Effect of Nitrogen and Other Alloying Elements on the Low-Temperature Brittleness of Steel. I : Correlation of Nitrogen and Carbon

著者	ISHIZAKI Tetsuro, IMAI Yunoshin
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	17/18
page range	61-69
year	1965
URL	http://hdl.handle.net/10097/27217

Effect of Nitrogen and Other Alloying Elements on the Low-Temperature Brittleness of Steel. I
Correlation of Nitrogen and Carbon*

Tetsurô ISHIZAKI** and Yûnoshin IMAI

The Research Institute for Iron, Steel and Other Metals

(Received May 27, 1965)

Synopsis

U-notch Charpy tests were performed with steels containing 0.3 to 0.4% of manganese, 0.15 to 0.25% of silicon, 0.003 to 0.005% of phosphorus, 0.015 to 0.030% of sulphur, 0.003 to 0.019% of nitrogen, 0.03 to 0.82% of carbon and copper in order to clarify the effect of nitrogen and carbon on the low-temperature brittleness of carbon steel. The results obtained were as follows. 1. The transition temperature rises with increasing content of nitrogen and carbon. 2. The effect of nitrogen becomes greater with lowering grade of carbon steel. 3. The transition temperature rises sharp up to about 0.008% nitrogen content, beyond which it rises gradually. 4. The effect of nitrogen is observable in low-carbon α-Fe, but less in hypoeutectoid structure, and not in eutectoid structure.

I. Introduction

Many works have been made of the low-temperature brittleness of steels, but all were concerned with the effect of the transition temperature on the mechanical properties around room temperature or below it. In these works, however, the effects of elements constituting an alloy disagreed with one another, and so the present study was carried out to clarify the effects of nitrogen and elements constituting the alloy on the low-temperature brittleness, and to explain the cause of this brittleness.

II. Experimental method and preparation of specimens

Specimens were prepared from electrolytic iron, iron alloys and pure metals selected with emphasis on nitrogen content, and melted in a high-frequency furnace. They were deoxidized with manganese and silicon, and nitrogen was added in the form of nitrogenized manganese. Potassium ferricyanide and calcium cyanamide were used in part, but other methods of adding nitrogen failed in showing any difference. After casting, they were forged into bars 12 mm$\times$12 mm, air-cooled from 950°C, machined into bars 10.3 mm square$\times$12 cm (corresponding to two Charpy test-pieces), heated at 550°C for 3 hours and cooled at the rate of 1°/min.

* The **1174th** report of the Research Institute for Iron, Steel and Other Metals.
** Technical Development Department, Fuji Iron and Steel Co., Ltd.

(Cooling below 300°C was done at a slower rate). The bars were processed with grinder and made into test-pieces with notches. V-notch was adopted instead of U-notch in the case where it was difficult to fracture completely and where there was little need of comparative test.

The specimens were heated and cooled as follows: (1) the specimens were put in liquid nitrogen; (2) temperatures below -100°C were obtained by using liquid nitrogen and lagging materials; (3) the specimens were put in alcohol and cooled by passing liquid nitrogen in copper pipe from -100°C to 0°C (c.f. Fig. 1); (4) the

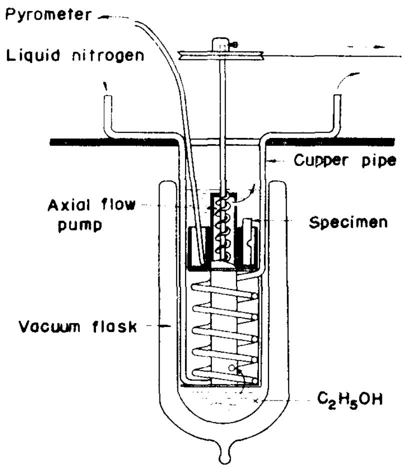

Fig. 1. Apparatus for specimen cooled.

specimens were held in water and ice at 0°C; (5) the specimens were cooled with ice from 0°C to room temperature; (6) the specimens were heated in water from room temperature to 70°C; (7) the specimens were heated in oil from 70° to 300°C.

The impact test could be carried out mostly in 3 to 5 seconds. It was found from the preliminary test that the fall in temperature was within 3°C and so no correction was necessary.

