification reduced the results to average grain area in square millimeters. The data presented here were obtained from the examination of over 200 samples. Nearly all points on the curves are the averages of values obtained from at least two samples.

The factors which affect grain growth in a metal of this kind are (*a*) composition, (*b*) amount of deformation, (*c*) temperature of annealing, (*d*) time of annealing, and (*e*) history previous to deformation. We have purposely avoided, as far as possible, gradients of any kind. Undoubtedly strain gradients are present, but we have made every effort to keep them uniform in all samples. The composition was maintained constant throughout, as was the previous history, all samples being chill cast in a steel mold. The variables which we are concerned with are, then, temperature of annealing, time of annealing and amount of deformation.

Ultimate Grain Size

Several investigators[2,3] have shown that the ultimate grain size is a function of temperature, that is, at any constant temperature there is a maximum average grain size which depends on the temperature. We have determined the values of the ultimate grain size at various temperatures from 100°. They are shown in Table I for 36% deformation.

Table I

Values for Ultimate Grain Size at Various Temperatures

Temp. °C.	Ultimate grain size		
		Volume, cu. mm. × 10^6	
	Area, sq. mm. × 10^4	Obs.	Calcd.
100	59	453	1,180
150	325	5,860	5,250
200	650	16,500	16,300
250	1188	40,950	40,800

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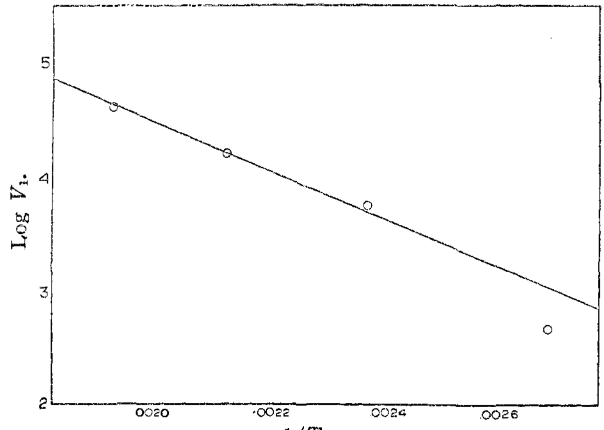
[2] Czochralski, "Grundprinzipien der Technologischen Kornverfeinerung," Forschungsarbeiten auf dem Gebiete des Ingenieurswesens, August, 1919.

[3] Rassow and Velde, *Z. Metallkunde*, **12**, 369 (1920).

In calculating the volumes we have assumed that $A^{3/2} = V$, where A is the area and V the volume. This assumption seems amply justified by the appearance of the samples, which show no directional orientation.



1/T.

Fig. 1.

In Fig. 1, the logarithm of the grain volume is plotted against the inverse of the absolute temperature. From this curve it is evident that the volume is an exponential function of the temperature and may be expressed by $V = Be^{(-A/T)}$, A and B being constants. By using this equation in the form $\log V = C-(D/T)$, and the values $C = 8.37$ and $D = 1970$, we get results which agree with the observed values as shown above.

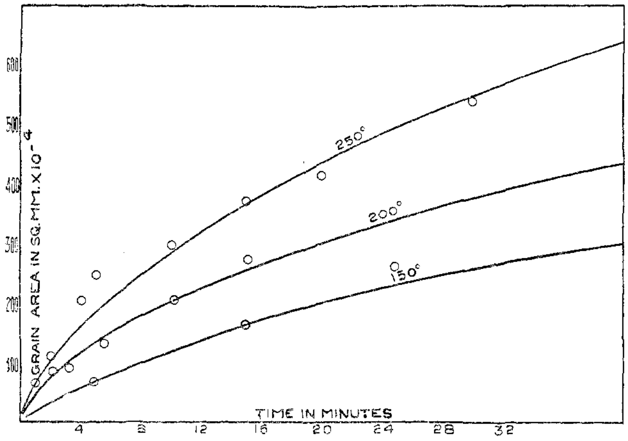


Fig. 2.

