The influence of nitrogen on the low temperature brittleness of steel has been investigated. In particular, it was systematically studied under the coexistence of other elements which have a chemical affinity for nitrogen. Among those studied, Ti, Al and V have a strong affinity, Si and P a moderate and Cu, Sn and As a weak affinity. All these alloying elements were found first to diminish the effect of nitrogen by forming nitrides or reducing the solubility of nitrogen in α-iron, and then to reveal their own effect with increasing content.

**Introduction**

The low temperature brittleness of steel has long been the subject for study of many investigators from different angles. With the development of modern industrial plants and traffic facilities, the demand for steels reliable at low temperatures is rapidly increasing, and with the increasing amount of steels employed in this temperature region, accidents due to steel fracture are also increasing. In order to find the way of preventing these accidents, extensive studies of the low temperature brittleness of steel are being conducted in many countries. Most investigations of this phenomenon have been concerned with the comparison of the transition temperature. But it should be remembered that the transition temperature depends not only on the size and shape of the specimen but also on the method and speed in the destructive test. Moreover, we cannot find any organic correlation between the results obtained by different testing methods currently used, and cannot even apply the law of similarity to those obtained by one and the same method. If the testing method is fixed, the factors affecting the results can be divided into two groups, say, the mechanical and the metallurgical; the straining velocity, the magnitude of internal stress, the position and shape of notch, and the size of the test-piece belong to the first group, while the sort and structure of steel, the chemical composition, the method of heat treatment, the degree of fatigue and the effect of welding belong to the second. Thus, this phenomenon should be discussed on the ground of the dislocation theory of crystals and stress-strain theory of solids as well as on the metallurgical ground. Since detailed discussions are impossible in a limited time now available, it is felt necessary to confine ourselves to the influence of the chemical composition, the most important factor in the metallurgical aspect of low temperature brittleness. Studies in this field have been made, of course, by many investigators in the past, but their results did not always agree with each other. They differed considerably according to the different methods of steel-making; in case of insufficient deoxidation, for example, the transition temperature was generally high. From this fact, we may infer the possible influence of oxygen and nitrogen, but the former cannot be supposed to play an important role in the common steel which always contains a small amount of carbon, manganese and silicon. From these considerations, we were led to investigate the influence of nitrogen, of which little was known at that time.

As for the influence of the secondary treatment such as the heat treatment...
important factor next to the chemical composition), the following fact is known: that a high transition temperature is observed for those steels in which quench-ageing and strain-ageing easily proceed or a large internal stress is apt to be produced. On the other hand, according to our own study as well as others' of quench and strain-ageings in steel it has been established34 that the main factor responsible for these phenomena is nitrogen dissolved. These facts also indicate the importance of the part played by nitrogen in the low temperature brittleness of steel.

It has widely been accepted that the nitrogen dissolved makes steel brittle, but detailed and systematically conducted studies have not yet been published on this subject, and especially on the correlation between nitrogen and other coexisting elements in steel there are known only the works of Geil35 and Sawamura18 who studied the influence of AlN. These investigations were performed at about the same time as the present one.

We shall present some of the results obtained in a series of our experiments, which were planned in order to clarify the connection between nitrogen and the low temperature brittleness of steel.

Preparation of Specimens

Electrolytic iron was melted in a high-frequency furnace and nitrogen was added in the form of either manganese nitride, calcium cyanamide or potassium ferricyanide. Any perceptible difference has not been observed between the effects of the nitrogen introduced in different ways. Deoxidation was brought about by making use of Mn and Si, and the initial amount of them in the charge was controlled so that the final product still contained 0.3-0.4 per cent and 0.15-0.25 per cent Si. The content of P in the specimen ranged from 0.003 to 0.005 per cent, and that of S from 0.015 to 0.030 per cent. There was a general trend that a high carbon content corresponds to a high sulphur content (carbon was contained of the amount between 0.03 and 0.85 per cent). At any rate, the effect of S was hardly observed; the presence of Mn is likely to explain this fact. (This topic will be discussed on another occasion.)

Ingots of square section, $35 \times 35 \text{ mm}^2$, were forged into square rods of the size $12 \times 12 \times 120 \text{ mm}^3$, air-cooled from 950°C, and then machine-worked into square rods of the size $10.5 \times 10.5 \times 120 \text{ mm}^3$. They were further heated in vacuum for 3 hr. at 550°C, and then cooled down to room temperature at the rate of 1°C. per minute. Finally, they were finished with a grinder into standard Charpy testpieces.

Experimental Procedure

In all experiments, Charpy's testing machine of 30 m.kg. capacity was used. The specimen holder was not cooled (or heated). The specimen was cooled (or heated) in advance within a cold (or hot) bath placed by the side of the testing machine, and then mounted on the machine as quickly as possible. As the bath liquid for cooling, either water, ice and water, alcohol or liquid nitrogen was used respectively according to different temperatures required. For heating, an oil bath was employed.