On the assumption that the relation of the absorbed energy to the testing temperature can be expressed by a gentle curve, the transition temperature was shown by taking the arithmetical mean of the highest and the lowest value of such a curve. In making out the curve, one shows frequently the lowering of the impact values in two steps (For example, they are presented when the quantity of elements of alloys to be added is large). According to the above method for determining the transition temperature, in case the curve for the impact value of the test temperature assumes the form in which temperature lowers in two steps, (the case where the upper and the lower transition temperature can be observed separately will be described in another report), it will be inaccurate, and furthermore, the change in the highest impact value will affect the transition temperature.

Consequently, in the present study, data were taken mainly on the largest absorbed energy which seems to have bearing on the toughness of steel, i.e. on the impact value at 0°C in the sense that it is representative of practical impact values and the transition temperature.

III. Experimental results

The effect of carbon on the low-temperature brittleness of steel is great when carbon is contained below 0.02%, being soluble in α-Fe, because it makes an interstitial solid solution (of which a report will be made in the next issue), whereas carbon in commercial steel is in the state of carbide. By heat-treatment, carbide assumes various shapes, becomes a factor of varying the notch sensibility, and prevents the slip-deformation of α-Fe in various extents. For comparison, therefore, it is necessary to make the shape of carbide uniform. It is possible to do so by the same heat-treatment, especially in the case where contents of alloying elements are less. The experiments were performed after this method but each time a certain unusual change occurred in structure. The specimens consisting of 0.3 to 0.4% of Mn, 0.15 to 0.25% of Si, 0.003 to 0.005% of P, 0.015 to 0.03% of S, N≒0.003% and various amount of C (Figs. 2 and 3), those consisting of N≒0.010%

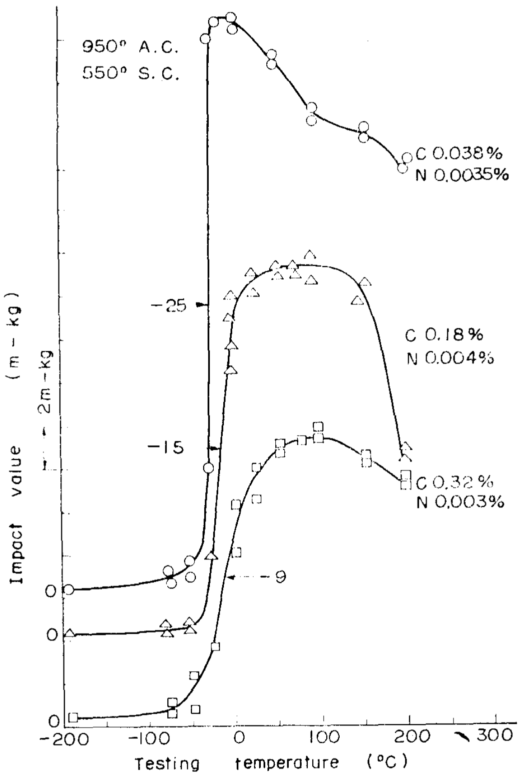

Fig. 2. Effect of temperature on impact value of C steel.

and various amount of C (Fig. 4) and those consisting of C≒0.40% and various amount of N (Fig. 5) were used. A tendency was observable that sulphur content increased, though little, with the increase in carbon content, and this was attributable to gas carbon used in making white pig iron.

It was found that the structures of the specimens were ferrite+pearlite in which pearlitic part increased with the increase in carbon content, whereas ferrite grain size tended to become fine with the increase in carbon and nitrogen content (6 to 8 G.S.N.). It was also found(1) that a small amount of string-like carbide was