Rate of Crystal Growth at Constant Temperature

In order to fix the relation of time to grain growth at constant temperature we selected 250° and 36% deformation as constant conditions and measured the grain size after various times of annealing, Fig. 2 shows the values obtained. From this curve, it is evident that the velocity of grain growth may be expressed by an equation of the form, $dx/dt = k\,(V-x)$, where V is the total amount of alloy available for crystal growth and x is the amount used up at the time, t. By integrating and evaluating the integration constant we obtain $k = \frac{1}{t} \log \frac{V}{V-x}$, where k is the velocity constant of crystal growth. The value of V is the equilibrium volume discussed above, 40,950 × 10^6 cu. mm. for 250°. The values of k, from the above equation, are given in Table II.

TABLE II

VALUES OF k

t Min.	Grain area in sq. mm. × 10^4	Grain vol. in cu. mm. × 10^6	k
0.5	42	272	0.0052
1.0	68	561	.0060
2.0	113	1,202	.0064
4.0	207	2,980	.0082
5.0	253	4,025	.0088
10.0	304	5,302	.0060
15.0	376	7,295	.0057
20.0	415	8,450	.0051
30.0	537	12,450	.0052
240.0	1188	40,950	...

Considering the inherent inaccuracies in grain size measurement, these values seem very satisfactory. The two values at 4 and 5 minutes are obviously out of line. The average value of k, neglecting these two points, is 0.0060. This represents the velocity of crystal growth at 250°. Fig. 3 shows some of the photomicrographs of these samples.

Similar experiments were made at 200° and 150°. The results are shown in Fig. 2 and the constants summarized below.

Temp., °C.	150	200	250
k	0.0100	0.0085	0.0060

Effect of Deformation

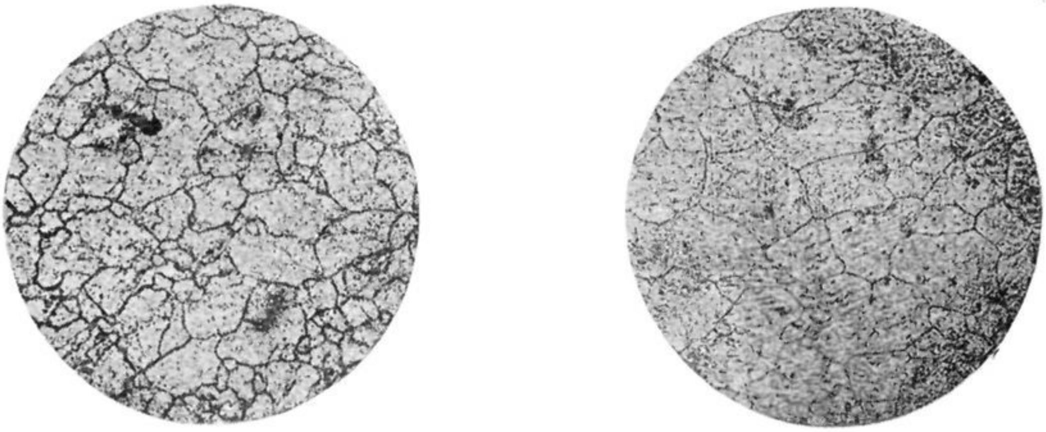
We have determined the effect of deformation on grain size by varying the reduction in length between the limits 20–65%, keeping all the other

