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Effect of Nitrogen and Few Other Elements on Strain Aging of Steels*

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Synopsis

Many investigations were carried out on the strain aging of steels but few were reported on commercial steels. In succession to the work on the effect of nitrogen on the strain aging in steels, the effects of Al, Ti, Si, Mn, As and Cu were examined.

I. Introduction

The aging observable in cold-working and that observable after cold-working co-exist in the strain aging of steels. In general, the former type is named the blue-brittleness and the latter the strain aging. The study on the blue-brittleness was reported in our last report,[(1)] and so the correlation between the strain aging and the content of nitrogen in steel was examined in succession and the correlation between Al, Ti, Si, Mn, As, Cu and nitrogen could be ascertained.

II. Preparation of specimen and method of experiment

The materials used for preparing specimens were electrolytic iron, electrolytic manganese, metallic silicon, Ti-Si alloy, arsenic and electrolytic copper, and were melted in a high frequency electric furnace. In order to vary the nitrogen content, a sufficient amount of $CaCN_2$ and nitrogenized manganese which was nitrogenized in the stream of pure nitrogen were used.

After forging, the specimens were heated at 950°C for 15 minutes and air-cooled, from which the tensile test-pieces, 35 mm in parallel part, and 6 mm in diameter, were machined. To eliminate the effect of machining the specimens were heated at 550°C for 3 hours and then slowly cooled at the rate of about 1°C per minute. After tensile loading, the specimens were aged at room temperature, and then, the tensile strength (σ_B), the yield strength (σ_S), the elongation (δ) and the reduction of area (ϕ) were measured. As the rate of cold-working the percentage of elongation was taken, and only the specimen which was cold-worked within an error of ± 1 per cent was used for the readjustment of the experimental result, because the value of elongation after the strain aging was affected especially by the variation of the rate of cold-working. The experiment was carried out with specimens cold-worked by 6~20 per cent. The effect of chemical composition on the strain aging was not in-

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(1) Y. Imai and T. Ishizaki, Sci. Rep. RITU, A 4 (1952), 553.

fluenced by the degree of cold-working. Accordingly, the experimental results will be explained on the specimens subjected to a definite degree of cold-working of 9 ~16 per cent. The strain aging is of course affected by the aging temperature, but the present experiments were carried out at room temperature for convenience sake.

III. Results of experiment

1. Effect of nitrogen

The chemical composition of the specimens was as follows: C≒0.01 per cent, Si=0.1~0.15 per cent, Mn=0.12~0.16 per cent, P≒0.004, per cent, S≒0.009 per cent. Fig. 1 shows the correlation between the rate of increase in the yield strength – the ratio of the difference between the yield strength after aging and the maximum strength at cold-working to the maximum strength at cold-working – and the aging time. Until the aging time of 200 hours, the rate of increase in the yield strength

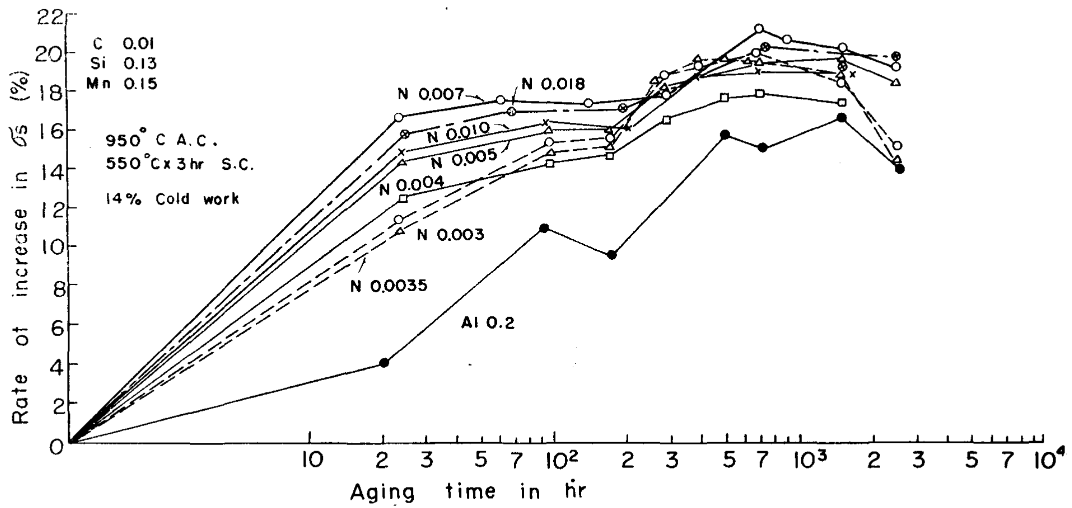

Fig. 1. Relation between aging time and rate of increase in σ_S.

with the increase of nitrogen content was remarkable, but after remaining a little, it reached the same degree. Though the strain aging was recognized in the specimens denitrogenized by the addition of Al, the degree of the strain aging was very small, that is, at the first stage of strain aging the rate of aging was fast in the specimens containing more nitrogen, but at the later stage the difference of the rate decreased, and from about 200 hours the degree of strain aging reached the same amount. In this case, however, the increase of the rate appearing in two steps at about 200 hours was not so clear. From the fact that the diffusion velocity of carbon is slow compared with that of nitrogen as shown in the last report on blue-brittleness, it will be seen that the later stage of strain aging is due mainly to the carbon.

The correlation between the rate of increase in the yield strength and the content of nitrogen is shown in Fig. 2, in which the results at about 22 hours, 200

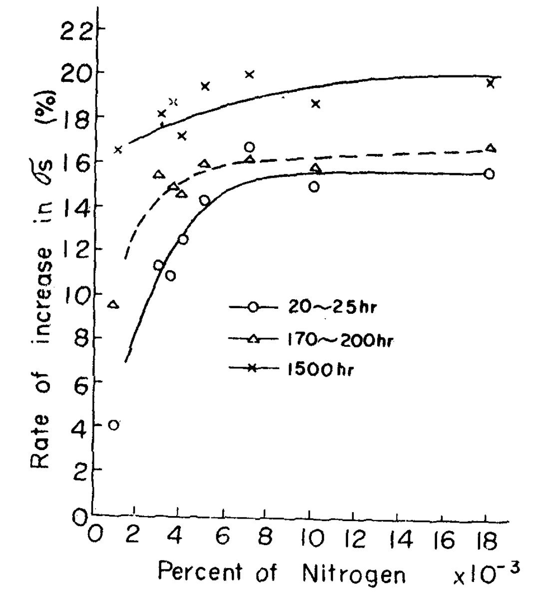

Fig. 2. Relation between rate of increase in σ_s and nitrogen in steels.

hours and 1500 hours are representatively shown. As seen in the figure the rate of increase in the yield strength with the increase of nitrogen content is remarkable up to about 0.006 per cent of nitrogen and then somewhat slowly.

From the result of the tensile strength, the relations similar to those shown in Figs. 1 and 2 were obtained, though the result was not so clear in comparison with the case of the yield strength.