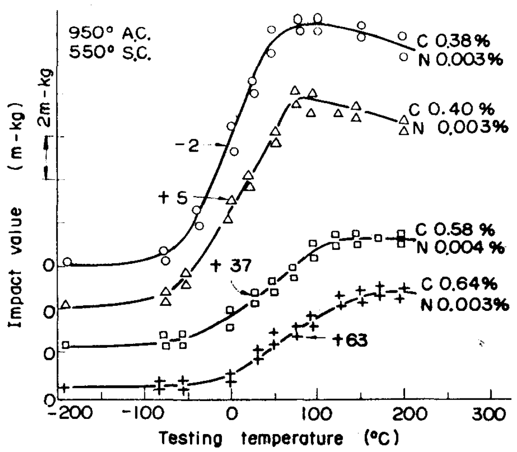

Fig. 3 Effect of temperature on impact value of C steel

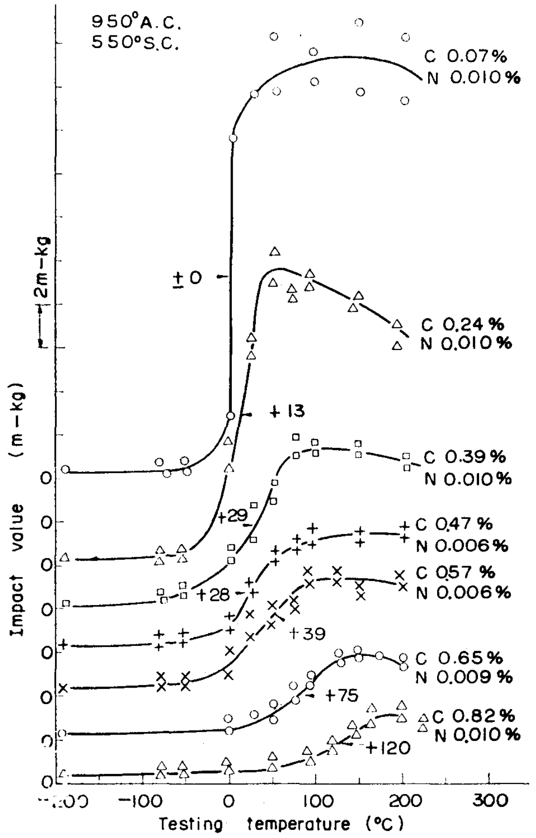

Fig. 4. Effect of temperature on impact value of C steel.

produced in low-carbon steel (less than 0.3% of carbon), (this is especially noticeable in lower-carbon steel). The string-like carbide was observed in low carbon steel

(1) K. Kikuchi, Tetsu-to-Hagané, **37** (1951), 570.

even when nitrogen content increased, or limmed or Al-killed. The results of the experiments are shown in Figs. 2 to 5, in which the numerals show the transition temperatures. Of low carbon steels, there were some which could not completely be fractured, for which the impact values were simply given. As seen clearly in the figures, no tendency was observed to lower the impact values in two steps, and the shape was rather gentle within the experimental errors. The relation between the largest impact value and the carbon content is shown in Fig. 6, in which the

