Nitrogen as an Alloying Element in Steel : Effect of Nitrogen on Quench-Aging of Steels

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Nitrogen as an Alloying Element in Steel.
Effect of Nitrogen on Quench-Aging of Steels*

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Synopsis

The present investigation was carried out in order to ascertain the effect of nitrogen on the quench-aging of steels containing 0.02~0.03 and 0.15~0.20 per cent carbon. The specimens tempered at 700°C for 3 hours after quenching at 950°C were requenched at 300~700°C after heating for 3 hours at respective temperatures and then aged at 30, 50 and 100°C. From the present investigation the following conclusions were obtained: (1) There is a distinct correlation between the nitrogen in steel and the quench-aging; (2) By the addition of nitrogen stabilizer such as Al or Ti, or by the fusion in vacuum the aging due to nitrogen is reduced; (3) The specimens containing less than 0.005 per cent of nitrogen revealed aging due to carbon.

I. Introduction

It is generally said that the nitrogen solubility in α-iron is about 0.1 per cent at the eutectoid temperature, 590°C, and about 0.001 per cent at room temperature(1); hence, the quench-aging seems to be due to the precipitation hardening(2). Though many works have been reported on this problem, quantitative results are few. To this day, it has not yet been clarified whether or not the quench-aging is due to oxygen, carbon or nitrogen contained in steel. Eilender and Wasmuht(3) examined the quench-aging of steels containing 0.01~0.015 per cent carbon and 0.004~0.040 per cent nitrogen, and found that nitrogen gave rise to the quench-aging, but they have not reported the effect of the carbon content on the quench-aging. In the present study, the effect of nitrogen content on the quench-aging of steels was investigated, together with those of carbon and oxygen contents.

II. Materials and methods

The specimens for the present experiment were prepared as follows: 2.5 kg of electrolytic iron containing small amounts of phosphorus and sulfur was melted in a high frequency electric furnace; after deoxidization with manganese and silicon (each 0.2 per cent), the melt was cast into a 35 mm square bar, which was forged to a cylindrical bar, 13 mm in diameter. After air-cooling at 950°C, it was machined into bars, 10 mm in diameter and 25 mm in length, and they were oil-

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* The 976th report of the Research Institute for Iron, Steel and Other Metals.

(1) Y. Imai and T. Ishizaki, J. Japan Inst. Metals, **16** (1951), A-334.

(2) Y. Imai and T. Ishizaki, J. Japan Inst. Metals, **17** (1952), A-110.

(3) W. Eilender and R. Wasmuht, Arch. Eisenhüttenwes., **3** (1930), 659.

quenched at 950°C and then tempered at 700°C for 3 hours to globulize the carbides. Nitrogenized manganese produced from electrolytic manganese by nitriding in nitrogen gas at 840°C and $CaCN_2$ were used(4) for the purpose of increasing the nitrogen content and decreasing the oxygen content. The carbon content in the specimen was kept above the solubility(1) in α-iron so that carbon could be saturated (0.02~0.03 per cent). Low carbon steel (0.15~0.2 per cent) was prepared by adding white pig iron produced from electrolytic iron with gas carbon.

The experimental method was as follows: after heating at 700, 650, 600, 550, 500, 400 and 300°C for 3 hours, the specimens were water-quenched, and then aged at 30, 50 and 100°C, and the age-hardening degree was shown by V.P.H. Two specimens were used for this experiment, and measurements were carried out 3~5 times and the mean value was taken.

