Changes in the Density of Silver with Annealing and Cold Working

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Abstract

With pure silver bar the changes of its density with the heat treatment and with the cold working were measured, and their relations were made clear in a systematic manner. The presence of minute cavities in the metal is discussed on the basis of the experiments. Finally, the process of obtaining the criterion value of the density of silver is proposed.

With respect to the density of metals and alloys several invetigations have been made in various ways. In the present experiment silver, more than 99.95% pure, was used as a specimen, and its density was measured after several annealings and cold rollings. The specimens which the writer examined were prepared by rolling (to about 50% reduction in thickness) cast silver bars, into long bars, the cross section of which was 4 mm × 10 mm. For annealing an electric resistance furnace was used, its temperature being measured by a thermo-junction. The porcelain pipe of the furnace which contained the specimens could be evacuated to a pressure lower than 0.1 mm Hg, or be filled with nitrogen or other gases of the same atmospheric pressure. The temperature of the furnace was raised to a given value in about 30 or 40 minutes, and was kept there for about 3 hours; then the specimens were left to cool in the furnace. A chemical balance was used for the density measurements. Before weighing in water, first the metal piece was sealed in a glass tube after the evacuation to a pressure lower than 0.1 mm. Hg., then the thin neck of the sealed glass tube and the glass tube itself were broken in the pure water previously boiled. This process was to get rid of the effect of the gas adhering to the surface of the test piece. In determining the density of the specimen necessary corrections due to the buoyancy of the air and the change of the densities of water and silver with temperature were always made. In the present experiment the values of the densities of all the specimens were recalculated to those at 17°C.

The changes of density of the specimens caused by successive annealings were seen to be represented by similar curves obtained by annealing in any furnace: air, nitrogen or vacuum, as seen in Figs. 1, 2, 3. In these curves we can see clearly that there is a maximum density at the annealing temperature of about 200°C–300°C, and a minimum density at about 600°C–800°C. In the following the writer will consider the significance of the parts, A, B, C, D in the above curves.