In the case of rather a large amount of alloy elements we sometimes observed a two-stage decrease in the curve of absorbed energy plotted as a function of testing temperature, the first abrupt decrease at the fracture-transition temperature and the second at the ductility-transition temperature. This phenomenon will be discussed elsewhere.

Different definitions of the transition temperature are adopted by different investigators3,36. It is not easy to determine the temperature definitely at which the maximum absorbed energy begins to decrease,
because this happens rather gradually at the transition. The temperature at which equal amounts of shear type and cleavage type fractures are observed coincides approximately with the transition temperature derived by the method of arithmetic average, but it is not convenient for the present purpose because of the non-uniform distribution of different kinds of fractures.

Taking the temperature of a constant impact value as the transition temperature is also inadequate, because the range of values is rather wide for the impact values in our experiment. We adopted for defining the transition point the temperature at which the absorbed energy is equal to the arithmetic average of the values at the points on both sides.

**Experimental Results**

On the Correlation Between Carbon and Nitrogen — Fig. 1 shows some examples of the impact value versus temperature curves obtained in our experiments. In Fig. 2 the transition temperature is plotted as a function of the carbon content for various values of the nitrogen content. It is clearly seen that the transition temperature rises with increasing carbon content, rather slowly in the low carbon range and rapidly in the high carbon range. For fixed carbon content, the transition temperature rises with nitrogen content; the effect of nitrogen is relatively large in low-carbon steels, but small for high-carbon steels, and becomes negligible in the eutectoid region.

We can imagine many possible reasons for this rise with carbon content of the transition temperature, but it is most plausible to assume that the increase in the volume of the pearlite region plays the most important role. It is because that the rise of the transition temperature is nearly proportional to carbon content\(^{24,37}\). (In reality, the curve is downward convex, see Fig. 2.) Fig. 3 shows the influence of nitrogen on the transition temperature in the case of C, 0.40 per cent and Si, 0.20 per cent. This curve shows a break at about 0.008 per cent N, up to which the transition temperature rises rather steeply (7°C./0.001 per cent N), but more slowly above this point (3°C./0.001 per cent N). We shall present a full account concerning the form of this curve on another occasion. It is worth noting, however, that the rapid rise of the transition temperature below 0.008 per cent N is caused by the suppressing effect on slip deformation (movement of dislocations) of the nitrides precipitating in \(\alpha\)-Fe below about 300°C. during the cooling process in preparing the specimen, and that the remaining nitrogen precipitating between about 300° and 550°C. is less effective to suppress the slip deformation.

The results as shown in Figs. 2 and 3 cannot be attributed to the formation of thread type boundary carbides\(^{37}\) because in a microscopic study we have not observed any correlation between this process and the content of nitrogen and carbon. The difference in grain size cannot also be responsible for these results, because it is a well-known fact that the transition temperature decreases in general with decreasing grain size\(^{17-20,29}\) while the grain size decreases with nitrogen content\(^{6-8}\).

Correlation Between Phosphorus and Nitrogen — Fig. 4 shows the effect of phosphorus and nitrogen on the transition temperature of 0.40 per cent carbon steel when both elements coexist. While the nitrogen content is small, the rise of the transition temperature with increasing phosphorus content is not very fast, but for large nitrogen content this rise becomes rather remarkable (about 60°C./0.1 per cent P at N 0.010 per cent). It has also been found that the effect of nitrogen on the transition temperature increases with increasing phosphorus content.

Since phosphorus is an element to reduce the solubility of nitrogen in \(\alpha\)-Fe, it would
naturally be expected to suppress to some extent the action of nitrogen itself as in the case of As, Sn, etc., described later. The existence of this effect could not be realized in our experiment, because the nitrogen content was fixed in those specimens containing phosphorus between 0.005 and 0.05 per cent.

Influence of Nitrogen Stabilization with Al or Ti — Fig. 5 shows the results for the carbon steel containing 0.006 per cent N as well as those containing in addition 0.05, 0.1 and 0.2 per cent Al. These experiments were carried out in order to study the effect of nitrogen stabilization by the added element. For comparison, the results in Fig. 2
for the case of 0.003 and 0.010 per cent N are reproduced here in dotted curves. The figures indicating Al content refer to that in the initial charge. The amount of alloyed aluminium in the specimen was about 0.03, 0.05 and 0.12 per cent respectively for each content of 0.05, 0.1 and 0.2 per cent in the charge, and the relative amount of alloyed aluminium increased slightly with carbon content. The fact that the drop in the transition temperature due to the nitrogen stabilization with aluminium is relatively large for low-carbon steels compared to that for the case of high carbon content is in accordance with the result in Fig. 2 that the effect of nitrogen has the same trend. It is to be noted that the transition temperature, when nitrogen is stabilized by aluminium, is lower than that for the case of N 0.003 per cent in low-carbon steels, but the situation is reversed in high-carbon steels. This fact could not be explained unless the influence of aluminium other than nitrogen stabilization were taken into consideration. In fact, we can imagine that the effect of nitrogen predominates in low-carbon steels over the other effects to elevate the transition temperature (the effect of alloyed aluminium and other possible effects not discussed here; one of the most important among them is perhaps that of carbon) while the latter predominate in high-carbon steels over the former effect which is known to be small in them. Thus, if we consider the effect of nitrogen
stabilization alone, the drop in the transition temperature to be expected in 0.35-0.40 per cent carbon steel must amount to about 20°C.

