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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	13
page range	57-66
year	1961
URL	http://hdl.handle.net/10097/27023

Nitrogen as an Alloying Element in Steels.
The Effect of Nitrogen on the Tempering of Cold-Worked Steels*

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(Received January 23, 1961)

Synopsis

The present investigation has been carried out to ascertain the effect of nitrogen on the tempering of the cold-worked steels. On steels containing various percentage of nitrogen, manganese, aluminium and titanium, the magnetic and electrical properties have been measured under the condition of cold-working and tempering. From these investigation it has become clear that: (A) The changes at about 100, 250 and 400～550°C begin to appear with the addition of nitrogen and become conspicuous as the nitrogen increases. (B) The relief of cold-working stress begins to appear at the temperature of about 300°C. (C) The change at about 100 or 250°C is due to the precipitation of nitrogen or carbon. (D) The changes at about 400～550°C and 650°C are due to re-solution of nitrogen and carbon respectively. (E) The effect of nitrogen is reduced as manganese increases.

I. Introduction

Studies have been made by many workers(1)～(8) on changes in the properties of steel caused by cold-working and on changes in the properties by tempering of cold-worked steel, and recently there have been many studies on the hardening up to about 300°C(9). However, only a few studies have been made on the effect of nitrogen on it. Köster(2) et al. reported that the hardening was accompanied with the precipitation and re-solution of nitrogen and carbon compounds(10), but recent studies have made it clear that the nitrogen in steel plays the principal role in the quench- and strain-aging(11)～(13). The present study was made to

* The 1015th report of the Research Institute for Iron, Steel and Other Metals. Read at the Annual Meeting of the Japan Institute of Metals, in Tokyo, Apr., 1953.

(1) W. Köster, H. V. Kockritz and E. H. Schulz, Arch. Eisenhüttenwes., **6** (1932/33), 55.
(2) W. Köster, Arch. Eisenhüttenwes., **2** (1928/29), 503; **3** (1929/30), 533.
(3) L. B. Pfeil, J. Iron Steel Inst., **118** (1928), 167.
(4) K. Tamaru, Kinzoku-no-Kenkyu, **6** (1928), 87.
(5) G. Shinoda and M. Kawasaki, J. Jap. Inst. Metals, **14B** (1950), No. 8, 12; **15B** (1951), No. 5, 199.
(6) J. H. Andrew and H. Lee, J. Iron Steel Inst., **145** (1942), 153.
(7) M. Balicki, J. Iron Steel Inst., **151** (1945), 181.
(8) G. Sacks, Iron Age, **161** (1948), 78.
(9) Y. Imai, No. 9 Report of 5th Committee Meeting of Japan Institute of Metals.
(10) Y. Imai and T. Ishizaki, J. Japan Inst. Metals, **16** (1952), A-110, A-148.
(11) Y. Imai and T. Ishizaki, ibid., **10** (1953), 318.
(12) Y. Imai and T. Ishizaki, ibid., **17** (1953), 209.
(13) Y. Imai and T.Ishizaki, Speech at Meeting of Japan Inst. Metals, April 1954.

ascertain the idea that nitrogen should have some effect on the changes in the properties of steel described above.

II. Preparation of specimens

Electrolytic iron was melted in the high frequency electric furnace and cast into cubes of 35 mm by changing deoxidizing and denitrifying methods using Mn, Si, Al, Ti, etc. Calcium cyanonitride and manganese nitride were used for the addition of nitrogen(14). Steel ingots were made into 4 mm ϕ in size by the forging-roller, and those which would undergo tempering in hydrogen stream were tempered at 710°C for 30 hours, and specimens of ϕ 2.5 mm and those of ϕ 2.1 mm were prepared by drawing. These specimens were made perfect tempering specimens by heating them up to 900°C and cooling in the furnace and further heating at 550°C for 3 hours and cooling down at 1°C/min. They were then worked into 1.7 mm ϕ by drawing (care was taken to prevent temperature from rising during the working). The degree of working was 53 and 34 percent respectively.

The specimens were allowed to stand at room temperature for 6 months in order to get sufficient strain-aging. They were tempered at 50 to 700°C for 1 hour each and cooled at 1°C/min, and they were allowed to stand at room temperature for 8 months to get further sufficient strain-aging. Then the measurement of the specimens were made. Carbon content in the specimen was slightly more than the carbon solubility in α-Fe, carbon compound being barely observable under microscope. An analysis showed that 0.2 to 0.03 % of C, 0.11 to 0.20 % of Si (the margin being due to the difference in Mn content) and about 0.003 % of P and about 0.008 % of S were present. As the effect of nitrogen depends upon Mn content, explanations are to be made on Mn contents in specimens by dividing them into 0 % of Mn (less than 0.01 %), 0.15 % of Mn (0.14 to 0.17 %) and 0.25 % of Mn (0.23 to 0.25 %).