TABLE III

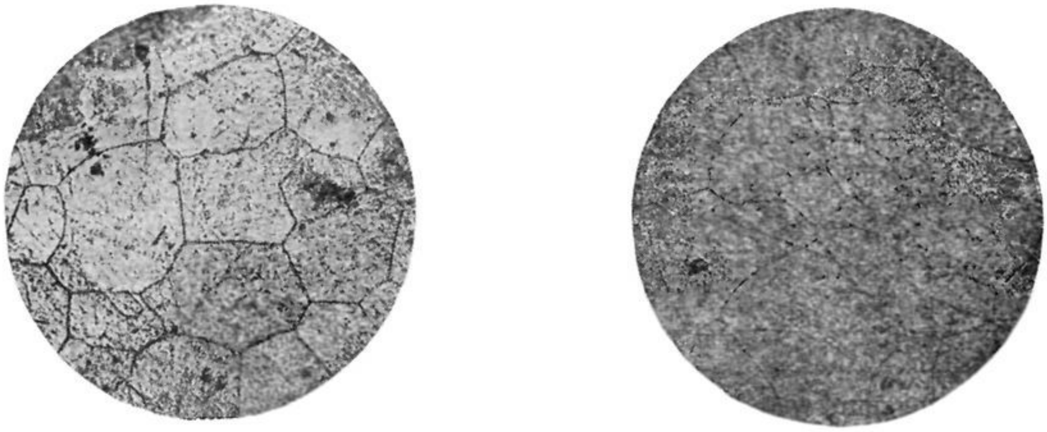
EFFECT OF DEFORMATION ON GRAIN SIZE

% Deformation	Grain area Sq. mm. × 10^4	Grain vol. cu. mm. × 10^6	$\frac{1}{\text{Grain vol.} \times 10^{-2}}$
20	900	27,000	0.370
30	495	11,000	0.910
40	343	6,350	1.575
54	260	4,190	2.388
65	218	3,220	3.106

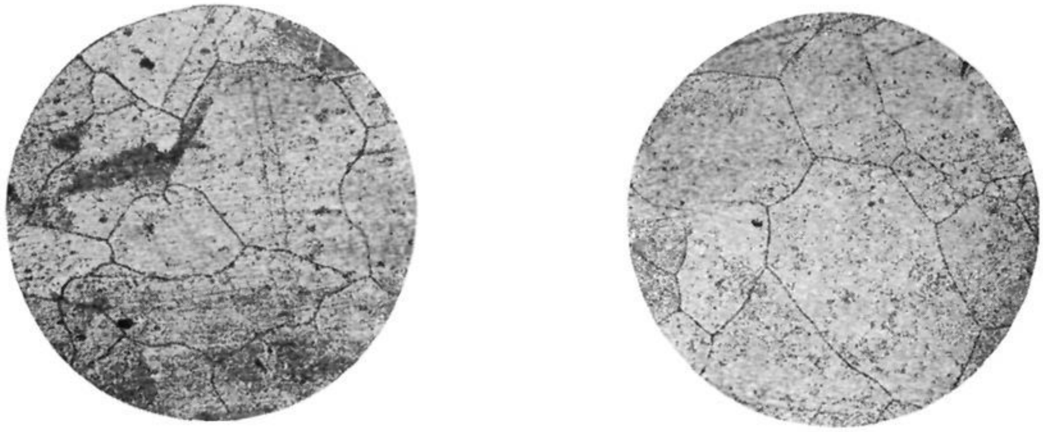
variables constant. Table III shows the values obtained from samples annealed at 200°, for two hours.



$^1/_2$ min. at 250° (× 100). 1 min. at 250° (× 100).



4 min. at 250° (× 100). 5 min. at 250° (× 100).



15 min. at 250° (× 100). 20 min. at 250° (× 100).

Fig. 3.

Since the effect of increased deformation is probably to increase the number of crystal nuclei, we have compared the deformation to the inverse of the grain volume (number of crystals per unit volume) in Fig. 4. It is evident from this curve that the number of grains per unit volume is a linear function of the reduction in length of the slug, or for this particular shape of slug, $N = KD + C$, where C is the minimum deformation which will allow grain growth at the temperature studied.

The photomicrographs of this series are shown in Fig. 5.

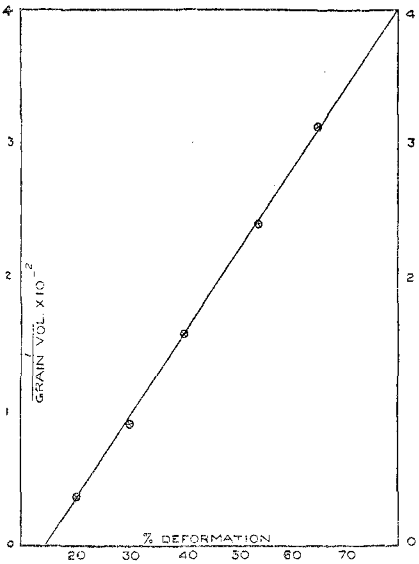


Fig. 4.

Theoretical Discussion

In a deformed crystal conglomerate the crystals are broken up by glide planes and the fragments oriented in a random manner. This has been clearly shown by Jeffries and Bain.[4] An X-ray reflection pattern of a single crystal showed no lines. By deforming this crystal, however, the entire spectrum was obtained indicating that the crystal planes after deformation were distributed in practically a random manner like those of a powder. (That this arrangement is, however, not entirely random but that the fragments tend to assume a definite orientation to the deforming force has been shown by Körber[5] and by Polanyi.[6])

Since the formation of these glide planes represents an expenditure of energy, it is reasonable to suppose that the atoms which are concerned in the formation of the glide plane are at a higher energy level than the atoms farther away. A deformed crystal conglomerate, on this assumption, represents a more or less random distribution of the energized atoms in the mass.