Figs. 3 and 4 show the correlations between the aging time and respectively the elongation and the reduction of area. The elongation or the reduction of area decreases with the increase of the nitrogen content. The strain aging occurred sharply in two steps at about 200 hours, but on account of large errors in the

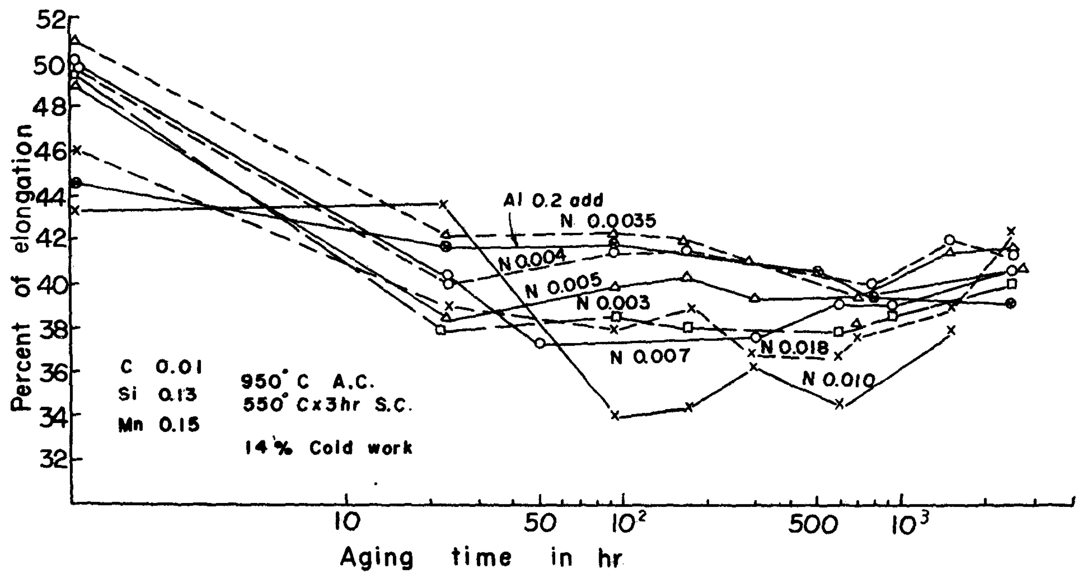

Fig. 3. Effect of aging time on elongation.

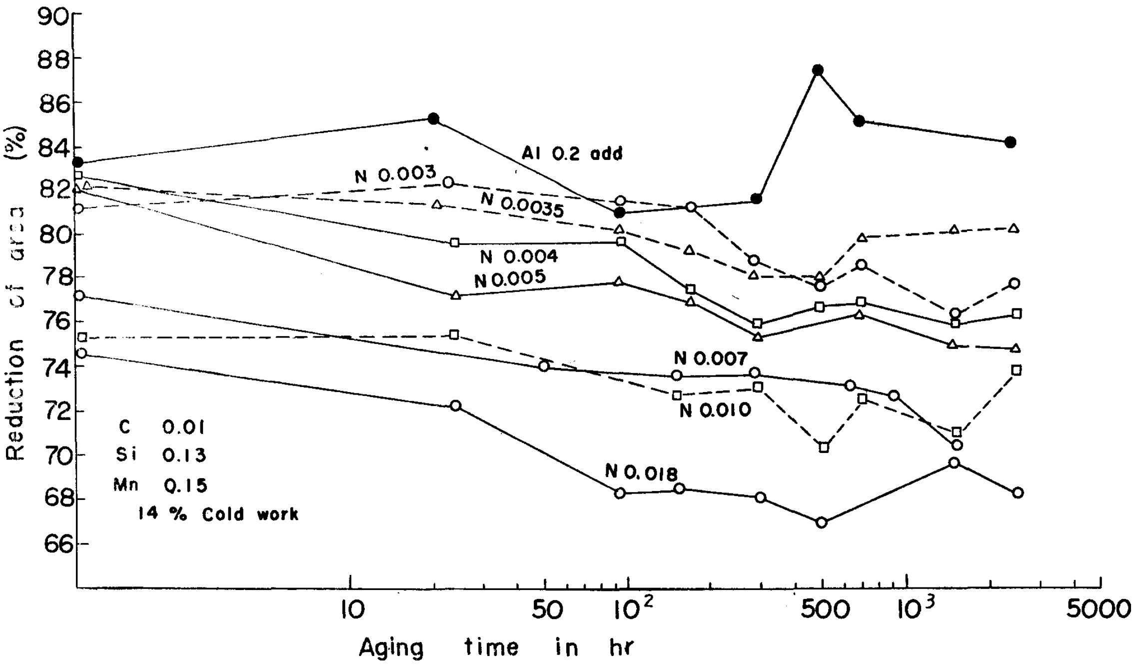

Fig. 4. Effect of aging time on reduction of area.

measurement of the elongation or the reduction of area further experiments should be done to clarify these phenomena. So, the strain aging was discussed mainly by the rate of increase in the yield strength or the increased amount of the yield strength, and accordingly, the data of the elongation and the reduction of area were used only for reference.

From the above results it was seen that the strain aging related closely to the solubility of nitrogen in α-iron, and that it is necessary to consider the aging due to carbon. Fig. 5 shows the results on steels in which the nitrogen content was controlled by the additions of nitrogenized manganese and $CaCN_2$. All the specimens were cold-worked as fast as possible after cooling from 550° either slowly or rapidly, and then the strain aging was examined. The experiment on the rapidly cooled specimens was done from the view-point that the rate of strain aging in specimens the containing more than 0.006 per cent nitrogen, being constant in the state of slow cooling, is increased with the increase of nitrogen contained in α-iron by rapid cooling. The reason for this is that the rate of strain aging increases with the increase of nitrogen or carbon content in α-iron. In this case the stress by rapid cooling is small, and therefore accordingly, the strain aging is affected mainly by the increase of nitrogen or carbon in α-iron. In the slowly cooled specimens the same result as in Fig. 1. was obtained. The strain aging shown in Fig. 1 takes place sharply in two steps at about 200 hours, but in this case it appeared at the side of long time. This difference may be due to the increase of carbon content and to the different aging temperature. From the results it is seen that the increased amount of yield strength in the rapidly cooled specimens is higher than that in the slowly cooled ones, and that the rate of aging in the former

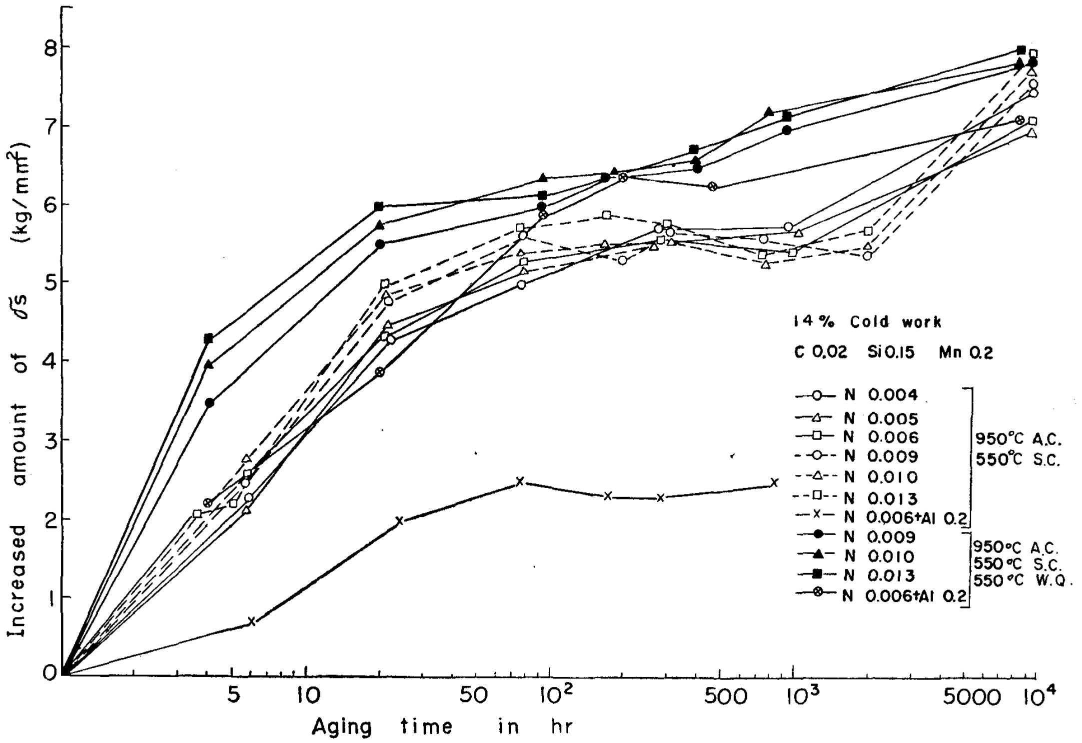

Fig. 5. Relation between aging time and increased amount of σ_S.