III. Experimental method

Measurements were made, by means of a ballistic ammeter method, of the initial permeability μ_0, the maximum permeability μ_{max}, the coercive force Hc and the residual induction Br with specimens 1.7 mm $\phi \times 100$ mm, and electric resistance with the same specimens at room temperature. Measurements of μ should have been made at temperature near -20°C(15), but because of the apparatus used, they were made only at room temperature. μ_0 were measured at 1.95 Oe.

IV. Experimental results

Figs. 1 to 3 show the relation between the tempering temperature and μ_0 of the specimens 53 % cold-worked containing respectively 0 %, 0.15 % and 0.25 % of Mn. As clearly seen in the figures, five changes could be observed, namely, a slight decrease of μ_0 at about 100 and 250°C (this became clearer with the changes

(14) Y. Imai and T. Ishizaki. J. Japan Inst. Metals, **16** (1952), A-17.
(15) J. L. Snock, Physica, **6** (1939), 161.

in Hc and Br), a sudden increase of μ_0 at about 300 to 400°C, the lowering of μ_0 from about 400° to 550°C and a decrease of μ_0 at about 650°C. According to Köster et al.(2), a slight decrease of μ_0 both at about 100 and 250°C is due to the precipitation of nitrogen and carbon compounds. The experiment being performed after sufficient strain-aging of the specimens, the value of μ_0 of the specimens before the tempering was low ; consequently, the precipitation caused by tempering was not clearly observable (Changes in Hc and Br were observable even in the case of small changes). As described later a comparison of the values before and after the treatments will indicate that the effect of nitrogen has a great deal to do with it.

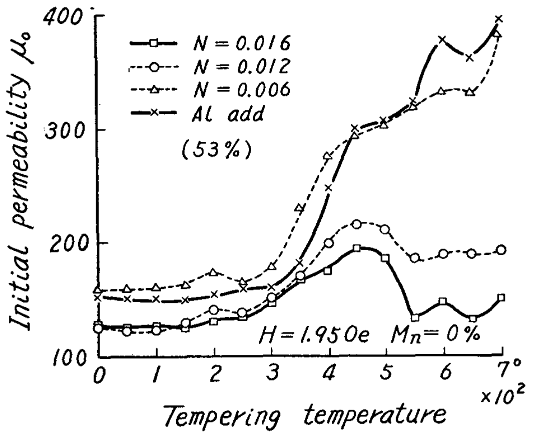

Fig. 1

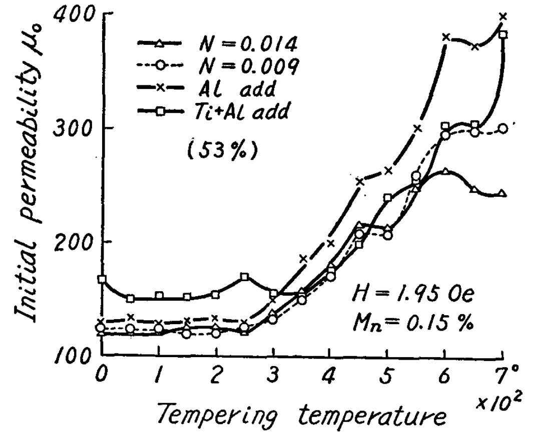

Fig. 2

The recovery of μ_0 at about 300 to 400°C was a phenomenon common to all the specimens, which seems to be, according to the results of studies by many workers(16), due to the release of stress by cold work. (recovery of crystals and recrystallization).

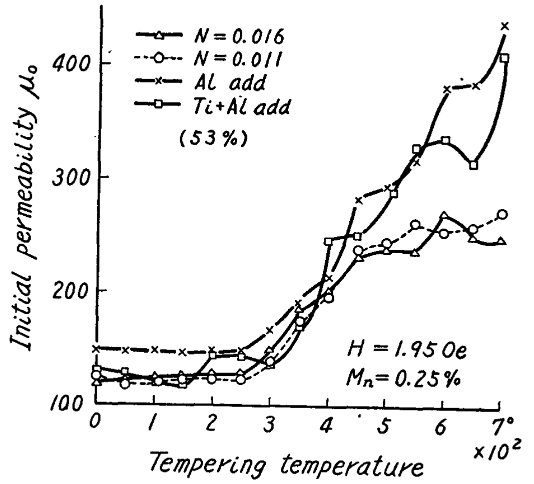

Fig. 3

As clearly seen in the figure, the lowering of μ_0 at about 400 to 550°C was greater in those in which nitrogen content was larger, and smaller in those in which nitrogen was fixed by Al or Ti. This change is under the effect of the cooling rate, tempering and aging, it seems that the nitrogen already precipitated is present as solid solution again due to the disappearance of stress by cold work and an increase in solubility in α- iron(17) and lowers the value of μ_0 by re-precipitation at the time of cooling. This change and the changes observable at 650°C are considered to correspond to the maximum at about 600°C shown in the result of measurement performed by Nishiyama et al.(18) by electrode potential.