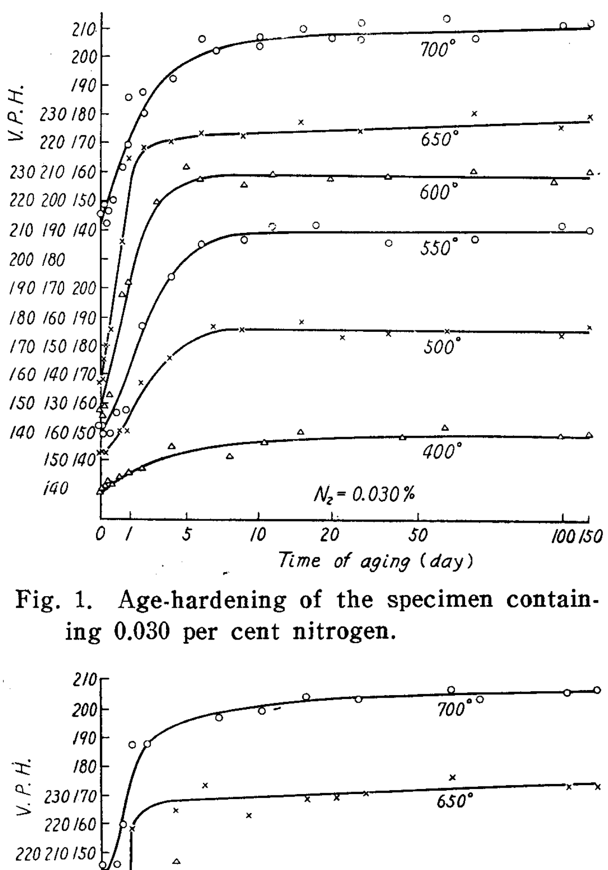

Fig. 1. Age-hardening of the specimen containing 0.030 per cent nitrogen.

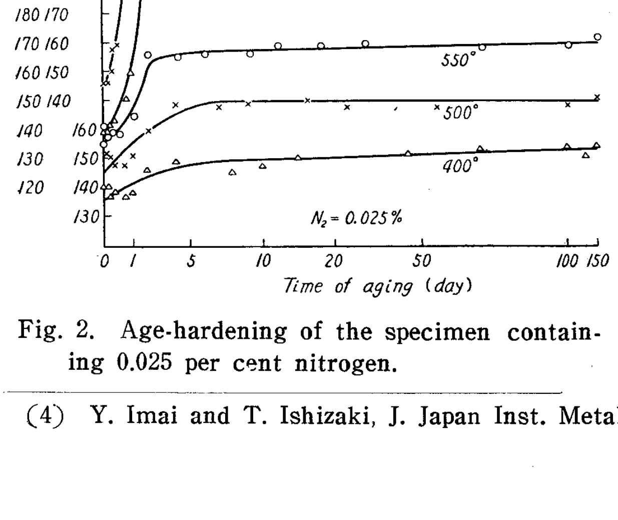

Fig. 2. Age-hardening of the specimen containing 0.025 per cent nitrogen.

III. Experimental results

Figs. 1~7 show the results on the age-hardening for the specimens containing 0.02~0.03 per cent carbon, 0.2 per cent manganese, 0.1 per cent silicon and various amounts of nitrogen and aged at 30°C for 150 days. Fig. 1 shows the results for the specimen containing 0.030 per cent nitrogen and quenched at 400~700°C; in all cases the age-hardening was observed, and with the rise of quenching temperature the increase in hardness due to aging became remarkable. In the case of quenching at 700°C, however, the degree of hardening was rather low and the aging rate decreased, that is, in the specimens quenched below 650°C, an almost constant value of hardness was obtained after aging for about 7 days, whereas the specimen quenched at 700°C showed a gradual increase of hardness after more than 7 days. This tendency was observed in all cases shown in Figs. 1~7. This seems to be due to the increase

(4) Y. Imai and T. Ishizaki, J. Japan Inst. Metals, **16** (1852), A-17.

in the solubility of carbon which prevents the nitride from being educed. Moreover, this may have connection with the results by Josefsson and Kula[(5)], that is, in the determination of nitrogen content by internal friction method, the decreasing velocity of Q^{-1}_{Max} was small in the case of steel containing carbon and nitrogen

