The Influence of the Occluded Gases on the Change of Density of Silver by Annealing

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Abstract

By annealing cold rolled pure silver bars successively at higher temperatures, density measurements and microphotographic examination were made at every stage of annealing. It was found with some specimens that by annealing at about 700°—800°C the decrease of density was enormous, and that in this case the occluded gases gushed out of the specimens by opening many small canals along the crystal boundaries during the annealing. The change of the density by the annealing at high temperatures was explained by the assumption that some gases are occluded in small cavities in the specimen, and that these gases expand in the cavities and escape by diffusion through the softened or molten crystal boundaries even when no trace of the small canals was detected.

Silver more than 99.95 % pure was used in this study. It was prepared for the experiment by rolling (to about 50 % reduction in thickness) cast silver bars into long bars, each cross section being 4 mm × 9 mm. Silver specimens cast in vacuum were also used, and these are indicated by the sign (V) in the following figures. When successive annealing for about 3 hours at different temperatures had been done on such a specimen, the density was measured, and the writer found that it generally assumed the typical variation form of A-B-C-D,[1] as is shown in Figs. 1 and 2. Next after subjecting the same specimen to a cold hammering or a cold rolling, the change of its density was measured. Thus have been brought to light[2] somewhat systematic connections between the changes of density and its mechanical treatments.

Now in order to find clearly how the changes of density above mentioned are connected with the internal crystal structure, microscopic photographs were taken of the specimen at various stages of the density curves.

In Fig. 1 the values of density for 4 different specimens (G), (H),

1. A. Igata: These Memoirs, **19**, 215 (1936).
2. A. Igata: These Memoirs, **20**, 35 (1937).

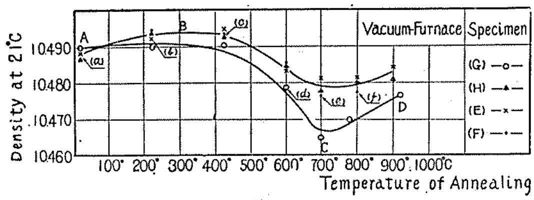


Fig. 1

(E) and (F) are plotted, and the micro-photographs at the stages (a), (b), (c), (d), (e) and (f) are shown in Figs. 1 a, 1b, 1c, 1d, 1e and 1f in Plate I. In this case the decrease of the density at the C state is not very great, and no peculiarity in the microphotographs is observed, except the general growth of the silver crystals with increase of the annealing temperature. Fig. 2 is obtained with two specimens (2) and (3) which were prepared by rolling the silver bars cast in vacuum. In this case the decrease of the density at the C state and its subsequent increase at the D state is very small, and no peculiarity in the microphotographs other than the general growth of the silver crystals with increase of the annealing temperature could be detected as in the case of Fig. 1. The writer has examined many other specimens, and in all cases when the diminution of density at the C state is slight no peculiar difference among the microphotographs at the corresponding stage of the specimens was perceived. But it happened with some speci-

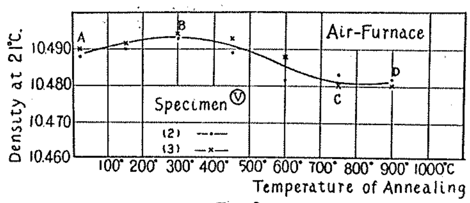


Fig. 2.

mens that the diminution of density at the C state is very great, as shown in Figs. 3 and 4. By taking microphotographs at the C state in this case it was found that many small holes are formed at the crystal boundaries, through which some gases seem to have gushed out from the inside of the specimen. Figs. 3d and 3e in Plate II are taken at the stages (3d) and (3e) in Fig. 3; and Fig. 4f and 4g in Plate II are taken at the stages (4f) and (4g) in Fig. 4, where the diminution of the density at the C state is enormous, and the holes at the crystal boundaries are much more remarkable.

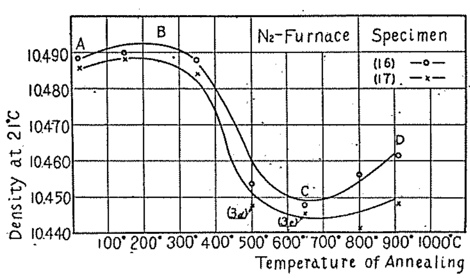


Fig. 3

The furnaces that were used in the present experiments were air-furnace, nitrogen-furnace and vacuum-furnace, and no remarkable difference was detected because of change of the furnace.