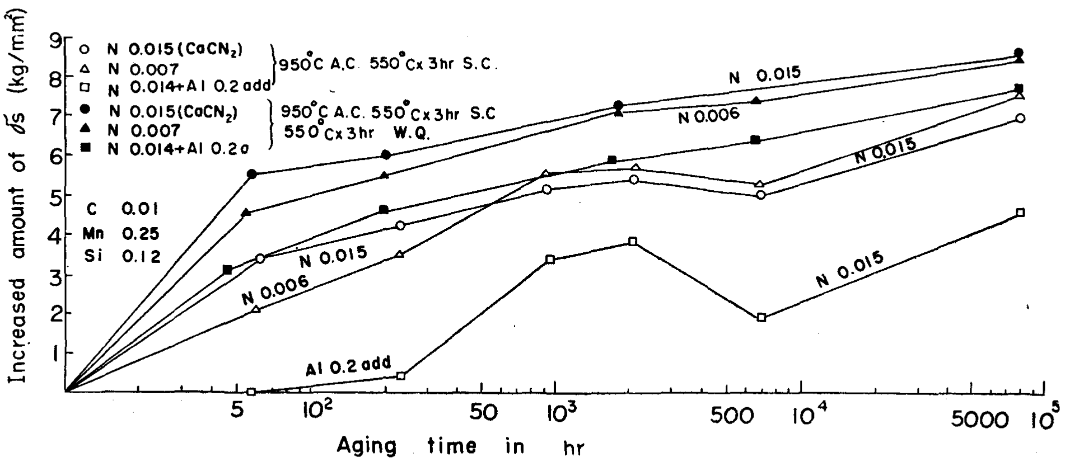

Fig. 6. Relation between aging time and increased amount of σ_S.

is fast. The slowly cooled specimens showed the constant rate of strain aging, but the rate in the rapidly cooled specimens increases with the increase of the content of nitrogen in the range of short aging time. With the progress of aging the difference in the aging rate decreases and finally the rate becomes the same value at about one year. It is noticeable that in the specimens, in which the nitrogen was stabilized by the addition of Al, the rate of aging is faster when rapidly cooled than when slowly cooled. It is due to a large amount of strain aging that the sharp two-step aging is impossible to be recognized. (cf. Fig. 7)

The result of the elongation or the reduction of area on these specimens was all the same as the above, except that the value either of the elongation or of the reduction of area in the rapidly cooled specimens was lower than those in the slowly cooled specimens.

The results of the specimens in which the $CaCN_2$ was used to increase the nitrogen contents were similar to that shown in Fig. 5, though not so clear on account of a small number of specimen. The sharp of two-step aging was clearly seen in the slowly cooled specimens containing a small amount of nitrogen, but not in the rapidly cooled specimens, because of a large amount of strain aging.

Fig. 7 shows the result of specimens containing a small amount of nitrogen or of carbon. The electrolytic iron was melted, and then Al or Ti was added either to the inside or to the outside of the high frequency electric furnace to vary the degree of the deoxidizing, the denitrogenizing or the decarbonizing in various

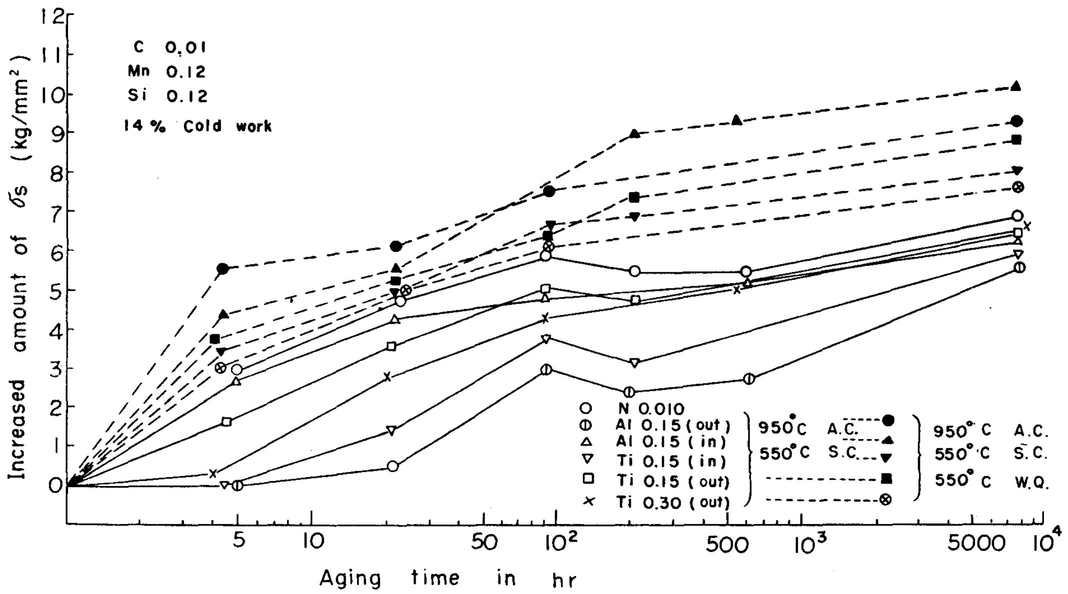

Fig. 7. Relation between aging time and increased amount of σ_S.

ways. The strain aging on the specimens obtained by adding Al to the inside of the furnace was remarkable. This is due to the absorption of nitrogen after the addition of Al. When Al was added to the outside of the furnace, the nitrogen was fixed most effectively, and accordingly, the strain aging became small. The specimens obtained by adding Ti to the inside of the furnace showed a small degree of strain aging, whereas the specimens obtained by adding Ti to the outside of furnace showed the imperfection of denitrogenizing. This is due probably to the imperfection of Ti-treatment because of high melting point of it. Therefore, it was impossible to clarify quantitatively the effect of nitrogen or of carbon. However, the sharp of two-step aging clearly appeared, and became obscure with the increase of the amount of strain aging.

2. Effect of Si

The chemical composition of the specimens was follows: C≒0.01 per cent, Mn≒0.15 per cent, N≒0.006～0.008 per cent and Si≒0.2～2.5 per cent. The content of nitrogen has a tendency of decrease with the increase of the content of Si, but as its amount is in the range in which the rate of strain aging is constant, the effect of Si on strain aging can be examined.

Fig. 8 shows the tensile strength (σ_B), the yield strength (σ_S) (Δ.... upper yield strength, ○.. lower yield strength), the elongation (δ) and the reduction of

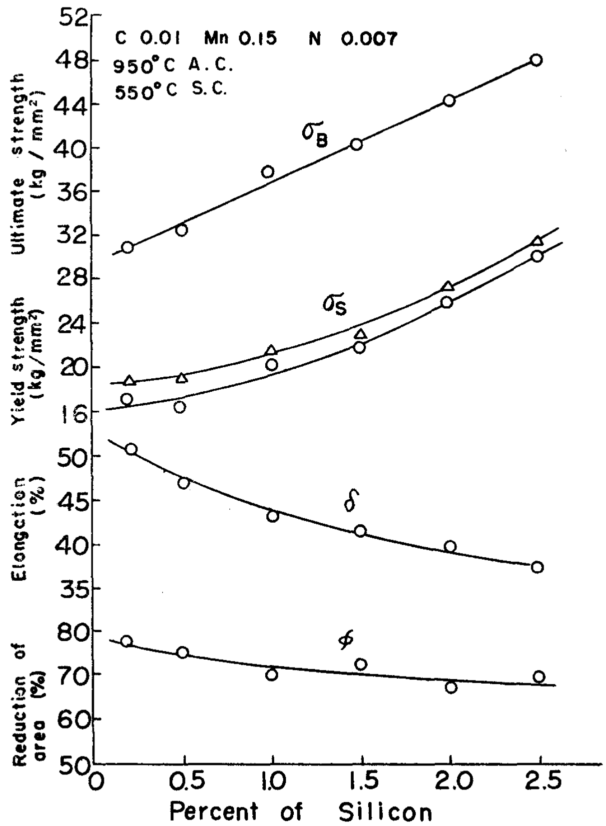

Fig. 8. Effect of silicon on mechanical properties.