(16) G. Shinoda, M. Tanaka and K. Suzuki, J. Japan Inst. Metals, **14B** (1950), No. 10, 25.
(17) Y. Imai and T. Ishizaki, ibid., **15A** (1951), 276.
(18) Z. Nishiyama and M. Yamamoto, ibid., **15B** (1951), No. 1, 7.

The lowering of the value of μ_0 at 650°C is a phenomenon common to all the specimens, which is considered to be due to the resolution of carbon compound, similarly to the change due to the resolution of nitrogen, as it is also affected by the cooling rate and aging at room temperature.

The changes due to the difference in the grain size deserve our consideration. Therefore, a consideration is given, based on the experimental results obtained by Nishiyama et al.[18] and on the view of Ruder[19] that although the grain size has some effect, other factors, such as purity, the method of making specimens, the size of the specimens and heat-treatment, are so important that each of them can easily cover any effect caused only by the grain size.

A comparison of Figs. 1 to 3 with one another reveals that the effect of nitrogen is small in those in which Mn content is large especially in case on the changes at 400 to 550°C. This is perhaps attributable to the same cause that we observed in the study of precipitation of nitrogen that the presence of manganese makes effect of nitrogen smaller.[20] In figures Al add. or Al+Ti add. means the specimens in which nitrogen is stabilized by 0.2 % Al or 0.15 % Ti+0.15 % Al after the addition of nitrogen by 0.015 %, and, as clearly seen in the figure, the values of μ_0 are high at temperatures above 400°C, showing that the effect of nitrogen is small in this range. It is conceivable from this and what has been described above that there is hardly any change up to about 300°C in the case of iron with high purity and its value abruptly rises with uniform change due to the disappearance of stress at about 300°C.

Figs. 4 to 6 show the values of μ_{max} of the 53 % cold-worked specimens. Simi-

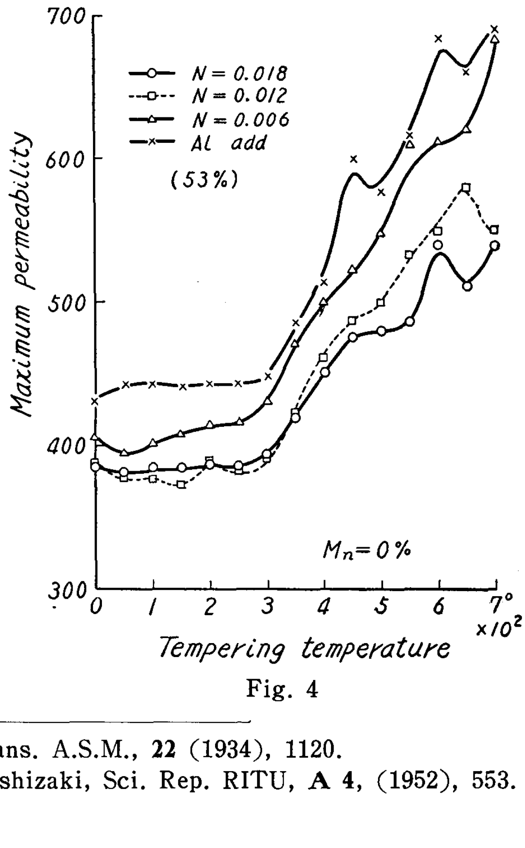

Fig. 4

(19) W. E. Ruder, Trans. A.S.M., **22** (1934), 1120.
(20) Y. Imai and T. Ishizaki, Sci. Rep. RITU, **A 4**, (1952), 553.