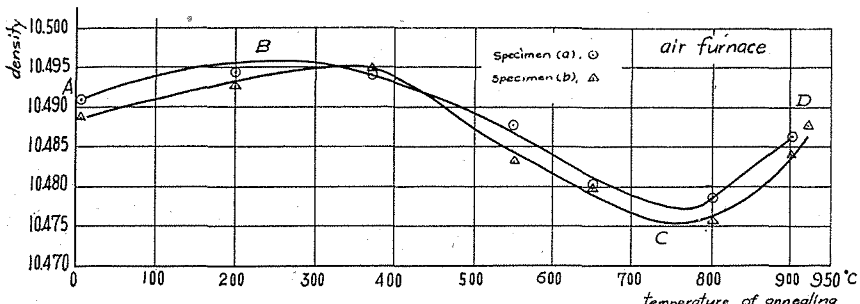

Fig. 1

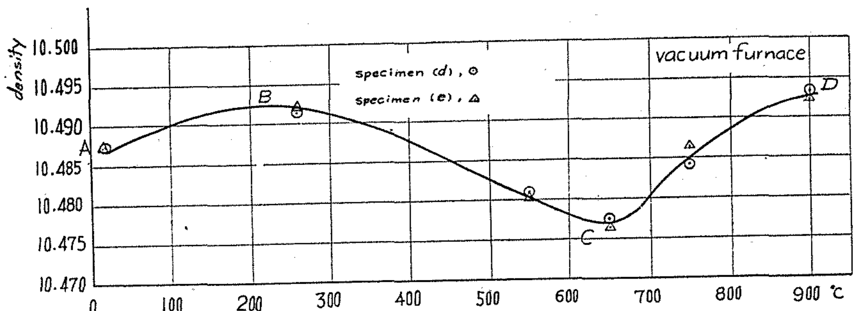

Fig. 2

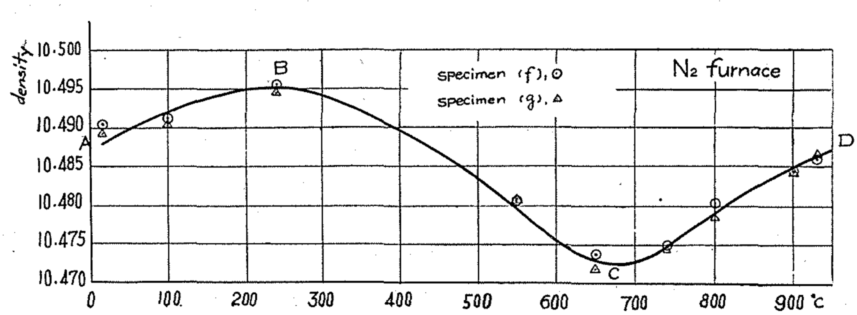

Fig. 3

It is natural that the density at the part A is different according to the previous history of the specimen such as casting, forging, cold working and heat treatment. The difference between the densities at the points A and B, as is seen in Figs. 1, 2, 3 and 10, is approximately of the order of $5/10^4$ of the density. This increase seems to be due to the recovery from the density decrease caused by the presence of the internal stress at the beginning. That this decrease is caused by the rolling to about 50%–70% reduction in thickness is shown in Fig. 4: that is, when the specimen in the B state is subjected to the rolling to 60%, its density decreases by $5/10^4$, and after the annealing at 210°C it increases again by the same amount.

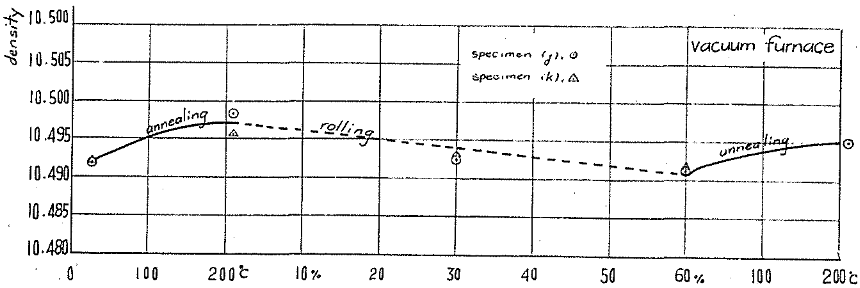

Fig. 4

When the degree of rolling increases more than a certain degree, the annealing temperature to recover the density becomes gradually higher. For the specimens rolled to about 80%–90%, the recovering temperature is about 600°C, as seen in Figs. 11, 12. For the less rolled specimen, the recovering temperature becomes lower as is seen in Fig. 10. It seems, therefore, that the greater the amount of cold working the more difficult it is to get rid of the internal stress completely by the annealing.

Next, the increase of the density between the states C and D is, according to the writer's view, due mostly to the vanishing of the minute cavities present in the metal at the C state, though a small part of the increase may be caused by the complete removal of the internal stress. Therefore, the decrease of the density between the states B and C is due mostly to the production of the minute cavities. The fact that the value of density returns almost to the value at the state B by annealing at 900°C or more seems to be in accord with the above view. As seen in Fig. 5, by the cold rolling to about 60% the density of the specimens (m) and (n), both at the state C initially,