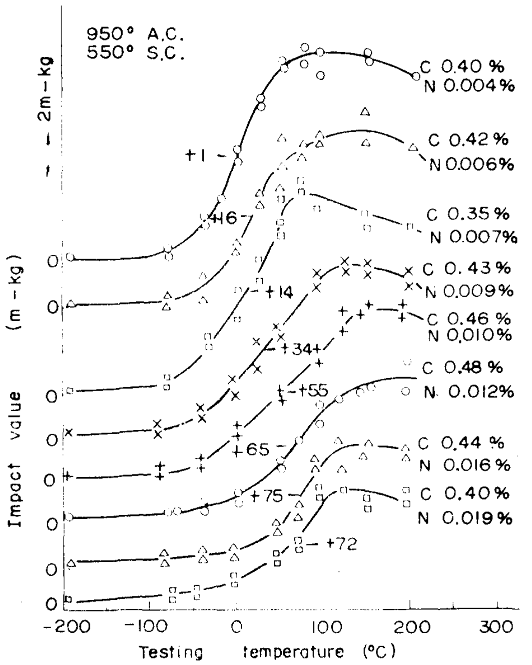

Fig. 5

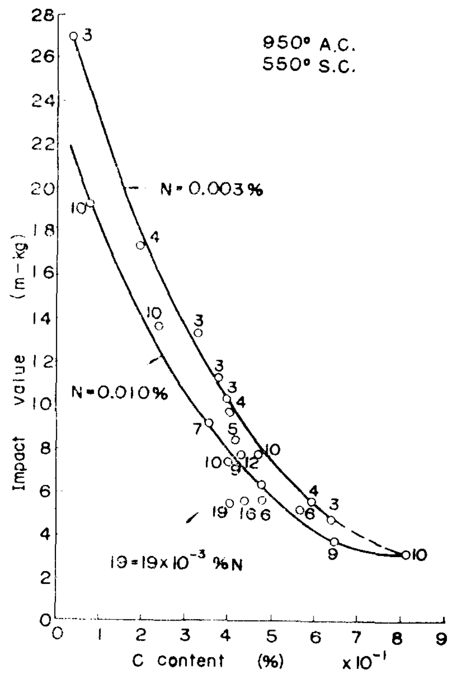

Fig. 6

Fig. 5. Effect of temperature on impact value of C steel.
Fig. 6. Effect of C and N content on max. impact value of C steel.

numerals show nitrogen content. It will be seen in the figure that the increase in nitrogen and carbon content lowers the largest impact values, making the steels more brittle. In the figure are drawn lines corresponding to N=0.003% and N=0.010%, showing that the effect of nitrogen disappears at the eutectoid structure. It is conceivable that this is due to the fact that nitrogen acts mainly on ferrite itself but little on the pearlitic structure.

Fig. 7 shows the relation between the impact value and the carbon content; the relation similar to that shown in Fig. 6 was observed more clearly; this was because the transition temperature was above 0°C. In Fig. 8 is shown the relation between the transition temperature was above 0°C. In Fig. 8 is shown the relation between the transition temperature and the carbon content; the transition temperature became high with the increase of carbon content (the result was the same as that obtained at the temperature at which the impact values given in Figs. 2 to 5 began to lower), but it was gentle in the low-carbon side and abrupt in the high-carbon side. When the carbon contents were the same, the transition temperature was higher in those steels with larger carbon content; similar to the case of impact value, the effect of nitrogen was great in the low-carbon side, and in the high-carbon side it tended to disappear, at least, the eutectoid structure. If a study is made of the effect of carbon on steel in which nitrogen content is less than in the present case (less than 0.003% N), it will be conceivable that the transition temperature rises more rapidly with the increase in carbon content. This will be discussed on another occasion.

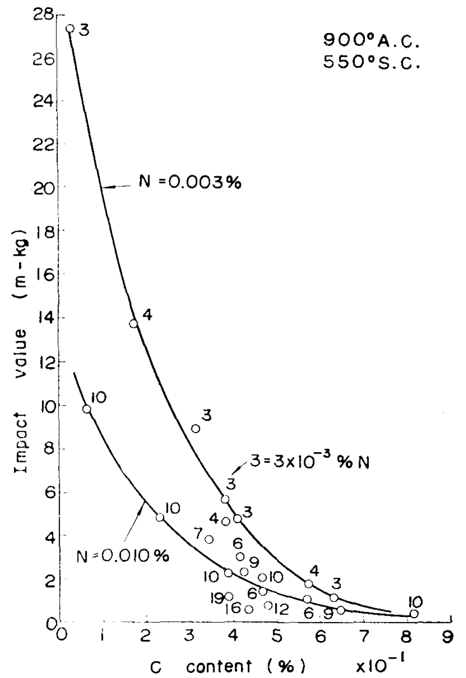

Fig. 7

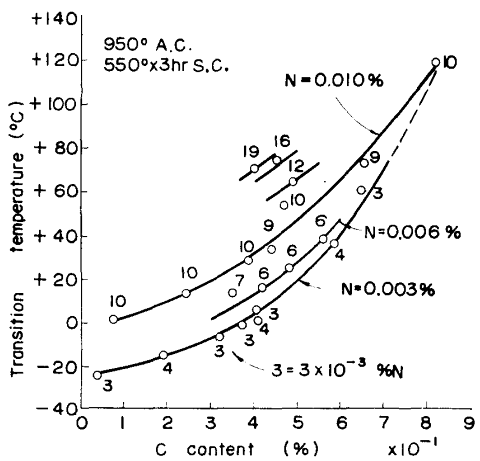

Fig. 8

Fig. 7. Effect of C and N content on impact value at 0°C of C steel.

Fig. 8. Effect of C and N content on transition temperature of C steel.