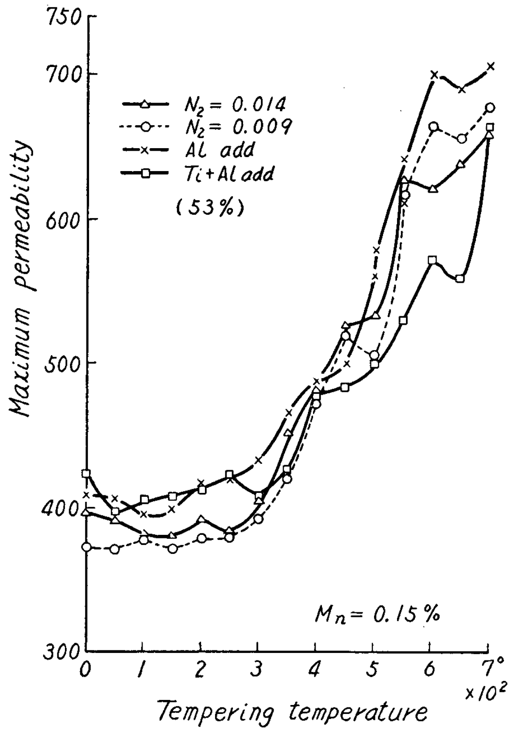

Fig. 5

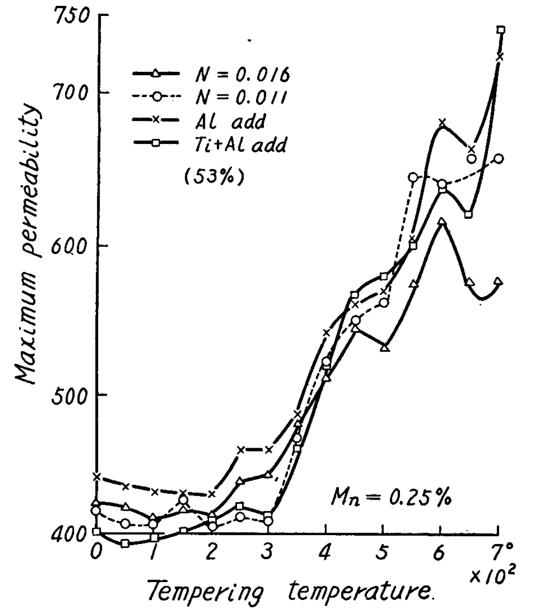

Fig. 6

lar to the case of μ_0, a slight lowering of the value of μ_{max} was observed at about 100 and 250°C, a sudden increase in the value with the disappearance of worked stress at about 300°C, and a lowering of the value at about 400~550°C and 650°C. They also show that the effect due to the difference in the content of nitrogen is smaller in those in which Mn content is high.

In the preceding section, we have described the changes observable in 53%-worked specimens, and in Figs. 7 to 10 is shown an example of the results obtained from 34%-cold-worked specimens. As in the case of 53%-worked specimens, some changes are observable in this case, but changes due to the difference in the