The mechanism by which recrystallization and crystal growth take place in this mass of unoriented crystal fragments is a current problem. Our experiments naturally give no direct evidence of this mechanism. We have found that whatever this process is, it has for the alloy studied four characteristics. It seems likely that these will be found to be of general application to crystal growth in deformed metals.

1. Crystal growth takes place with a velocity which may be expressed by the same equation as a monomolecular reaction, that is, the velocity at any instant is proportional to the final crystal volume less the mean crystal volume at that instant.

2. The velocity constant calculated in this way changes only slightly

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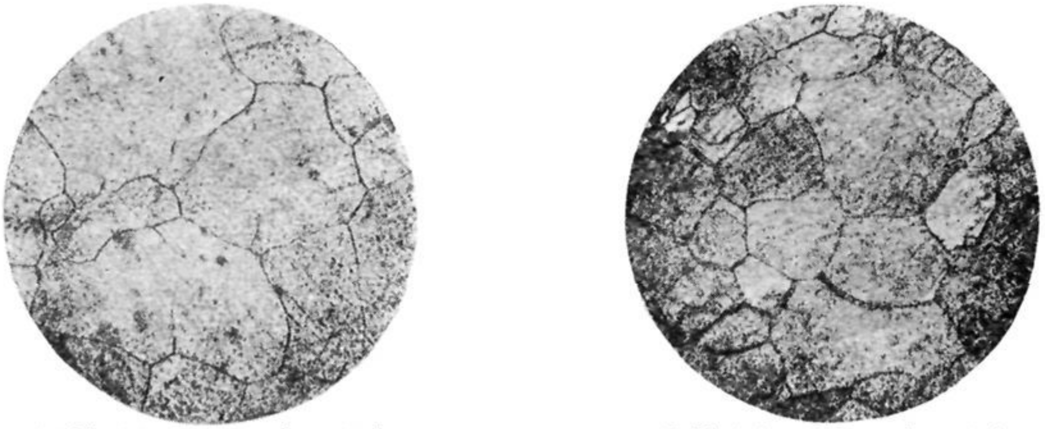
[4] Jeffries and Bain, *Chem. Met. Eng.*, 25, 775 (1921).

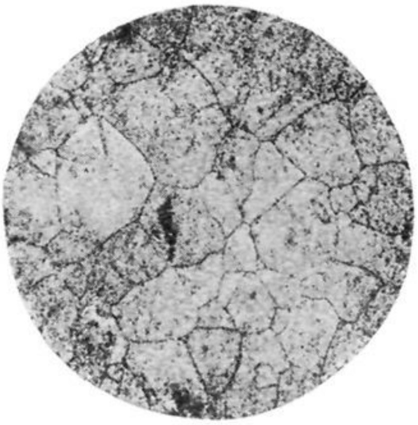
[5] Körber, *Stahl u. Eisen*, **42**, 365 (1922).

[6] Polanyi, *Z. Physik*, **17**, 42 (1923).

with the temperature, although the ultimate crystal volume changes greatly with the temperature.



20% deformation (× 100). 30% deformation (× 100).



40% deformation (× 100).

54% deformation (× 100). 65% deformation (× 100).

Fig. 5.

3. The relation found between ultimate grain volume and temperature is not inconsistent with the assumption that $V = Be^{(-A/T)}$, where V is the volume, T the absolute temperature and A and B are constants.
4. The final crystal volume is a linear function of the decrease in height of the slug.

The theories which have been proposed for grain growth do not in general lend themselves to calculations of the velocity of grain growth and its temperature function so that it is difficult to test their applicability. A discussion of the current theories is given by Fonda[7] who concludes that grain growth takes place by transfer of material across an "amorphous" phase from the small to the larger particles. It seems that if this theory were followed to its logical conclusion the recrystallization velocity should change much more rapidly with the temperature than we have found.[8]

Considering the theory of metal flow of Stark[9] which has been previously discussed by one of the present writers[10] we may arrive at certain relations. This theory considers a glide plane as formed by the separation of the atoms of the metal to such a distance that the free electrons of the metal become bonding electrons between the separating atoms, giving a sort of pseudo-molecular formation across the glide planes. The atoms so bound have of course additional energy, and when the temperature is raised to a point where there is sufficient amplitude of vibration of the atoms a rearrangement into the normal space lattice will take place.