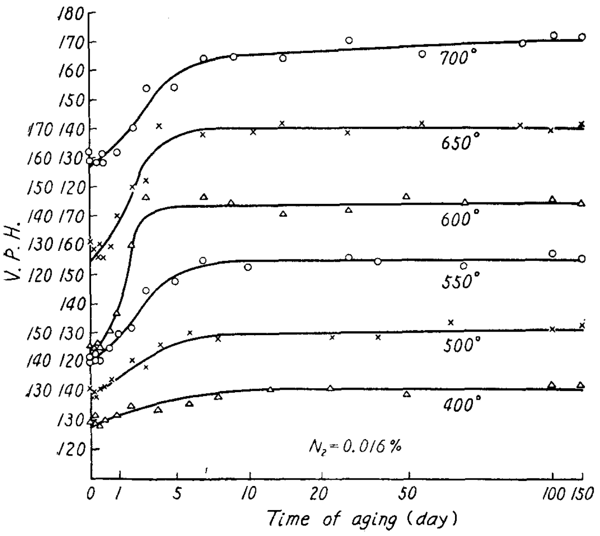

Fig. 3. Age-hardening of the specimen containing 0.016 per cent nitrogen.

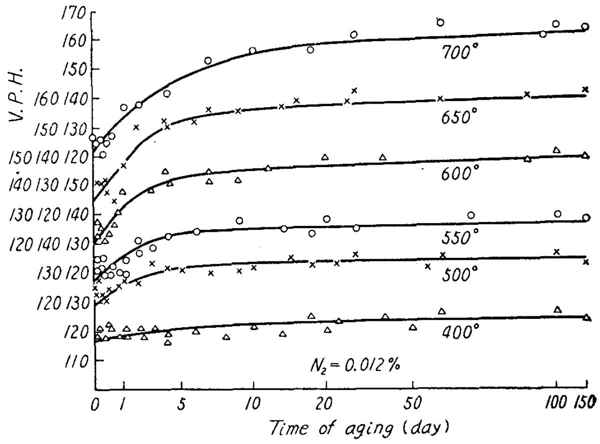

Fig. 4. Age-hardening of the specimen containing 0.012 per cent nitrogen.

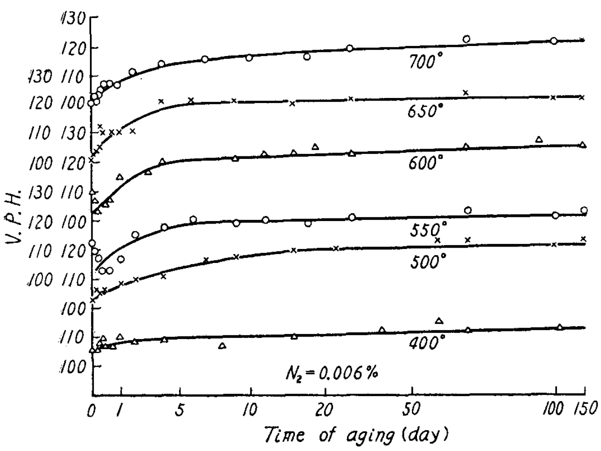

Fig. 5. Age-hardening of the specimen containing 0.006 per cent nitrogen.

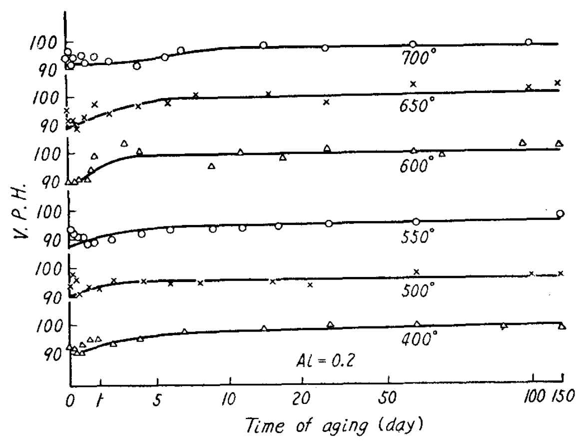

Fig. 6. Age-hardening of the specimen containing 0.016 per cent nitrogen with the addition of 0.2 per cent aluminium as the stabilizer of nitrogen.

though eutectoid reaction.