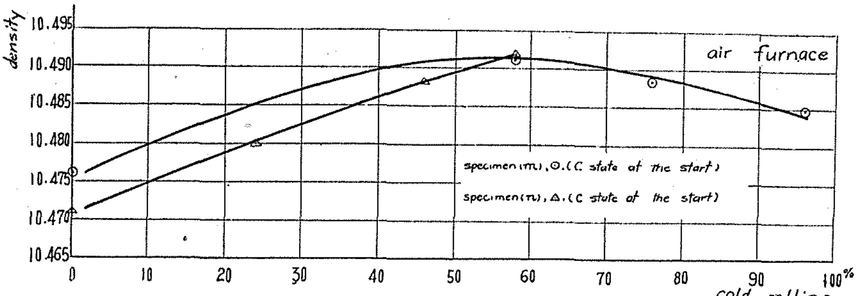

Fig. 5

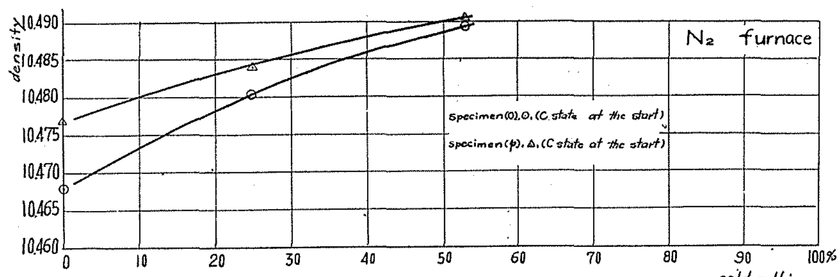

Fig. 6

approaches the B value, but does not coincide with that value. This seems to be caused by a small decrease of the density due to the increased internal stress produced by the cold rolling; and the value of the density thus obtained nearly coincides with the value at the state A. Similarly, as is seen in Fig. 6, the densities of the specimens (o) and (p) approach and come to the value of the state A by the process of successive cold rollings. From these facts it seems rather evident that nearly all the minute cavities can be vanished by cold rolling to about 60%. This fact can also be ascertained by the auxiliary experiments mentioned later. Still more, the necessity of about 60% cold rolling to vanish almost all the minute cavities seems to be inferable from Figs. 7 and 8.

Next let us consider again the state D. According to U. Yoshida and K. Koyanagi,[1] metal crystals having some distortion melt at their boundaries even at the temperatures below the melting point of the metal. This was confirmed by the writer from the fact that when two silver plates held tightly together were annealed at about 700°C for a long time they adhered together so strongly that it was a little

1. These Memoirs, **18** (1935).

difficult to separate them with the hands. When the minute cavities possessed by the specimens at the state C were heated at a higher temperature, tbey were filled gradually with the melted metal; and thus when the specimen cooled and contracted as a whole, its density became greater than in the state C. Therefore the rise between the points C and D in an ideal case is to recover or to exceed the value at the state B, as is seen in the specimens (d) and (e) in Fig. 2, which were annealed in a vacuum furnace.

When the specimens devoid of the cavities at the D state are subjected to successive cold rollings, they show successive decreases

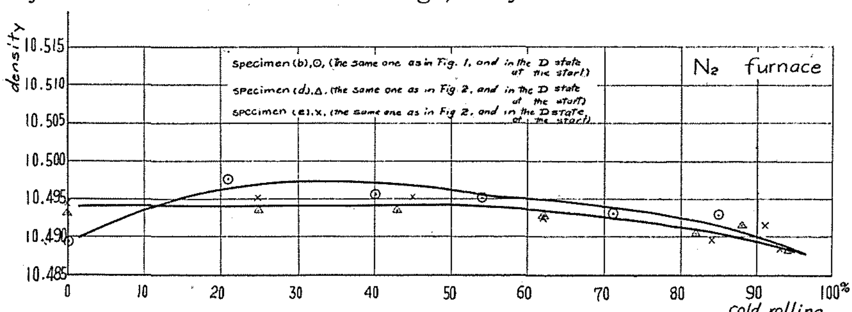

Fig. 7

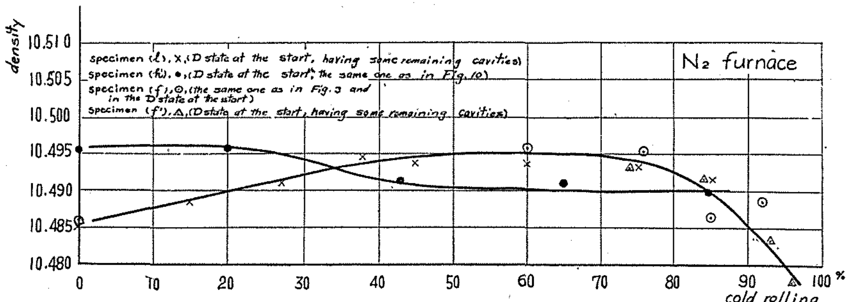

Fig. 8

of density as is seen in the specimens (d) and (e) in Fig. 7 and (h′) in Fig. 8. When the specimens (b) in Fig. 1 and (f) in Fig. 3, which seem to have some remaining cavities at the state D, are subjected to successive cold rollings, their densities increase gradually at first, depending on the amount of the cold rollings. As is seen from the curves corresponding to the specimens (b) in Fig. 7 and (f) in Fig. 8, the maximum densities of the specimens approach that at the B state.