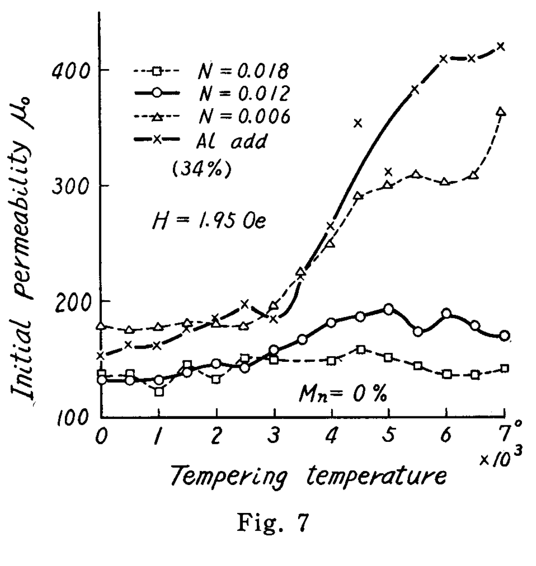

Fig. 7

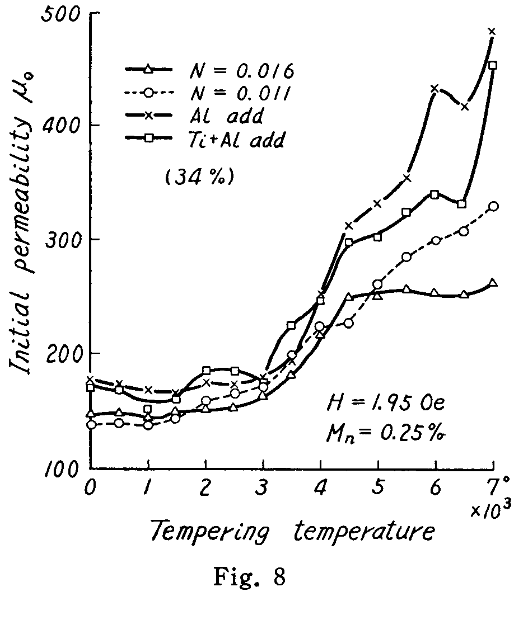

Fig. 8

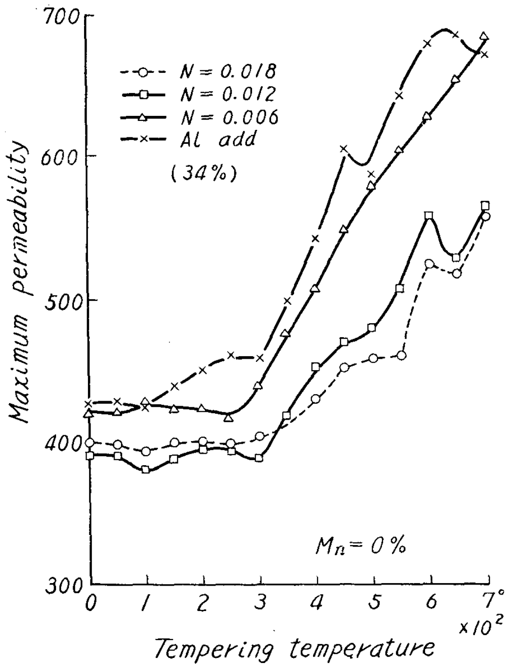

Fig. 9

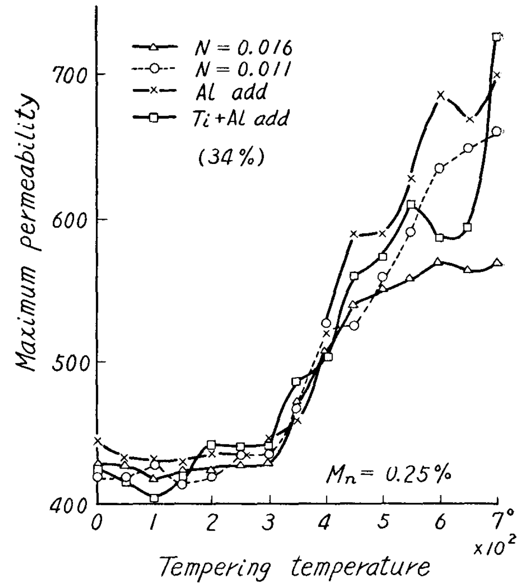

Fig. 10

degree of working cannot be observed, but those specimens which are low in the degree of working show high value in the range of low temperature.

Fig. 11 shows changes in Hc with the specimens without Mn. It can be seen clearly that rather obscure changes in μ_0 and μ_{max} become clearer in Hc at about 100 and 250°C and that the change is greater when nitrogen content is larger. The lowering in the value of Hc due to the disappearance of the strain is observable at about 300°C, Hc increases again at 450 to 500°C and increases further at about 650°C. It is to be noted that the increase of Hc at about 450 to 500°C is the larger in those containing nitrogen the more. For such phenomenon the same explanation can be given as in the case of μ_0 and μ_{max}.

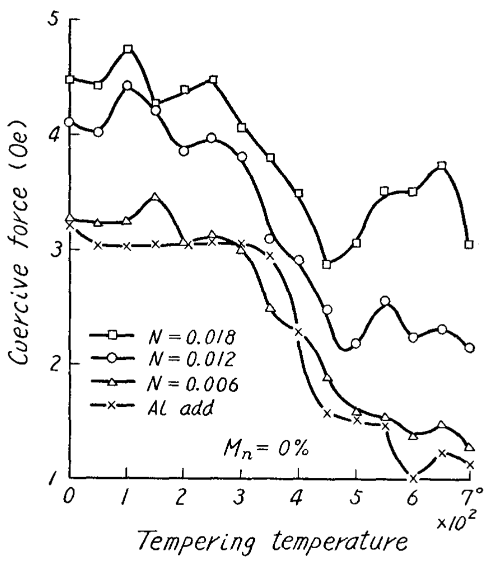

Fig. 11

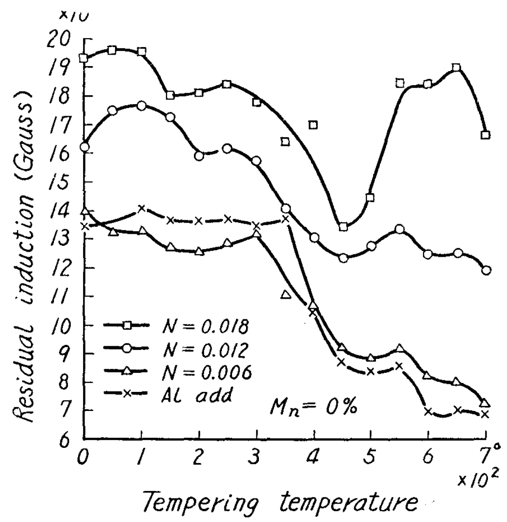

Fig. 12

Fig. 12 shows Br of the specimens which contain 0 % of Mn. Changes the same as those in Hc can be seen in it. When Mn is present in large amount, the effect of nitrogen becomes small as in the case of μ_0 and μ_{max}, but no change is observable in the result. The difference due to the degree of working is that the values of Hc and Br become lower in those in which the degree of working is less, but other results are the same as the other specimens.