Figs. 2~5 show the results on the age-hardening of various kinds of steel containing nitrogen of 0.025, 0.016, 0.012 and 0.006 per cent, respectively. They are similar to that shown in Fig. 1. The initial aging rate of the specimen referring to Fig. 2 is larger than those of the other specimens. This specimen was prepared by adding nitrogen only with nitrogenized manganese without accompanying $CaCN_2$, and the time of melting was 65 mins (high oxygen content one),

(5) Ake Josefsson, J. Met., **4** (1952), 161.

while it was 50~55 mins for the other specimens. Similar results were obtained also in the specimens containing less silicon. From the above results it seems that this phenomenon is due to the high oxygen or oxide content; therefore, the effect of oxygen content on the quench-aging of steels should also be investigated.

The specimen referring to Fig. 6 was prepared by adding 0.2 per cent aluminium after adding 0.016 per cent nitrogen, and that to Fig. 7 by adding 0.15 per cent titanium and 0.15 per cent aluminium to fix nitrogen. The degree of age-hardening remarkably decreased in both specimens.

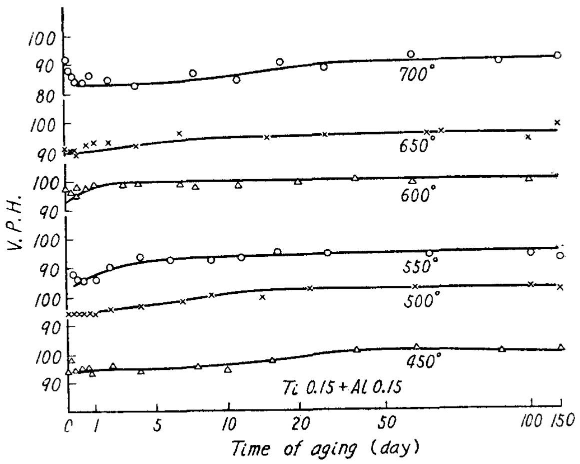

Fig. 7. Age-hardening of the specimen containing 0.015 per cent nitrogen with the addition of 0.15 per cent titanium and 0.15 per cent aluminium as the stabilizer of it.

Fig. 8 shows the relation between the nitrogen content and the degree of age-hardening. The mark ▲ indicates the result for the specimen annealed at 700°C for 3 hrs, △ refers to the specimen annealed at 700°C for 3 hrs and aged at 30°C for 30 days, × is of the case of heating at 600°C for 3 hrs followed by water-quenching, and ○ indicates the result for the specimen heated at 600°C for 3 hrs, water-quenched and aged

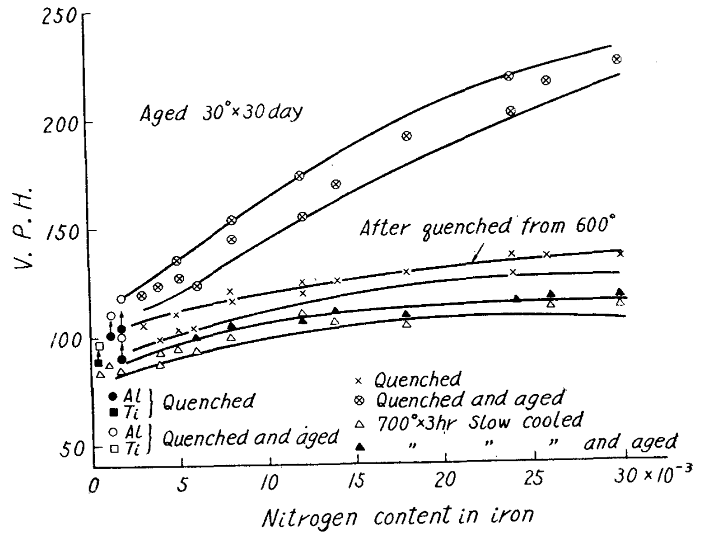

Fig. 8. Relation between the nitrogen content and the degree of age-hardening.

at 30°C for 30 days, in which the age-hardening seemed almost completely developed. In the left corner of the figure the hardness of the specimen in which nitrogen content was fixed by using aluminium and titanium is shown. (This amount of nitrogen is not the analytical value, but has an effect on the age-hardening.)

It will be noticeable that the increase in hardness is 10～20 in the case of the specimen containing 0.003～0.005 per cent nitrogen, and that almost the same degree of increase in the hardness is observed also in the specimen in which nitrogen content is fixed by using aluminium and titanium. This may be considered to be that the increase in hardness is due to the carbon content (0.02～0.03 per cent), because the dissolved amounts of both nitrogen and oxygen in α-iron seem to be fairly small.