The effect of AIN, produced as a result of nitrogen stabilization by Al, should be taken into account in principle, but it may be disregarded in practice. However, the effect of TiN in the case of the nitrogen stabilization by Ti cannot be ignored, because this compound is of a cubic form and of a larger size than AIN and, in consequence, exhibits a notch effect. Thus, when Ti is added, we have a transition temperature higher by up to 30°C than that for the case when Al alone is added (experimental data not presented).

Correlation Between Arsenic and Nitrogen — Fig. 6 shows the correlation between the effects of arsenic and nitrogen on the transition temperature of 0.35 per cent C steel. For the samples with low nitrogen content the transition temperature generally increases with increasing arsenic content. When the nitrogen content is high, the transition temperature first decreases as a result of the reduction of nitrogen effect by arsenic, and then increases with increasing arsenic content. The diminution of the effect of nitrogen in low arsenic content shows the diminution of the nitrogen solubility in α-Fe due to the presence of arsenic. The function of As seems to be explained by the following interpretation: if the solubility is reduced, then the amount of nitrogen, which precipitates below 300°C, and has a large effect on low temperature brittleness, is also reduced, and most nitrogen precipitates at higher temperatures in a harmless form.

The rise of the transition temperature curve in the region of the arsenic content higher than 0.3 per cent can probably be attributed to the primary effect of this element. It is further to be noted that the influence of As is supposed to consist only in reducing the solubility limit of nitrogen and not in acting as the so-called stabilizer by producing nitride, the presence of the latter action being evident in the case of Al.

Correlations Between Tin and Nitrogen, and Copper and Nitrogen — On expecting similar
results as arsenic for tin and copper, we studied the effect of Sn and Cu on the property of steel containing 0.35 per cent C and 0.006 per cent N.

Fig. 7 shows the effect of Sn. It is found that the transition temperature first decreases and, after passing through a minimum at 0.008 per cent Sn, rises rapidly with Sn content. The curve has a similar form as in the case of arsenic, but the slope at higher contents is steeper in Sn than in As. This difference may be attributed to the possible existence of the notch-effect due to thread-type boundary carbides in Sn-containing steel, as suggested from the fact that such carbides can be clearly observed at the crystal boundaries of α-Fe containing Sn.

Fig. 8 shows the effect of Cu. The minimum appears in the neighbourhood of 0.4 per cent Cu. The slope of the curve above this point is also steeper than that for the case of As, and the difference may be ascribed in this case to the precipitation of copper itself. These results are quite similar to those obtained for steels containing As, apart from the difference in magnitude of the effect. They are summarized as follows: tin and copper reduce the solubility of nitrogen and, in consequence, the influence of it, on the one hand, and they raise the transition temperature in 0.35 per cent C steel, on the other hand, as a result of their primary effect. (For low-carbon steels the results are not similar. They will be reported on another occasion.)

**Correlations Between Silicon and Nitrogen, and Vanadium and Nitrogen** — We have discussed above the effects of the elements Al and Ti which have a strong affinity for nitrogen, and those of P, As, Sn and Cu which have only a weak affinity. We shall now talk about the effect of Si and V, which are considered to have an intermediate affinity for nitrogen between the above two groups.

Fig. 9 shows the correlation between the effects of silicon and nitrogen, and Fig. 10 is a similar plot for vanadium and nitrogen.

The results shown in both figures are quite similar to those obtained on As. However, since both elements, vanadium especially, have a relatively strong affinity for nitrogen, we have to consider the effect of the nitride formation with these elements as we considered with Al. Thus, silicon and vanadium in steel are considered to play the following two roles: the first is the reduction of the primary effect of nitrogen by decreasing the amount of solid soluble nitrogen in α-Fe, and the second the nitrogen stabilization
accompanying the production of nitrides. In other words, the decreasing solubility of Si₃N₄ or VN in α-Fe, accompanied by the increase of Si or V content, diminishes the precipitates emerging below about 300°C and having a pronounced effect on low temperature brittleness and lowers the transition temperature, on the one hand, and in the high Si and V contents the primary action of these elements to elevate the transition temperature begins to appear, on the other hand.