It is clear from the descriptions made in the preceding sections that nitrogen has effect on them, and Figs. 13 and 14 show the results obtained from the specimens prepared by annealing in hydrogen at about 710°C, denitrified[21], worked and tempered. They show the changes in μ_0 and μ_{max} of the specimens containing 0.25 % of Mn and 0.016 % of nitrogen and nitrogen stabilized marked ● ▲ and not stabilized marked ○ △ and changes in Hc and Br, all of which were worked 53 %. That is, when the same specimen is treated by hydrogen, the values of μ_0 and μ_{max} are raised and those of Hc and Br are lowered, all of which are considered to be due to cold working; however, it will be known that the lowering of the values is due to the strain-aging caused by nitrogen (carbon) and that the lowering of the values by working is not so great.

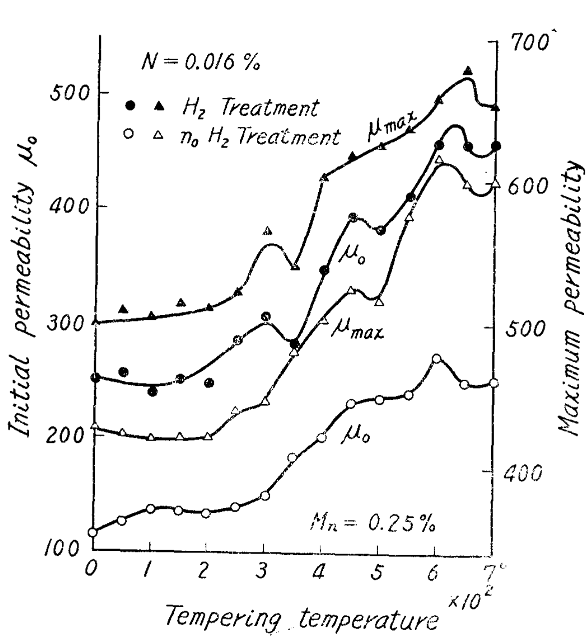

Fig. 13

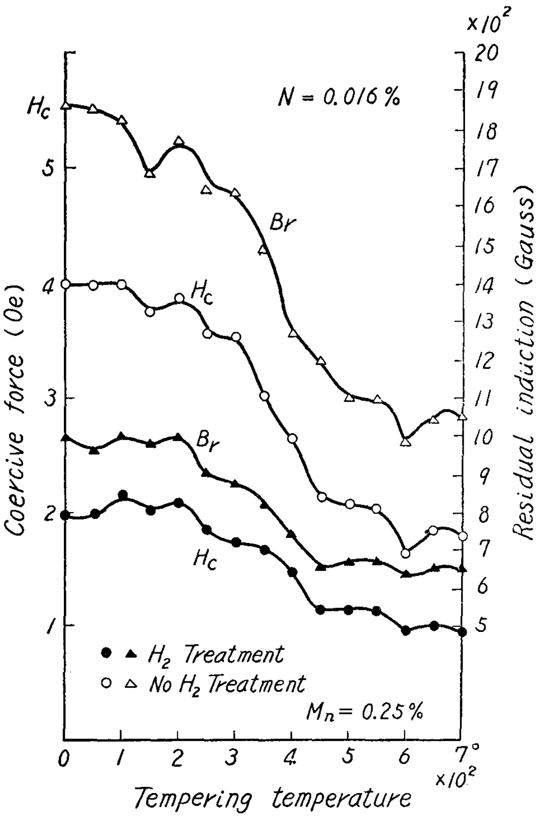

Fig. 14

In curves for μ_0 and μ_{max}, it is seen that the changes in hydrogen-annealed specimens in the range from 400 to 500°C are about the same as those in which nitrogen was stabilized with Al or Ti. (See Figs. 3 and 6). As observed in the changes in Hc and Br, the change observed by nitride crystallized at 300°C was

(21) Y. Imai and T. Ishizaki, J. Japan Inst. Metals, **14B** (1950), No. 10, 21.

small in the specimens treated with hydrogen. That is, a decrease in the effect of nitrogen can be observed in the specimen containing manganese.