As for the effect of oxygen content on the age-hardening, both in the case of high nitrogen specimen prepared by using nitrogenized manganese and $CaCN_2$ (the addition of $CaCN_2$ seems to make slag reducing) and in the case of the specimen prepared only with nitrogenized manganese, the same result was obtained as shown in Fig. 8. Therefore, oxygen content seems to have little effect on the age-hardening. (Of coures, the same amounts of manganese and silicon were contained in the specimen.)

Next, the results on the age-hardening of specimens containing 0.15 per cent carbon and aged at 30°C are shown in Figs. 9～13. The specimen for Fig. 9

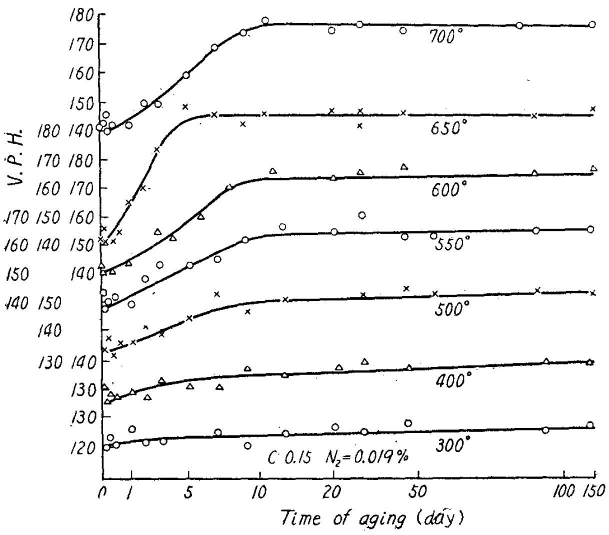

Fig. 9. Age-hardening of the specimen containing 0.15 percent carbon and 0.019 per cent nitrogen.

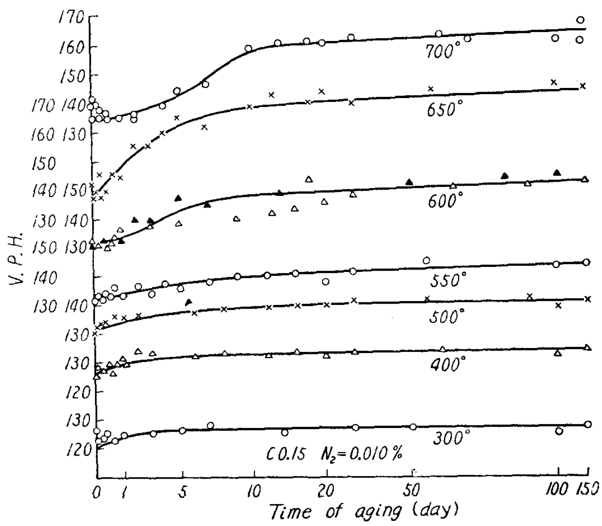

Fig. 10. Age-hardening of the specimen containing 0.010 per cent nitrogen.

contains 0.019 per cent nitrogen, that for Fig. 10 contains 0.010 per cent nitrogen, that for Fig. 11 contains 0.019 per cent nitrogen with the addition of 0.2 per cent aluminium to fix it, and that for Fig. 12 contains 0.019 per cent nitrogen with the addition of 0.15 per cent titanium and 0.15 per cent aluminium as the stabilizer of nitrogen. Fig. 13 shows the result for the specimen fused in vacuum. The results for these specimens are nearly the same as those containing 0.02～0.03 per cent carbon, that is, the larger the nitrogen content, the larger the age-hardening is, and the age-hardening decreases when the nitrogen in the specimen is fixed by adding aluminium or titanium. Further, it will be needless to say that the low age-hardening in the vacuum-fused specimen is due to low nitrogen content. Moreover, the specimens prepared by adding aluminium or titanium, or by vacuum fusion showed the hardening degree of 10~20 V.P.H., which became high with the rise of quenching temperature. From this fact it seems that the age-hardening in this case is caused by carbon.