Although the impact value lowers and the transition temperature rises with the increase in carbon content, as mentioned above, on the whole, they are proportional to the carbon content, of which the principal cause is to be found in the increase of volume of the pearlitic structure[(2)]. The string-like carbide observed at carbon content less than 0.3% would naturally raise[(1)(3)] the transition temperature, on account of which the change in the transition temperature was gentle in the low-carbon side.

Figs. 9 and 10 show the relation between the nitrogen content and the greatest impact value within the range of carbon content from 0.38 to 0.48% and that between the impact value and the transition temperature at 0°C, respectively. It is seen in the figures that the impact values in both cases lower with the increase in

(2) J.A. Reinbolt, Trans. ASM, **43** (1951), 778.

(3) N.P. Allen, J. Iron Steel Inst., **174** (1953), 108.

nitrogen content, and that the transition temperatures rise with the increase in nitrogen content, showing a large effect of nitrogen on the low-temperature brittleness of steel.

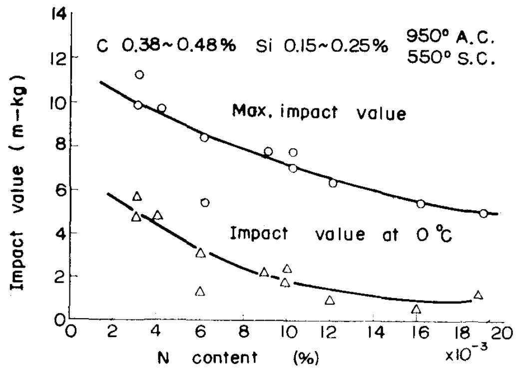

Fig. 9

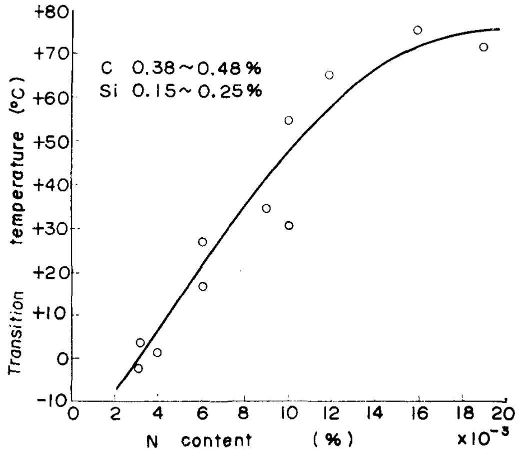

Fig. 10

Fig. 9. Effect of N content on impact value.
Fig. 10. Effect of N content on transition temperature.

Some workers[1] have reported that nitrogen accelerates the generation of string-like carbide in the low-carbon steel, which makes the steel brittle; but in the present experiments such a tendency was not observable. As will be reported later, it cannot be explained why the impact value lowers and the transition temperature rises with the increase in nitrogen content on the basis that a similar effect of nitrogen is observable in the quench-tempered steel; it is conceivable that the changes mentioned above are due to the effect of nitrogen itself on ferrite, and that if there is any effect of the string-like carbide, it will be due to the enlarged effect of nitrogen itself in the form of notch-effect.

It is said that the finer the grain size is, the lower the transition temperature is[4][5], but the grain size tends to be finer in the steel deoxidized by silicon, as in the present experiments, when nitrogen in the steel increase — (in the case of rimmed steel, when it is air-cooled, the grain size does not change with nitrogen content, and when it is gradually cooled over the interval of A_3–A_1 transition, the grain size becomes larger in the steel with larger nitrogen content) — and even if there is an effect of the grain size, it will be seen from the results of the present experiments that the effect of nitrogen is larger.

By using the results shown in Figs. 6 to 8, it is possible to obtain corrected values in the case of different carbon contents, and to obtain presumed values when carbon and nitrogen contents are determined.

Figs. 9 and 10 show the results obtained from the steel melted with 0.4% of carbon content as the goal. Carbon content increased with the increase in

(4) S.J. Rosenberg, J. Res. Nat. Bur. Stand., **27** (1941), 159: Trans. ASM, **30** (1942), 361.
(5) M. Williams, Welding J., **30** (1951), 572.

nitrogen content, and Figs. 11 and 12 show the results obtained by correcting carbon contents in the steel mentioned above. The corrections made the scattering of the points less, and the effect of nitrogen became smaller than the results shown in Figs. 9 and 10.