The phenomena similar to the magnetic properties above-described, were observed in the change in their electric resistance. However, it was impossible to obtain quantitative results as there were relatively many changes in the measured values. Fig. 15 shows an example of such cases. On the whole, it may be said that these changes can be observed at the same temperature at which the change in magnetic properties takes place.

We shall next show the relation between the change in properties and the amount of nitrogen induced by cold-working and strain-aging. Fig. 16 shows the values of μ_0 and μ_{max} obtained on the annealed specimen (furnace cooled from 950°C and kept at 550°C for 3 hours then cooled gradually) and on the specimens cold-worked and aged for 400 days at room temperature. It also shows that the larger the content of nitrogen, the lower the values are. The values on the specimens containing aluminium are shown in the left of the figure. Those containing much nitrogen show low values even without working; for example, the value of μ_0 of N_2 0.018 is about 180, which is equal in value to N=0.06 % after working.

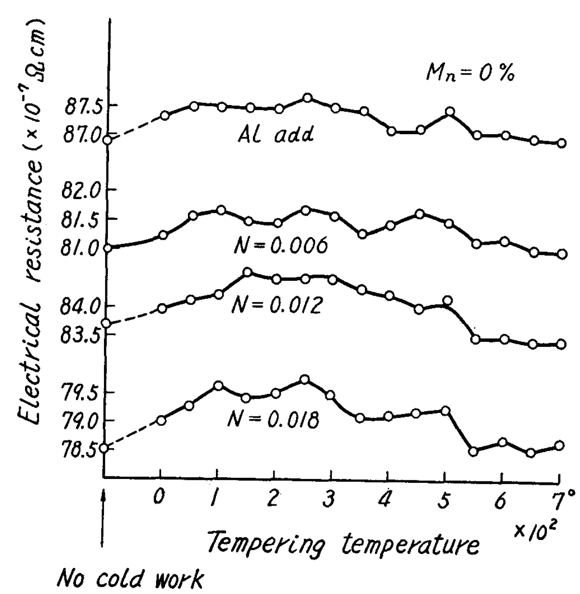

Fig. 15

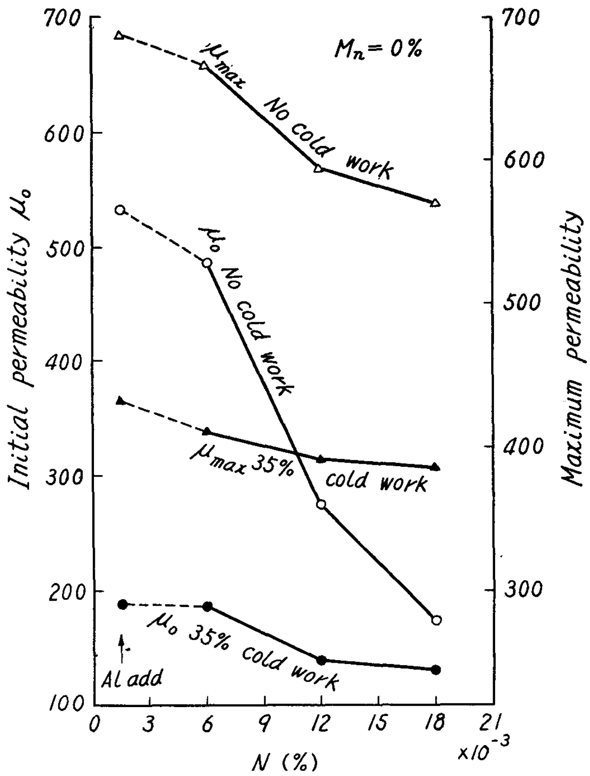

Fig. 16

Fig. 17 shows the results obtained from Hc and Br and is similar to Fig. 16. Figs. 18 and 19 show the results obtained from those specimens containing manganese; the results are similar. In Fig. 19 there is a case where annealing in hydrogen stream was performed, and it must be noted that in such a case the specimens, both with working and without working, showed considerably high