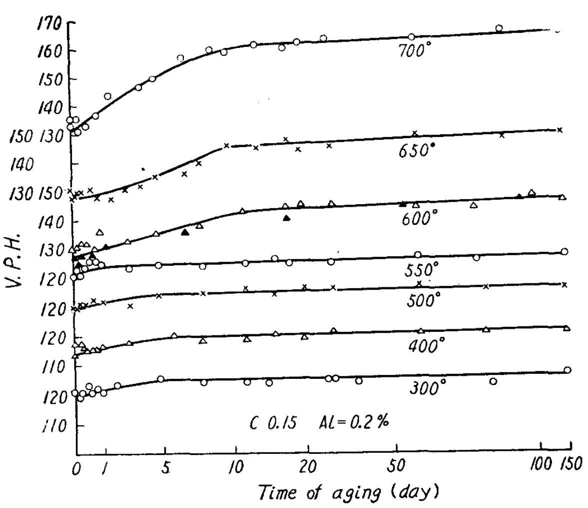

Fig. 11. Age-hardening of the specimen containing 0.15 per cent carbon and 0.019 per cent nitrogen with the addition of 0.2 per cent aluminium as the stabilizer of nitrogen.

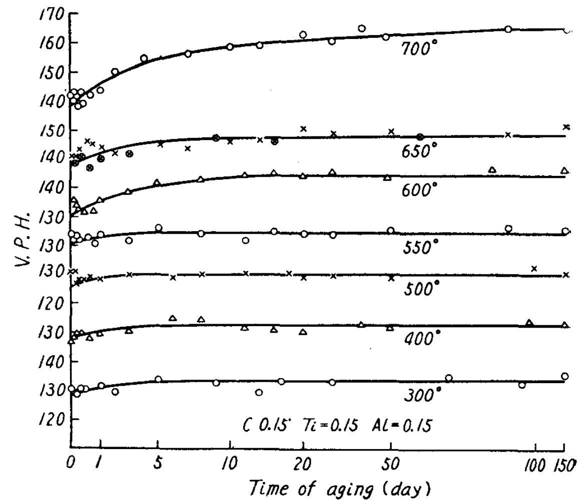

Fig. 12. Age-hardening of the specimen contaig 0.019 per cent nitrogen with the addition of 0.15 per cent titanium and 0.15 per cent aluminium as the stabilizer of it.

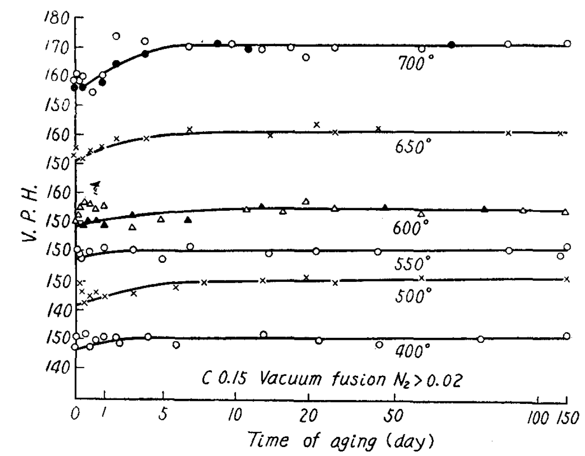

Fig. 13. Age-hardening of the specimen fused in vacuum.