area (ϕ). Fig. 9 shows the correlation between the rate of increase in the yield strength and the aging time. From Fig. 9 it will be seen that the strain aging occurs sharply at two steps. Both the aging due to nitrogen observed up to 200 hours and the maximum amount of aging decrease with the increase of Si. This is due to the circumstances that the Si has a remarkable affinity with nitrogen, and accordingly, the nitrogen is fixed by Si, resulting in the decrease of its solubility in α-iron. In the specimens in which the nitrogen was fixed by the addition of 0.2 per cent of Al, after the addition of 1 per cent of Si, the degree of the strain aging was not higher than that in the specimens containing of 1 per cent of Si, but is higher than that in the specimens containing 2 per cent of Si. One of the reasons for this is that the denitrogenizing becomes difficult with the increase of Si; the other is that the solubility of nitrogen in α-iron decreases by the existence of Si. As men-

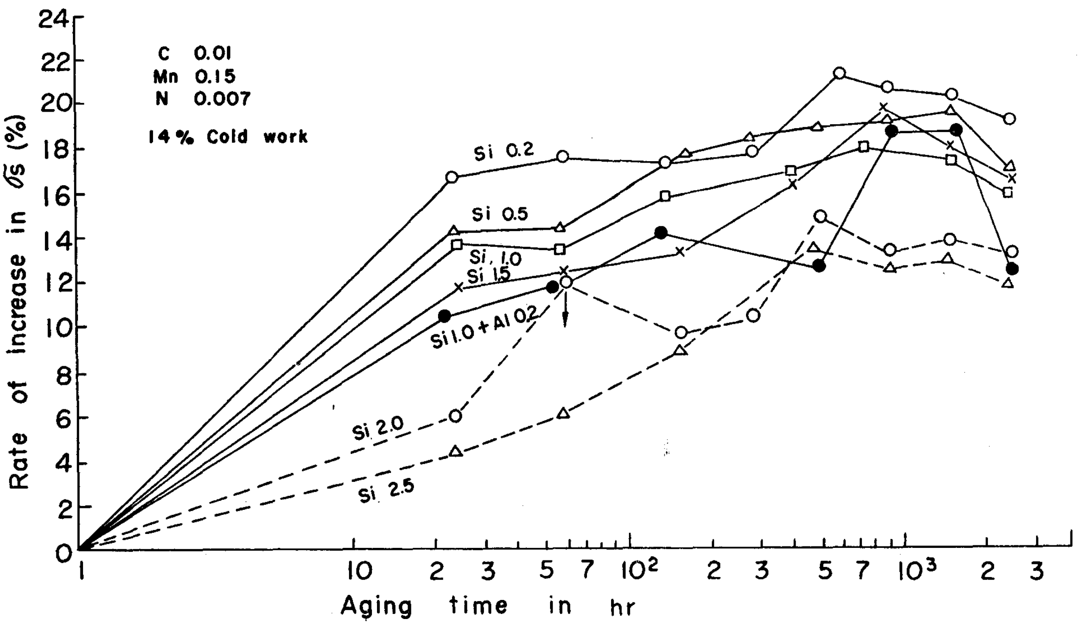

Fig. 9. Relation between aging time and rate of increase in σ_s.

tioned above the maximum amount of strain aging in the specimens denitrogenized with Al is higher than that in the specimens denitrogenized without Al. This will be explained in way as in the case of blue-brittleness, that is, the blue-brittleness due to nitrogen decreases with the increase of Si, and that due to carbon becomes conspicuous with the decrease of the blue-brittleness due to nitrogen. In other words, it is due to the fact that with the decrease of the solubility of nitrogen the solubility of carbon increases.

Fig. 10 shows the correlation between the rate of increase in the yield strength and the aging time. With the increase of Si-content the decrease of strain aging clearly appears. There is a difference between the value of 24~150 hours and that of 900~1500 hours. The former is due mainly to nitrogen and the latter to carbon. Fig. 11 shows the correlation between the elongation and the aging time. There is a tendency that the amount of elongation decreases with the progress of aging, but after the certain time the amount of elongation increases. It is remarkable that the increase of elongation appears in spite of the increase of yield strength or tensile strength.

3. Effect of Mn

The experiment was carried out on the specimens containing C≒0.01 per cent, Mn=0~2.5 per cent, Si≒0.15 per cent and N≒0.006~0.0075 per cent. The content of nitrogen was increased with the increase of the content of Mn.

Fig. 12 shows the mechanical properties. The tensile strength is in proportion to the increase of Mn-content, but the yield strength, the reduction of area and the elongation of specimens of low Mn content are fairly low. This is due probably to the unsoundness of the specimens resulting from the different amount of deoxidizing.

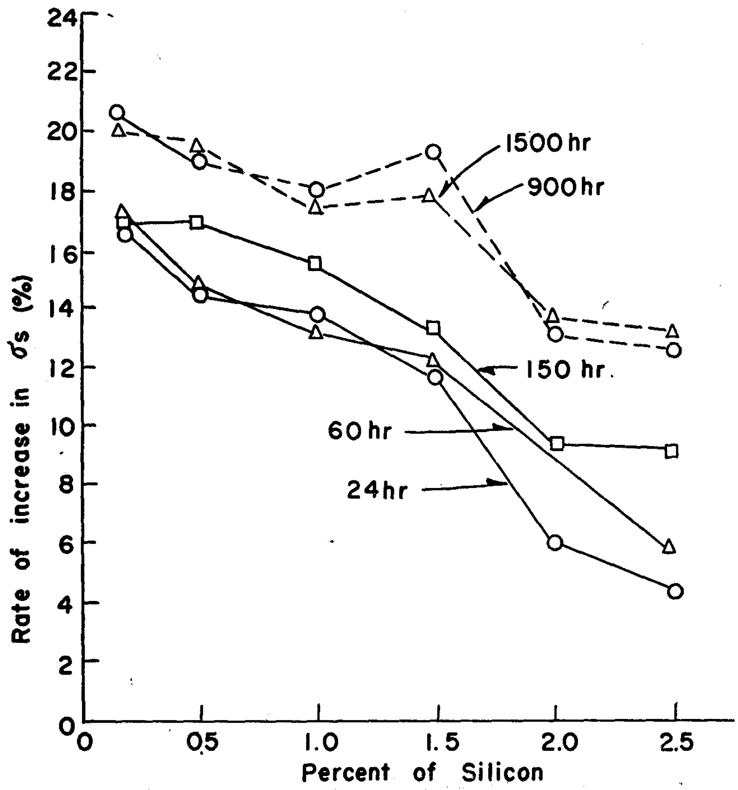

Fig. 10. Relation between rate of increase in σ_s and percentage of silicon.