For still higher contents of V the transition temperature decreases again. This is explained by the formation of VC which results in the reduction of the carbon content in steel. Similar results were obtained for Ti as an alloying element. Such phenomena associated with carbon will be reported on another occasion.

Summary

In the above, we have described the effect of nitrogen on the low temperature brittleness of steel and the influence of various alloying elements on it, and have shown that nitrogen causes a rise of the transition temperature of steel. This effect is largely due to the nitrogen which precipitates below about 300°C during the preparation process of the specimen, and the nitrogen precipitating above that temperature which causes the notch-effect is also effective to raise the transition temperature but to a lesser extent.

Phosphorus, arsenic, tin and copper reduce the solubility of nitrogen in α-Fe and suppress more or less the influence of nitrogen in their small addition. The elements with a strong affinity for nitrogen, such as aluminium and titanium, largely reduce the influence of nitrogen by stabilization. The elements with a moderate nitrogen affinity partly act in forming their nitrides and partly in reducing the solubility of nitrogen in α-Fe. Thus, the action of the alloying elements can be well explained by giving due consideration to their affinity for nitrogen, or their effect on solid solubility of nitrogen in α-iron, as well as to their primary function.

In concluding our report, we express our hearty thanks to Dr. T. Murakami for his valuable suggestions.

References

PAPERS DISCUSSED

1. Deoxidation and Inclusion Control for Alloy Steel, by W. Crafts & D. C. Hilty.
3. Progress of Special Steel-making Process in Japan, by Yoshio Ishihara.
6. Influence of Nitrogen on the Low Temperature Brittleness of Steel, by Yunoshin Imai & Tetsuro Ishizaki.

PROF. R. FAIVRE [Laboratoire de Physique de l’Etat Metallique de la Faculte Des Sciences, Nancy (France)]

Crafts and Hilty have used the iron-oxygen system to discuss their experimental results. I remember that my country, France, has made contribution on iron-oxygen system. Thirty years ago, my own master, Prof. G. Chaudron (Paris), more recently (1947) Chaudron and Benard, and last year (1955) Manors and Aubry (Nancy) gave important results on the subject.

DR. V. G. PARANJPE (Tata Iron & Steel Co. Ltd., Jamshedpur)

The first paper on temper-brittleness, somehow or other, has left me in a very confused state of mind. Maybe with the more rapid advances in the science of metallurgy, particularly into the dislocation theory, the whole thing will be clarified.

The physicist in propounding new suggestions based on dislocation theory would be rather wavering because he is conscious of the limitations of the knowledge that he has at his command. The atomic forces of only two or three of the alkaline elements have been fully analysed. I do not think that electronic and atomic forces in as complicated a structure as iron have been thoroughly understood as yet. The dislocation people
have been continually propounding the theory, but I do not think they mean that it is the solution. They are presenting a scheme of things which, to their mind, is a little more appealing.

Coming to the concrete fact of embrittlement the temper-embrittlement phenomena, as is clearly shown by the second paper, have been taken to be as a result of grain boundary precipitation. I think there is ample evidence to say that there is a precipitation. As to what the exact nature of the precipitate is, there is some doubt. The only possible embrittlement phenomenon which can be grouped with temper-brittleness on the basis of grain boundary precipitation is the one that follows immediately after quenching.

DR. B. R. NIJHAWAN (Dy. Director, National Metallurgical Laboratory)

I am fair in saying that I have partly succeeded in the object of my paper in having passed on my confusion of thought to others. I feel that carbon and nitrogen are connected in some way with embrittlement. The phenomena of temper-brittleness, strain-ageing, quench-ageing and hardenability are inter-related and should be treated together and not separately.

As regards dislocation theory, I believe it to be highly speculative. What is it that the old theory cannot explain and the dislocation theory does? Can the dislocation people tell me how boron additions of 30 parts to a million raise the impact resistance of steels?

DR. A. B. CHATTERJE (National Metallurgical Laboratory)

I have indicated in my paper the rival theories based on segregation and precipitation. Dr. Paranjpe has shown himself in favour of the precipitation theory which has been very much approved by McLean and Woodbain and others. The electron micrographs which I had shown were taken at a magnification of 10,000 after subjecting the specimens to an embrittlement treatment for about 120 hr. at 620°C and did not show any breakdown in coalescence while the coalescence of the carbides was quite clear. So I find myself in favour of the segregation theory and not the precipitation theory.

MR. VISVANATHAN (Tata Iron & Steel Co. Ltd.)

It has been stated that fine-grained steel has a lower transition temperature. How is it then that an addition of 0.2 per cent Al, which should render the steel coarse-grained, brings down the transition temperature?