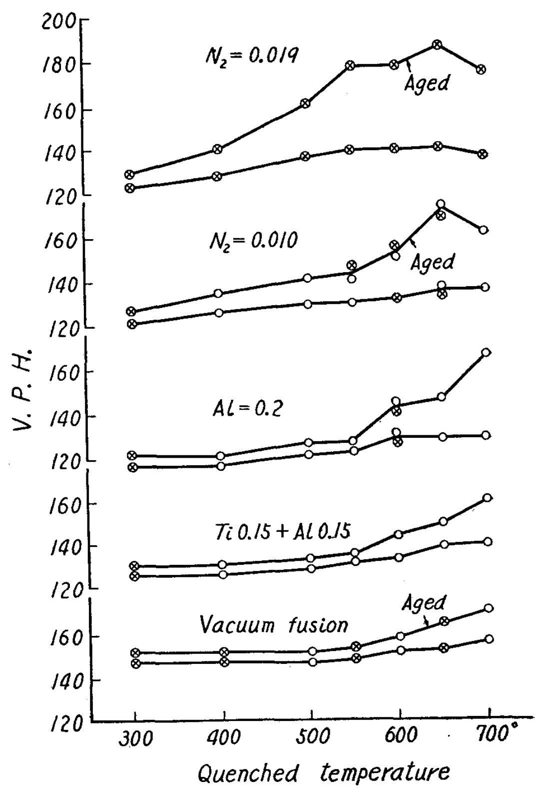

Fig. 14. Effect of quenched temperature on the degree of age-hardening in steels containing various amount of nitrogen.

Fig. 14 is the summary of the above results; in the figure the hardness of various steels immediately after quenching and the maximum hardness after aging are shown. In high nitrogen specimens, when quenched at about 400~500°C, the age-hardening occurred, at 600~650°C it showed the maximum hardness and at 700°C the degree of age-hardening decreased. As mentioned above, in the case of the specimen quenched at 700°C, the age-hardening progressed slowly (the increase of hardness was recognized even after aging for more than 300 days) as seen in Figs. 9 and 10, while in the case of low nitrogen specimens (Figs. 11, 12 and 13) the age-hardening increased with the rise of quenching temperature. From this fact it seems that the age-hardening due to carbon occurs. Moreover, the difference in the hardening rate was small, and the experimental values of hardness scattered and, therefore, it can be said, though not exactly, that the rate of age-hardening due to carbon is slower than that due to nitrogen.

Fig. 15 shows the hardening curves for the specimen containing 0.025 per cent carbon and 0.016 per cent nitrogen (the same as the specimen for Fig. 3) after quenching at 650°C followed by aging at various temperatures. As shown in the figure, in the case of the aging at 50°C the maximum hardness appeared after 10 hrs, in the case of 100°C it appeared after 2~4 hrs and at 150°C it was after 15 min. Moreover, in the case of the aging at 30°C the maximum value appeared by aging for about 7 days, which is seen in Fig. 3. The time taken to reach the maximum hardness becomes short, and the degree of age-hardening becomes small with the rise of aging temperature.

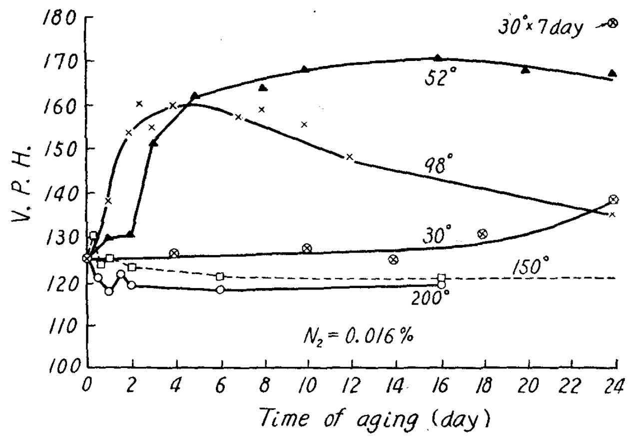

Fig. 15. Effect of aging-temperature on the age-hardening of the specimen containing 0.016 per cent nitrogen.

In the present experiment, the following facts were clarified: (1) the age-hardening occurs in two steps (600 and 650°C quenching in Fig. 2); (2) in an early stage of aging the hardness decreases and then begins to increase with the progress of aging (600 and 550°C quenching in Fig. 5).

Summary

(1) Nitrogen mostly affects the age-hardening of quenched steel.

(2) Carbon becomes a cause of age-hardening in the case of low nitrogen content, but the hardening degree is about 20 V.P.H. in spite of a suitable condition of hardening.

(3) The lower the aging temperature, the slower the aging rate and the larger the maximum hardness are.

(4) Oxygen (or oxide) seems to increase the aging rate, but its effect on the age-hardening is small.

Acknowledgements

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