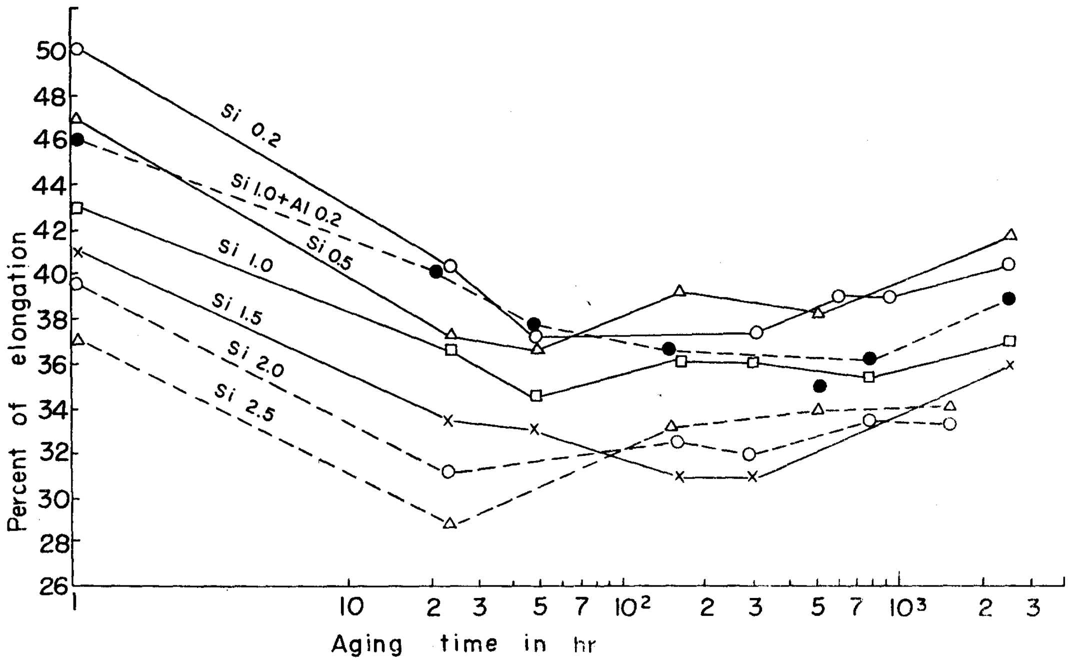

Fig. 11. Effect of aging time on elongation.

Figs. 13 and 14 show the correlation between the rate of increase in yield strength and respectively the aging time and the content of Mn. The same as in the case of Si will be seen, that is, the strain aging develops sharply at two steps, the

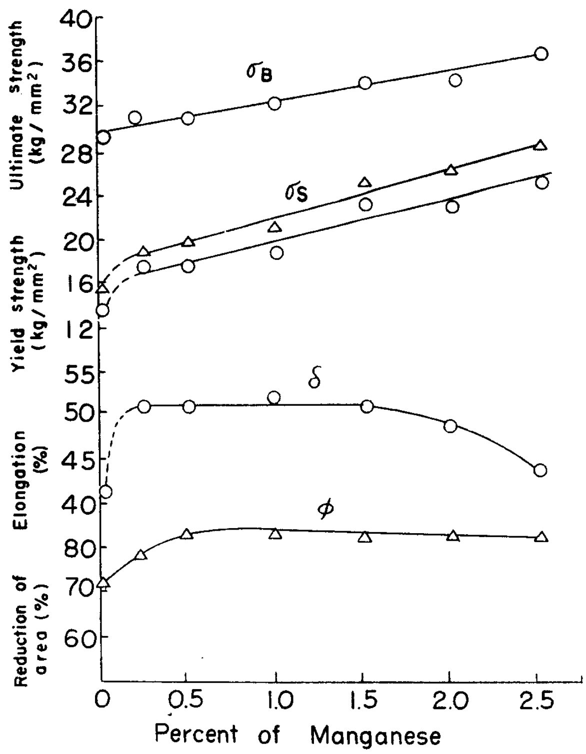

Fig. 12. Effect of manganese on mechanical properties.

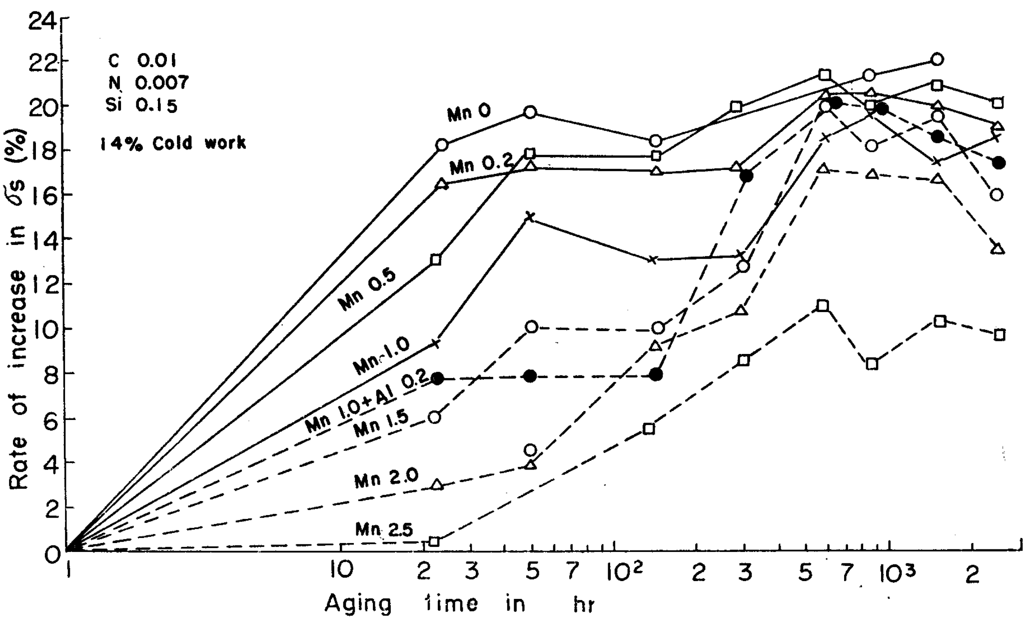

Fig. 13. Relation between rate of increase in σ_S and aging time.

former due mainly to nitrogen decreasing, while the latter due to carbon increasing with the increase of Mn content. Figs. 15 and 16 show the correlation between the aging time and respectively the elongation and the reduction of area. No anomaly was observable in the specimens containing a small amount of Mn, in

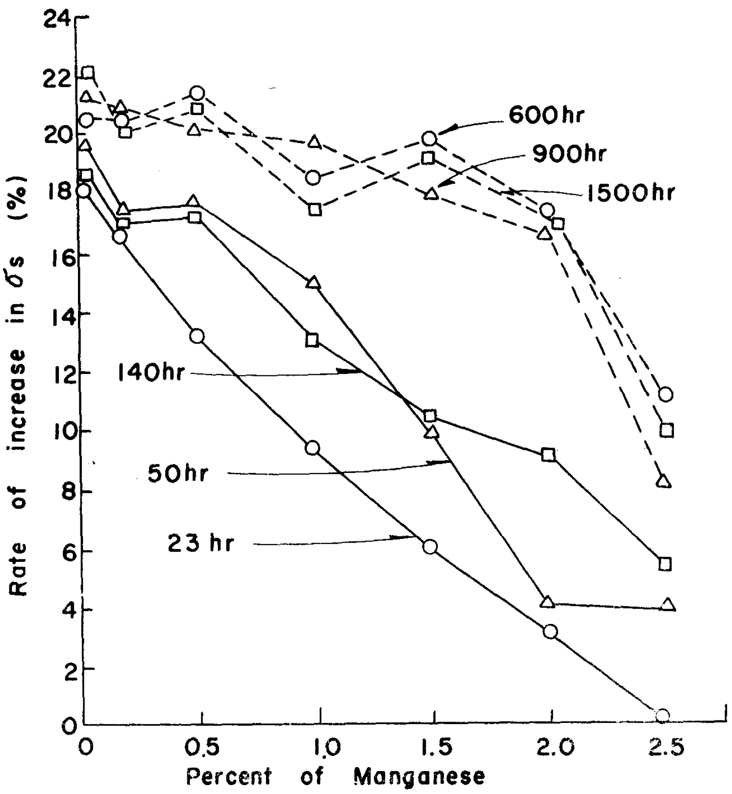

Fig. 14. Relation between rate of increase in σ_s and percentage of manganese.