The results obtained by giving successive annealings to the several specimens which were at the D state and cold rolled differently are

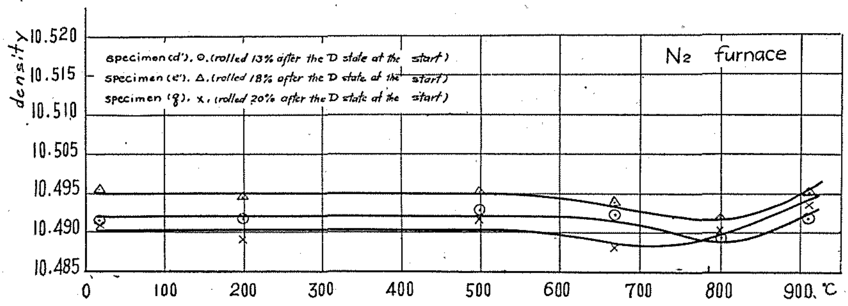

Fig. 9

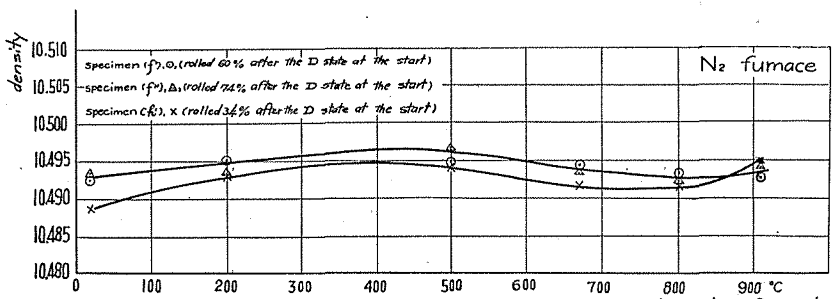

Fig. 10

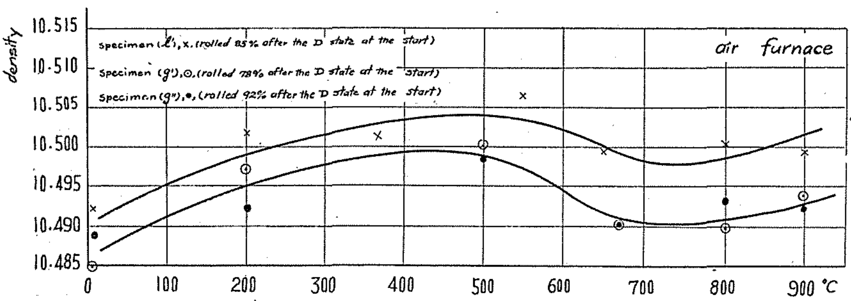

Fig. 11

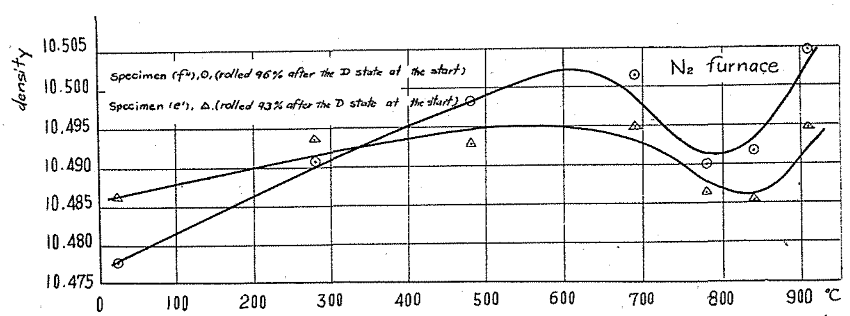

Fig. 12

shown in Figs. 9, 10, 11 and 12. With the specimens subjected to the rollings below 30% the rise of the density caused by the release of the stress could not be detected and the decrease of the density caused by the production of the cavities was not remarkable. With the specimens which were rolled within the range of about 40%–70%, the release of the stress occurred at about 400°C, and the difference between the A and B values was about $5/10^4$ of the density. With the specimens which were rolled very strongly to about 80% or 90%, the release of the stress took place at the annealing temperature of about 500°C–600°C, and the decrease of the density at the C state was about $1/10^3$ of the density, as is seen in Fig. 12.