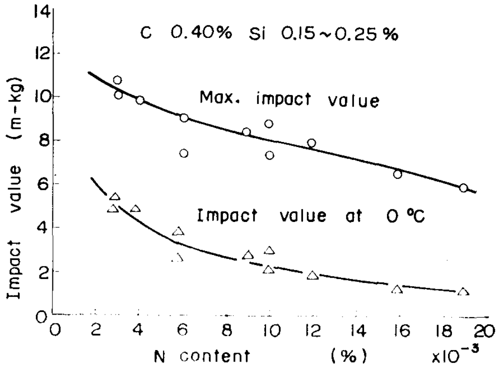

Fig. 11

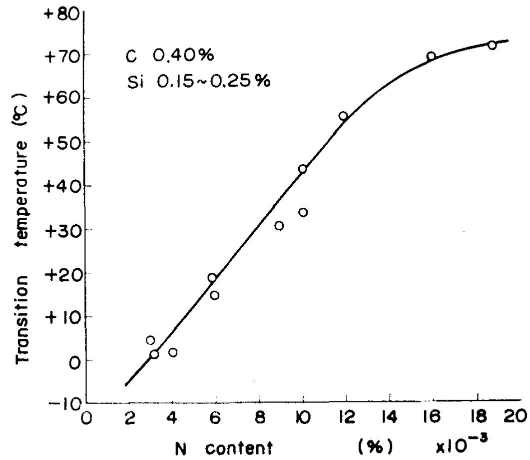

Fig. 12

Fig. 11. Effect of N content on impact value.
Fig. 12. Effect of N content on transition temperature.

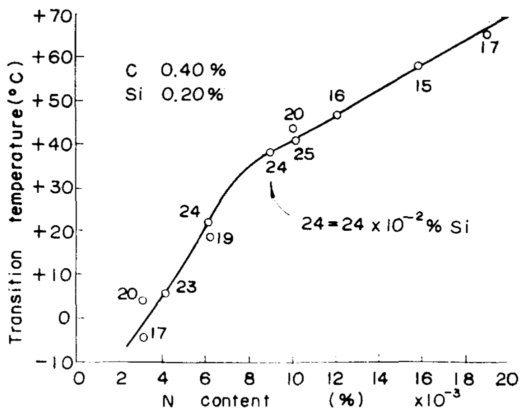

Fig. 13. Effect of N content on transition temperature of 0.4% C steel, contained 0.2% Si.

In these experiments, silicon content in the specimens used was 0.15 to 0.25%, but the effect of silicon is so great that it is necessary to make corrections according to silicon contents, as is reported in another paper. Fig. 13 shows the corrected results (the method of correction will be reported separately). It is seen in the figure that the scattering of measured points is less, and that the effect of nitrogen is reduced to greater extent than in the results shown in Fig. 12, because the high nitrogen specimen contains low silicon, as especially remarked in the above. The effect of nitrogen on the transition temperature (in the case of 0.4% of carbon content and 0.20% of silicon content) is represent by a curve having the inflection point when the nitrogen content is about 0.008%, and the transition temperature abruptly rises till the nitrogen content is 0.008% (7°C/0.001% N), beyond which it rises rather gently (3°C/0.001%). It will be explained separately why it assumes such a shape, but the nitrogen precipitated below 300°C — (including the case where it is lined on the axis of dislocation) — prevents ferrite from making slip-deformation, on account of which the transition temperature abruptly rises until nitrogen content is about 0.008%; when nitrogen content is more than 0.008%, the transition temperature rises more gently, because the nitride precipitated at the temperature above 300°C has an effect different from that of nitrogen precipitated below 300°C.

Summary

The experiments on the effects of carbon and nitrogen on the low-temperature brittleness of carbon steel revealed the following results.

(1) The low-temperature brittleness becomes sharp with the increase in carbon and nitrogen contents.

(2) The effect of nitrogen is greater in low-carbon steel.

(3) The transition temperature rises abruptly until nitrogen content is about 0.008%, beyond which it rises gently.

(4) The effect of nitrogen is observed in α-Fe, but not much in hypoeutectoid structure and becomes unobservable in eutectoid structure.