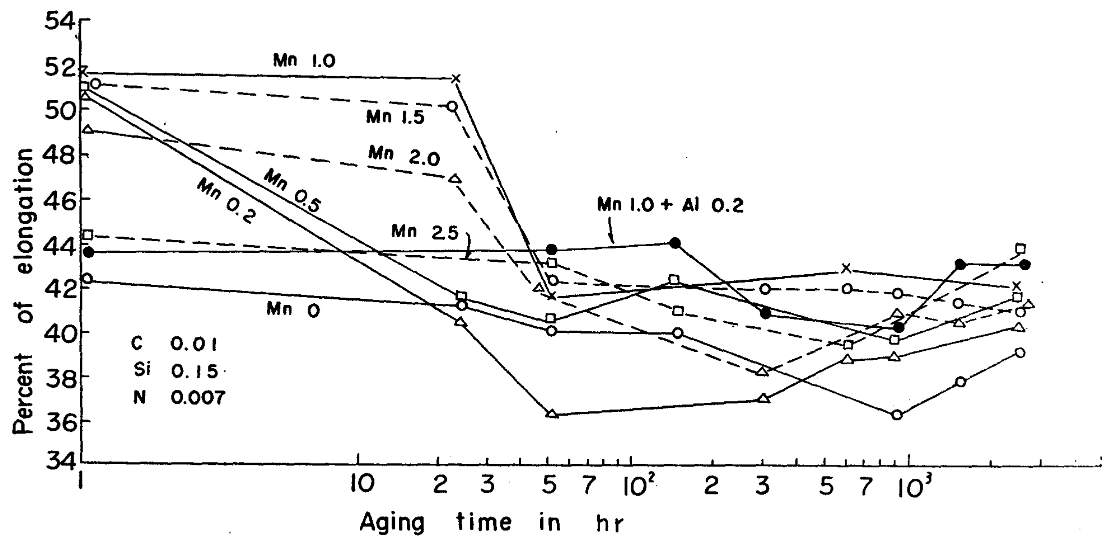

Fig. 15. Effect of aging time on elongation.

which the elongation or the reduction of area was low, that is, the effect of Si is the same as that of Mn.

4. Effect of As

As mentioned above, Si or Mn has a comparatively great affinity with nitrogen, and the effects of these elements on the aging were evident. Arsenic, however, has

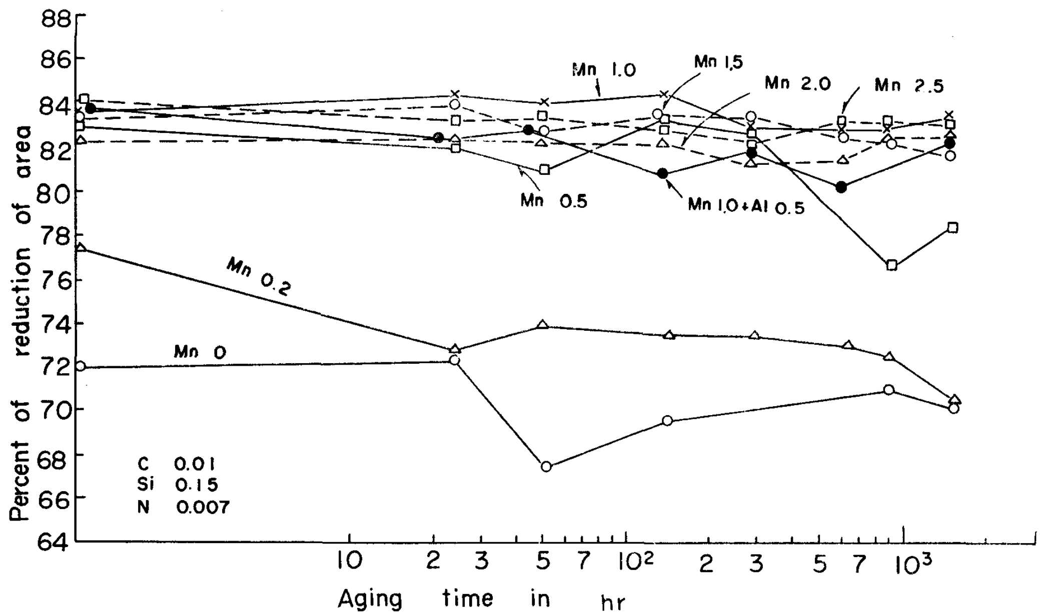

Fig. 16. Effect of aging time on reduction of area.

a small affinity; hence its effect was examined.

The composition of the specimens as follows: C≒0.01 per cent, N≒0.006 per cent, Mn≒0.2 per cent, Si≒0.2 per cent, As=0~1.2 per cent. Fig. 17 shows the mechanical properties. The each of them varied in proportion to the content of As. The mark ● refers to the specimens which were deoxidized with Al. The difference between the specimens which were deoxidized with Al and those to which was added no Al increased with the decrease of As.

Figs. 18 and 19 show the correlation between the rate of increase in the yield strength and respectively the aging time and the content of As. With the increase of As content, both the rate of increase in yield strength and the rate of strain aging decrease up to the As content of 0.2 per cent, but increase above this percentage of As. In the specimens deoxidized with Al, however, the amount of strain aging increases with the increase of As content. As shown in the result on the specimens deoxidized with Al, As has the increased effect of the rate of strain aging due mainly to carbon. These are well explained from the above-mentioned result. The fact that both the rate of increase in the yield strength and the rate of strain aging decreases up to the As content of 0.2 per cent, is due to the decrease of strain aging by nitrogen. These phenomena are due to the decrease of the dissolved amount of nitrogen in α-iron resulting from a small affinity of As with nitrogen.

The phenomenon that the maximum amount of strain aging of the specimens containing 0.5~1.2 per cent As is higher than that of the specimens containing 0.006 per cent nitrogen—(the constant amount of aging was seen in the slowly cooled specimens containing nitrogen above 0.006 per cent)— is due to the increase of the strain aging by the existence of arsenic, that is, the stress reduced by the cold-working in the specimens containing arsenic in the state of solid solution in

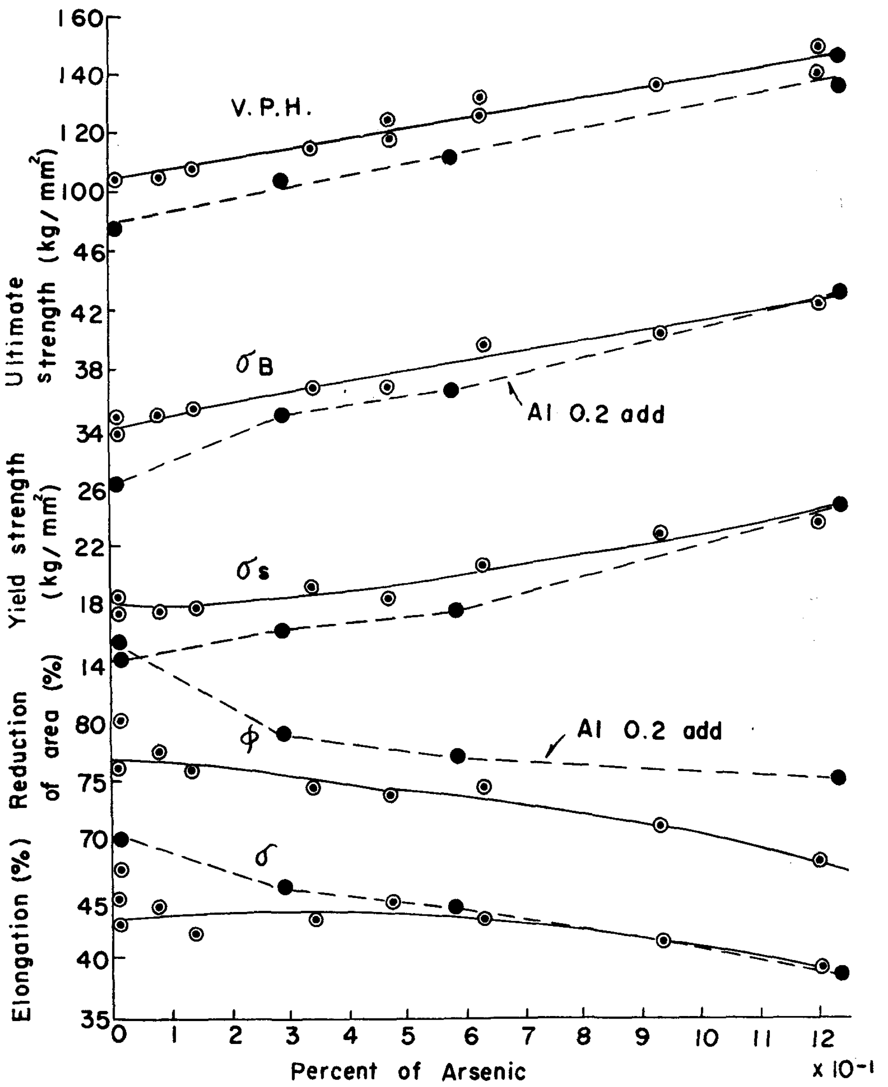

Fig. 17. Effect of arsenic on mechanical properties.