The velocity with which this transformation will take place will depend on the frequency of vibration of the atoms which changes only slightly with the temperature.

Temperature Coefficient of Final Crystal Volume.—Since the crystal volume is proportional to the number of atoms which have changed to the normal lattice the final volume at any temperature will be proportional to the number capable of changing over at that temperature. Now, if we assume a Maxwellian distribution of the energy among the energized atoms, the number with energy above a certain critical amount E, at any absolute temperature T, is given by $\eta = Ne^{(-E/kT)}$, where N is the total number of molecules and A is a constant. Hence the final volume V at any temperature will be of the form $V = Be^{(-A/T)}$. Our experimental results are not inconsistent with this theory.

Effect of Degree of Deformation.—Finally, the number of centers around which grain growth takes place is apparently a function of the amount of deformation. As the deformation is increased, the number of centers increases and, therefore, the final volume at any temperature decreases. This increase in number of centers seems from our experimental work to be a linear function of the decrease in length of the slug.

Our thanks are due to Mr. E. F. Salchow for taking the very many photomicrographs used in this work and to Mr. G. S. Rutherford under whose general supervision this work was done.

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[7] Fonda, *Genl. Elec. Rev.*, **25**, 309 (1922).

[8] Tammann, *Wied. Ann.*, **62**, 292 (1897).

[9] Stark, *Physik. Z.*, **13**, 585 (1922).

[10] Dean, *Chem. Met. Eng.*, **26**, 965 (1922). Dean, "Theoretical Metallurgy," John Wiley and Sons, N. Y., **1924**, p. 53.

Summary

1. Crystal growth of an alloy of 99% of lead and 1% of antimony has been found to take place with a velocity which may be expressed by the same equation as a monomolecular reaction, that is the velocity at any instant is proportional to the ultimate volume less the mean crystal volume at that instant.

2. The velocity constant calculated in this way is only slightly affected by the temperature.

3. The ultimate or equilibrium volume is an exponential function of the temperature and may be expressed by an equation of the form $V = Be^{(-A/T)}$.

4. The ultimate crystal volume is a linear function of the decrease in height of a cylindrical slug.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE OXIDATION OF HYDRAZINE. II. THE EFFECT OF OXYGEN ON THE DECOMPOSITION OF HYDRAZINE. THE REACTIONS WITH FERRICYANIDE IN ALKALINE SOLUTION, AND DICHROMATE IN ACID SOLUTION

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The Effect of Oxygen on the Decomposition of Hydrazine

In the first paper[1] the following experimental data had been incidentally collected on the decomposition of hydrazine sulfate solutions at various acid or alkali concentrations.

TABLE I

THE DECOMPOSITION OF HYDRAZINE IN THE PRESENCE OF AIR

Expt.	Concn. of hydrazine M	Acidity or alkalinity of the solution	Time	Decomposed %
19, Table I	0.11	H^+ = about 0.1 M[2]	2 months	0
4, Table IV	.008	H^+ = about 10^{-7}	2 hours	0.9
11, Table IV	.015	H^+ = about 10^{-7}	48 hours	8.1
19, Table II	...	alkaline	10 minutes	2.0
p. 864	.05	OH^- = about 0.5	5 minutes	0.9
p. 864	.05	OH^- = about 0.5	16 hours	20.0

These solutions were all in contact with air, and the opinion was expressed that the presence of oxygen is responsible for the rapid "decomposition" of hydrazine in alkaline solutions.

[1] Bray and Cuy, THIS JOURNAL, **46**, 858 (1924).

[2] This solution of hydrazine sulfate (0.11 M) gave a green color with methyl violet, indicating that the concentration of H^+ is about 0.1 M. For more exact evidence that the hydrolysis of $N_2H_6^{++}$ into $N_2H_6OH^+$ (or $N_2H_5^+$) and H^+ is nearly complete, see Bredig, *Z. physik. Chem.*, **13**, 314 (1894), and Bach, *ibid.*, **9**, 250 (1892).