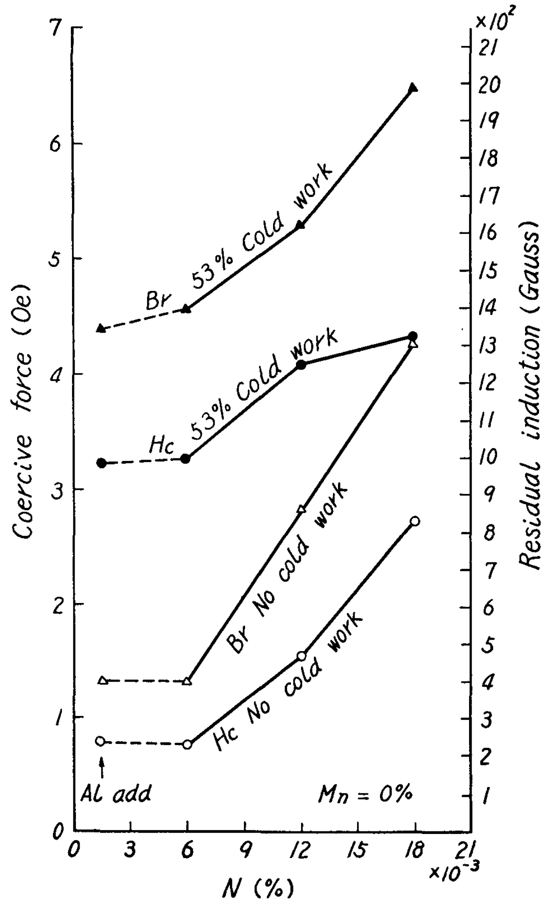

Fig. 17

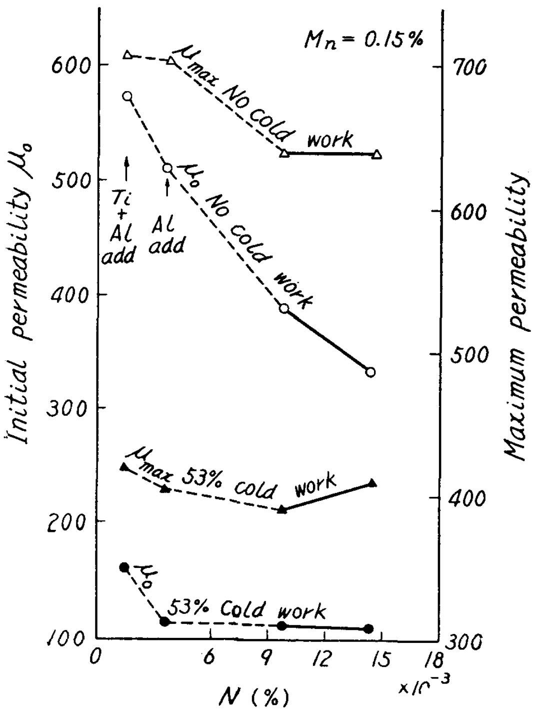

Fig. 18

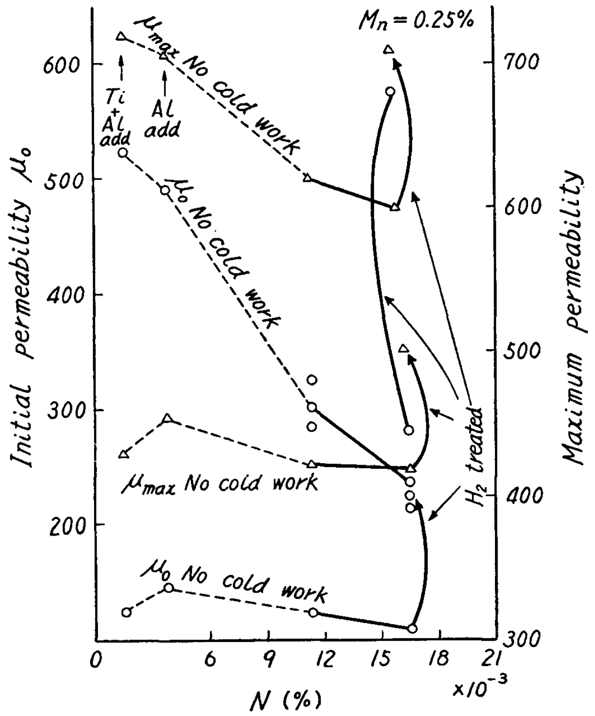

Fig. 19

value in case the denitrification (partial denitrification) was performed on them. A decrease in value appeared in the case of Hc and Br, but data is omitted.

Summary

(1) In tempering steels worked at room temperature, changes can be observed at 100, 250, 300 to 400°C, 400 to 500°C and around 650°C, and with the addition of nitrogen, more changes appear at 100, 250 and 400 to 550°C.

(2) All the changes are clearly observable in Hc and Br, but in μ_0 and μ_{max} they are not so clearly observable at 100 and 250°C.

(3) A clear relation is present between cold-working and strain-aging and the amount of nitrogen contained.

(4) The larger the amount of manganese, the less the effect of nitrogen will be.

(5) The changes at 100°C and around 250°C are accountable as phenomena on precipitation of nitrogen and carbon, those at 300 to 400°C as disappearance of worked-strain and those at 400 to 550°C and at 650°C as phenomena on re-precipitation of nitride and carbide after re-solution.