α-iron is larger than that in the specimens without As.

Though the strain aging with respect to the elongation or to the reduction of area was not clear, a tendency was seen that with the increase of As content both the elongation and the reduction of area did not decreased in a short range of time, and decreased in a long range of time. This shows that the strain aging due to carbon appears at the big state in a long range of time on account of containing arsenic.

5. Effect of Cu

An experiment was carried out on the specimens containing Cu in expectation of the effect similar to that of As. Fig. 20 shows the correlation between the mechanical property and the content of Cu. In the case of Cu content above 0.6 per cent, both the tensile strength and the yield strength increased, whereas both the elongation and the reduction of area decreased. This is due to the precipitation

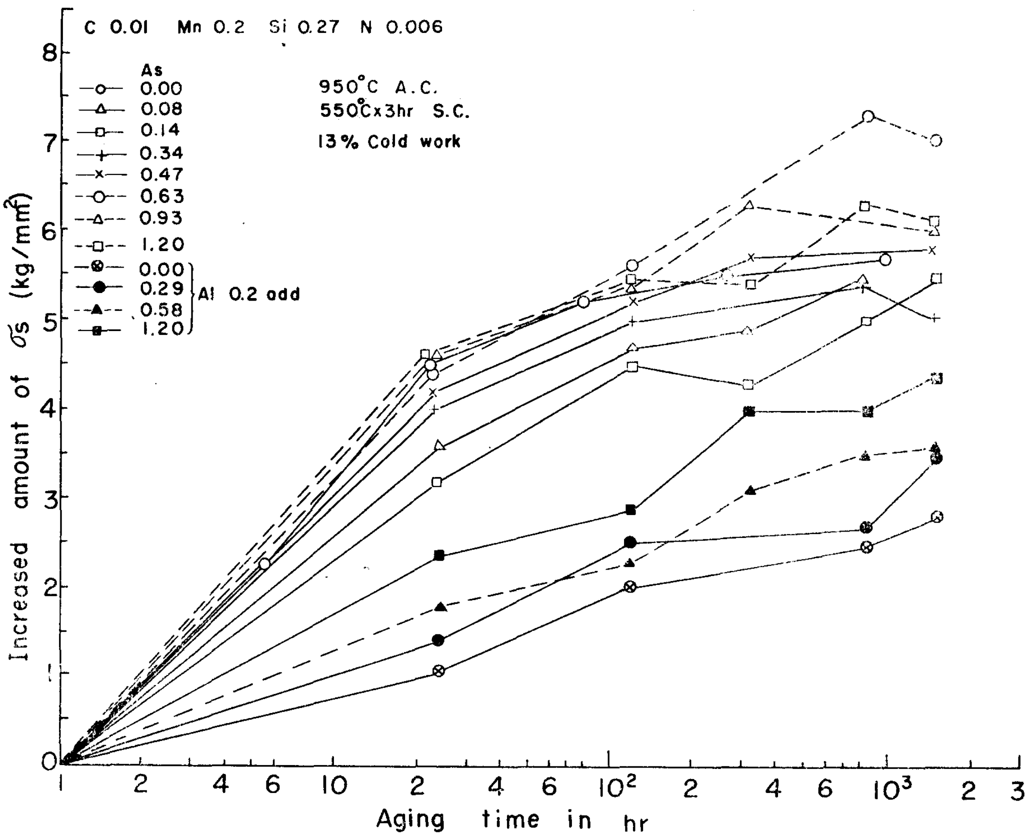

Fig. 18. Relation between aging time and increased amount of yield strength.

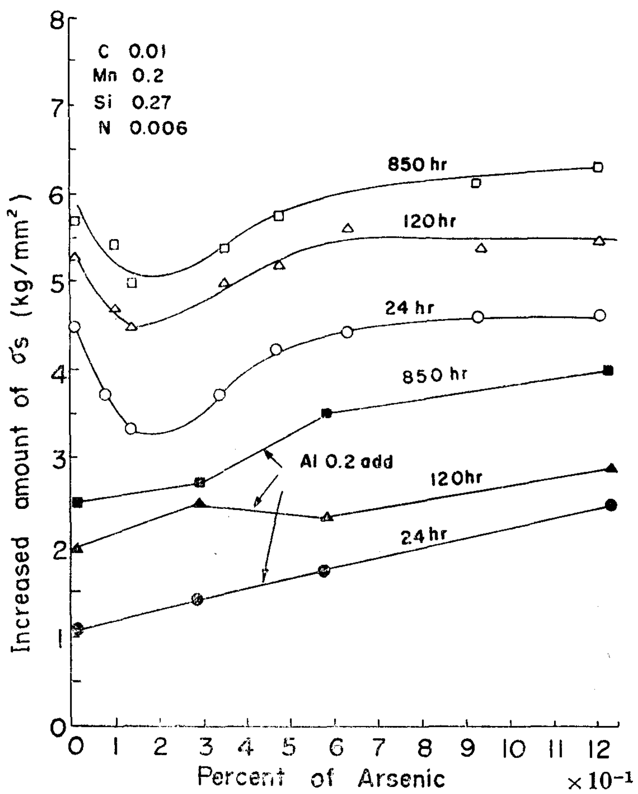

Fig. 19. Relation between increased amount of σ_s and percentage of arsenic.

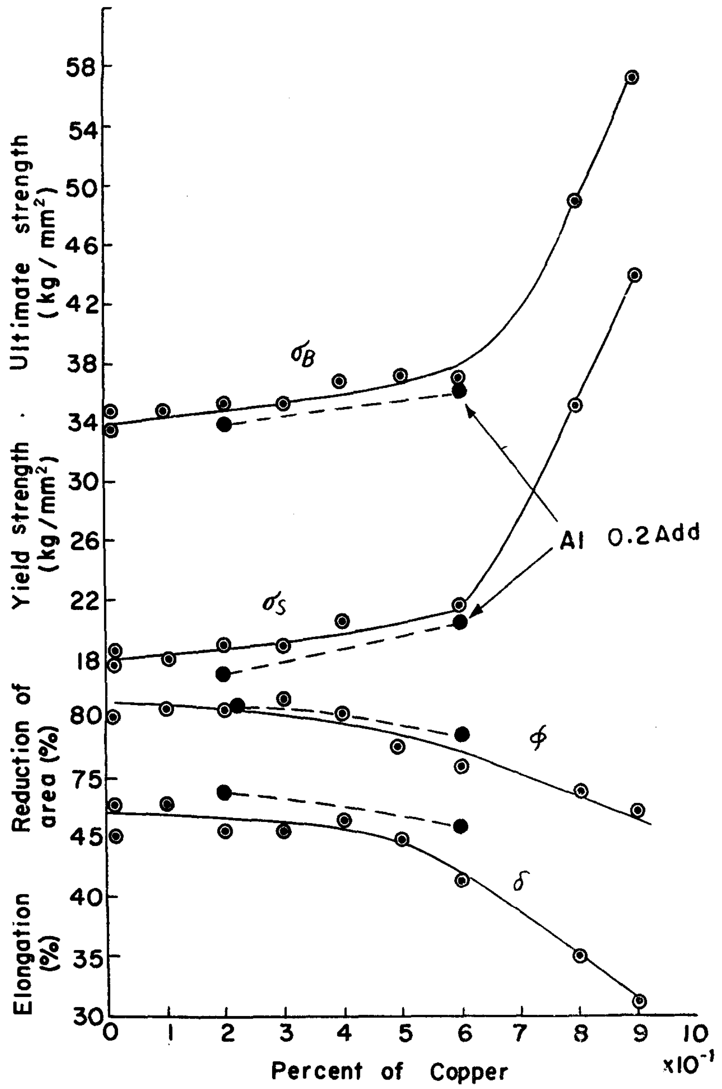

Fig. 20. Effect of copper on mechanical properties.