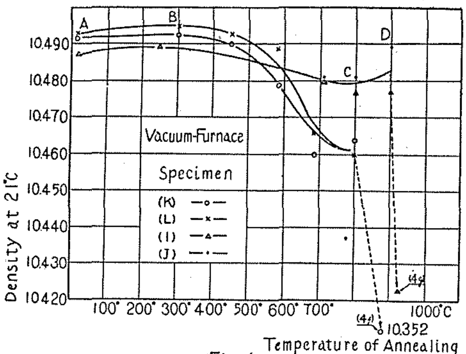


Fig. 4

Silver is said to have a property of absorbing oxygen at a high temperature in the course of refining metallurgy or casting, but it may be presumed that it goes even so far as to contain some other gases besides oxygen in some way of chemical combination, of absorption or of occlusion.

As is described before, violent expulsion of the occluded gases happens only at the crystal boundaries, and not through the crystal itself. This seems to show that a considerable amount of gas is accumulated and confined in narrow spaces of the crystal boundaries. If so, when such a specimen is heated to a temperature as high as 700° or 800°C, the metal will become very soft, especially at the crystal boundaries where it may even melt below the melting point as was pointed out by U. Yoshida and K. Koyanagi[1]; and the occluded gases, having being increased in its pressure to several times of its initial value, will gush out from the inside by opening many canals through the crystal boundaries. Since, judging by the aperture and the number of canals along the crystal boundaries, the amount of the occluded gases is estimated to be enormous, it is thought that a considerable amount of the gases must still be left in the specimen. enclosed in small cavities which are expanded when heated to a high temperature at the C state. The presence of the same circumstances can also be assumed in the case of the specimens with which no trace of the appearance of the small holes along the crystal boundaries at the C state is detected; and thus the decrease of the density at the C state seems to be caused, at least mainly, by the expansion of the small cavities containing occluded gases by being heated to a high temperature at the C state. The amount of decrease of the density depends thus upon the quantity of the occluded gases, and the former increases with the latter.

1. U. Yoshida and K. Koyanagi: These Memoirs, **18**, 9 (1635).

When the occluded gases are enormous in quantity, they cause a remarkable decrease of the density, and gush out violently by opening small canals along the crystal boundaries. On the contrary when the occluded gas is scanty in quantity, as in the case of the specimen obtained by vacuum casting, the decrease of the density at the C state is very small.

On further annealing the specimen at a temperature higher than that at the C state, the density of the specimen becomes generally greater than that at the C state and this state is denoted by the D state as is shown in Figs. 1, 2 and 3. According to the writer's view, the increase of the density at this state is due to the escape of the occluded gases in small cavities by diffusion through the softened or probably molten crystal boundaries, and to the subsequent partial filling up of the cavities by the softened or the molten metal at the crystal boundaries. As is seen in Fig. 2 and in Figs. 9 and 10 of the former report,[1] the increase of density from the state C to D is small when its decrease at the C state is small. Moreover when the specimen is cold rolled in proper degree after being subjected to the A-B-C-D annealing process, and then annealed again in the same way, the density at the C state in the second annealing process is much greater than that at the first C state and remains almost the same as that at the D state in the first annealing process, as is seen in Fig. 13 of the former report.[2] These facts seem to support the view described above that the recovery of the density at the D state is due to the escape of the occluded gases by diffusion through the crystal boundaries. In the cases of Figs. 3 and 4, where the quantity of occluded gases is supposed to be enormous and some has gushed out through the canals along the crystal boundaries, the gases still enclosed in the cavities will be of considerable amount; and the insufficient recovery of the density at the D state seems to have arisen from this fact together with the circumstance that the formation of many small canals at the C state makes the measured density smaller.

The change of density of cold rolled silver bar at the C and the D state of annealing is thus well explained qualitatively by the occlusion of some gases in the silver specimen. There will still be some other factors involved; and a clear understanding will, of course, be

1. A. Igata: These Memoirs, **19**, 215, (1936).
2. Ibid.

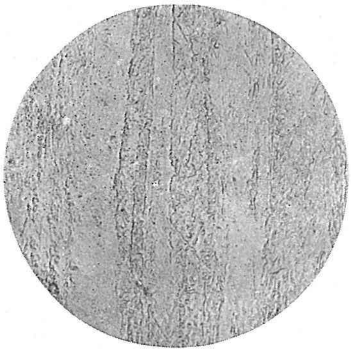
reached after a more exhaustive investigation on this subject; but now it has become evident that an enormous amount of gases is occluded in metals and that the mechanical and physical properties of metals are affected, at least to some extent, by the presence of occluded gases of such amount.