According to Fig. 12, where strongly worked specimens were annealed, the recovery to the B value by annealing was almost perfect. Judging from this, it seems almost certain that the cavities were not formed by the process of rolling. The amount of the decrease in the density which was caused by the production of the cavities differed according to the temperature at the B state and the history, especially the degree of cold working before the recrystallization.

From the experiments described above the manner of the change of the density of silver with the annealing and the cold rolling has now become very clear. As an example, the behavior of the density of the specimen (f), when it is subjected to the process of annealing and cold rolling alternately, is represented by the upper curve in Fig. 13. This curve seems to clarify the way to get the standard value of the density of a specimen of silver. Let the specimen arrive at

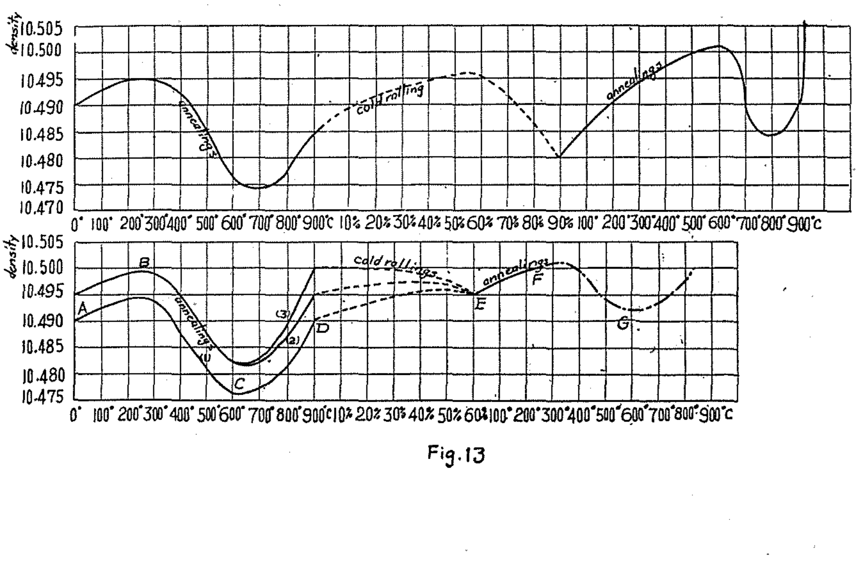

Fig. 13

the state D by passing through the path A B C D by successive annealings. This D state is not necessarily entirely devoid of minute cavities and a subsequent cold rolling to about 60% is to be done to destroy all the remaining cavities. The resulting internal stress is next to be released by the annealing at about 250°C, without forming any new minute cavities. Three curves drawn in the lower half of Fig. 13 show the values of the densities of three different specimens at various stages of such procedure of obtaining the standard value of the density. Among these three specimens, the one corresponding to the curve (1) seems to have had some cavities at first, as is revealed by a somewhat lower value of its density at the state B, and the other two corresponding to the curves (2) and (3) seem to have had almost no cavities at first, as is shown by the higher value of their densities at the B state which is almost the same as that at the state F. Irrespective of such differences in the porosity at the start their densities become the same at and after the state E, by the vanishing of the remaining cavities in the process of rolling; and by the subsequent annealing at about 250°C the density of all the specimens arrives at the standard value at the state F. The value of the density thus obtained with these three specimens at the standard state F is 10.502 at 17°C.

The present research has explained systematically the rather irregular changes in the density of a metal by the process of annealing and cold working.

In conclusion the writer expresses his sincere thanks to Professor U. Yoshida of the Kyoto Imperial University by whose kind suggestions and encouragement the present research was carried out.