hardening by Cu. Figs. 21 and 22 show the correlation between the rate of increase in the yield strength and respectively the aging time and the content of Cu. With the increase of Cu the amount of strain aging decreases, and then increases at about 0.3 per cent of Cu, and finally decreases when the precipitation hardening by Cu occurs. In the specimens denitrogenized with Al the amount of strain aging increased with the increase of Cu content up to about 0.6 per cent, that is, the effect similar to the case of As is seen which, however, was not clear on account of a small number of the specimen.

As in the case of As the strain aging increased with the increase of the dissolved amount of Cu in α-iron, but Cu has a decreased action of the strain aging due to nitrogen on account of the decrease of solid solubility of nitrogen.

The phenomenon, that the strain aging decreases in the specimens in which the precipitation hardening of Cu was recognized, shows that the strain aging decreases in the specimens which were hardened by the other function.

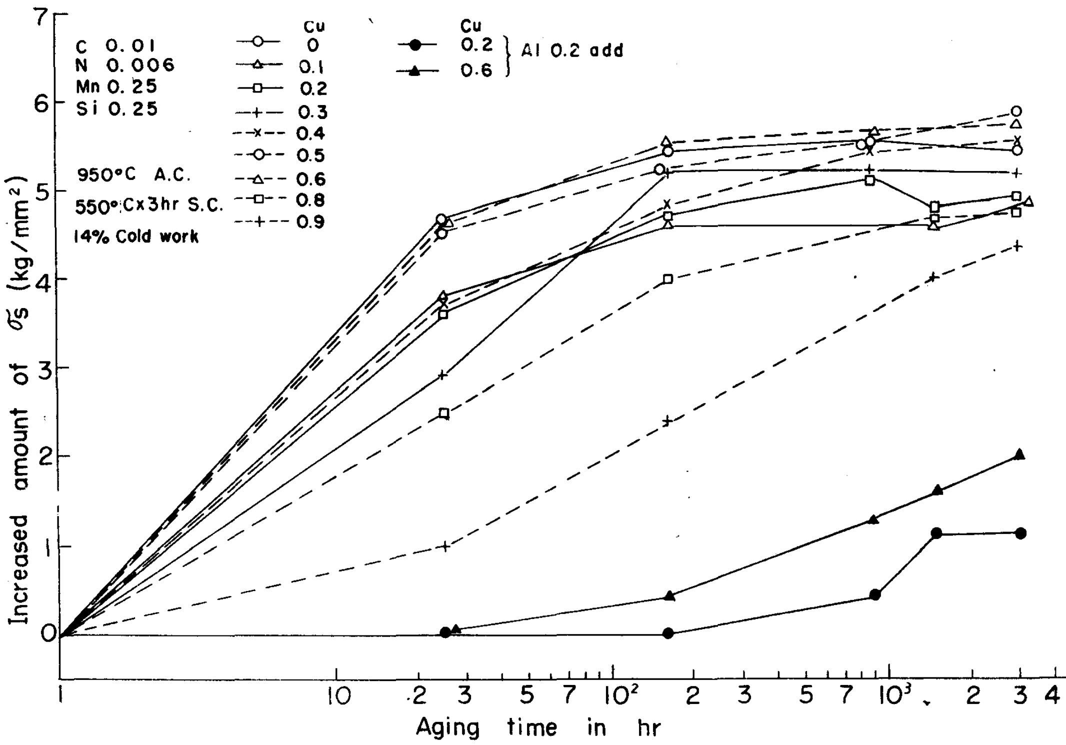

Fig. 21. Relation between aging time and increased amount of yield strength.

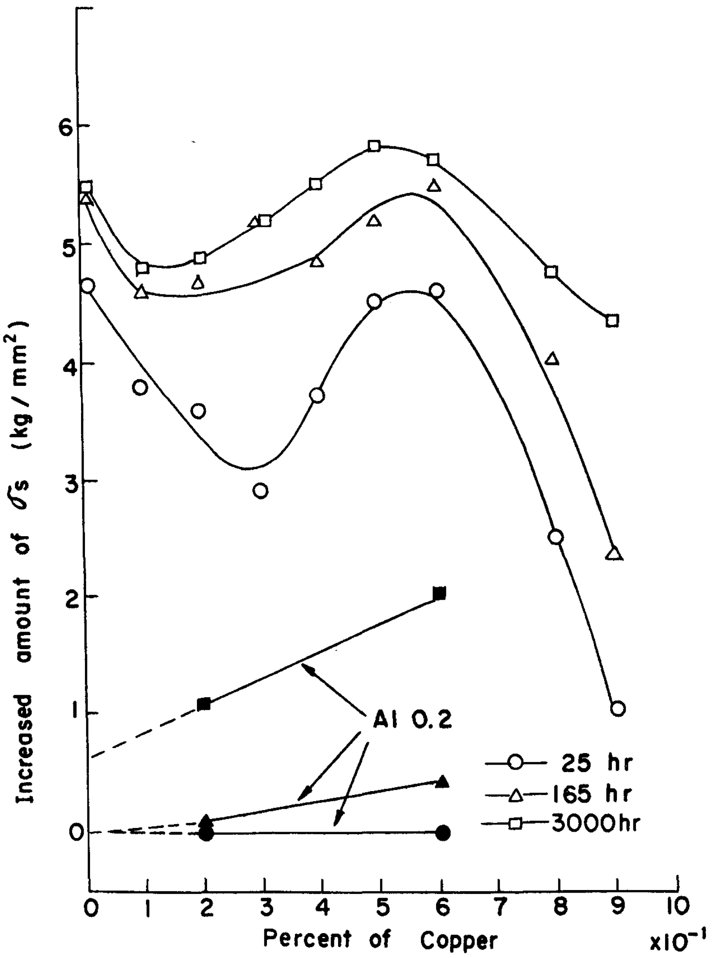

Fig. 22. Relation between increased amount of σ_s and percent of copper.

No clear correlation was observed between the elongation or the reduction of area and aging time. The reduction of area in the range of 800～3000 hours of the specimens denitrogenized by 0.2 per cent of Al after the addition of 0.2～0.6 per cent of Cu was especially high, the reason for which, however, is not clear on account of the small number of specimens.

Summary

The strain aging of iron were examined from mechanical properties, and the results may be summarized as follows:

(1) The strain aging occurs at two stages.

(2) The former stage of strain aging is due mainly to the nitrogen, and with the increase of nitrogen content dissolved in α-iron the rate of strain aging increases.

(3) The latter stage of strain aging is due to both the nitrogen and carbon.

(4) The strain aging is decreased by the addition of the element having a high affinity with nitrogen or carbon.

(5) The strain aging due mainly to nitrogen decreases on account of the decrease of the solid-solubility of nitrogen in α-iron by the existence of Si, Mn, Cu and As.

(6) The stress reduced by the cold-working increases with the increase of the dissolved element in α-iron as shown in the case of As, and accordingly, the amount of strain aging increases.

(7) The strain aging decreases in the specimens in which the precipitation hardening by Cu occurs.

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