Lastly the writer has estimated the total volume of the small cavities filled with occluded gases by assuming that the decrease of density at the C state is entirely due to the expansion of such small cavities. By taking the true and net density of pure silver as 10.502 at temperature 17°C, and that at the C state as 10.475[1] at 17°C, where no bursting out of the occluded gases has occurred, the total volume of the cavities at the C state becomes about 0.25 % of the volume of silver. In the case of Fig. 4, where the bursting out of the occluded gases has occurred, the density at the C state is about 10.422 at 21°C; and we obtain the value of 0.74 % as the minimum value of the total volume of the cavities. These figures themselves are not remarkable; but when the occluded gases of the volume of this order are dispersed in very tiny cavities rather evenly throughout the metal or along the crystal boundaries, as will actually be the case, their injurious effect on the mechanical properties will be of no inconsiderable degree. As to the pressure of the gases enclosed in small cavities, we must consider it to be very high, because at a temperature as high as at the C state of annealing, the occluded gases burst out of the metal sometimes through the softened crystal boundaries.

In conclusion, the writer humbly expresses to Prof. U. Yoshida of the Kyoto Imperial University his hearty thanks for his kind guidance through all these experiments. Also he should not forget to express his deep gratitude to Prof. Hanemann at der Technische Hochschule in Berlin who has afforded him much assistance in his studies and experiments during his stay in Germany.

1. A. Igata: These Memoirs, **19**, 215 (1936)

Plate I.



500×

Fig. 1a

500×

Fig. 1b

500×

Fig. 1c

100×

Fig. 1d

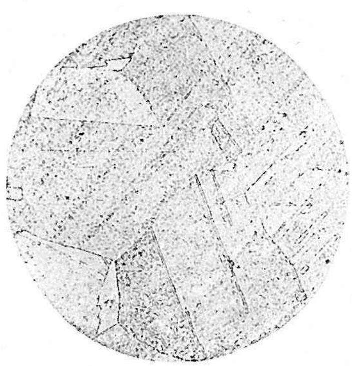


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Fig. 1e

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Fig. 1f

Plate II.

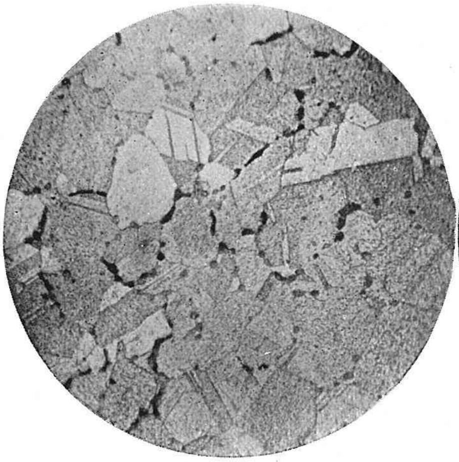

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Fig. 3e

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Fig. 3d

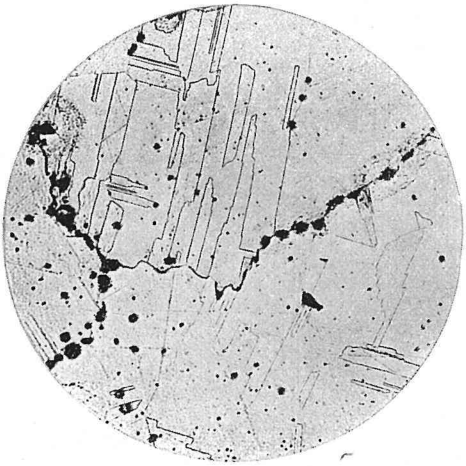

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Fig. 4f

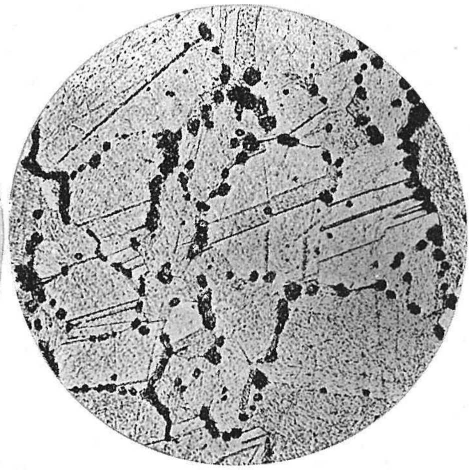

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Fig. 4g