DIFFUSION OF NITROGEN IN IRON–TITANIUM ALLOYS

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The production of alloy steels is a difficult problem of our steel industry, because the required alloying elements of which there is a shortage, are expensive and must be partly obtained from abroad. This is the reason why considerable amount of research has been carried out to develop alloy steels with adequate properties, which could be manufactured using alloying elements recovered from inland raw materials.

One of these alloying elements is titanium, a very important metal, as it was pointed out by Professor GILLEMOT in a lecture held at the Academy of Sciences [1].

TiO_2 content of our bauxites is abundant enough to make an economical production of either ferrotitanium or metal titanium possible when an appropriate procedure is applied after TiO_2 had been enriched in the red mud which is a by-product of aluminium production.

Even a few percentages of titanium has an important effect on the properties of steel, and, therefore, relatively large amounts of alloy steel can be produced using comparatively small quantities of titanium.

Accordingly, the extensive research which had been started to determine the different properties of titanium steels, were justified. This program includes investigations on the effects of titanium on the behaviour of steel during nitriding process, and this behaviour was the basic problem of the experimental work dealt with in this paper.

Nitriding experiments were performed on alloys obtained by the addition of titanium to armco iron of Swedish origin to reduce the disturbing effect of carbon contents to a minimum. The first series of these investigations were carried out with the aim of making clear the effect of titanium content, temperature of treatment, degree of dissociation of the ammonia during treatment, and time of treatment on the nitrided-case properties of the titanium steel.

Effect of titanium content on the properties of the nitrided case

A series of alloys with 0 to 4.25 per cent titanium content was made in a high-frequency induction furnace, using metal titanium as an alloying element. The titanium to carbon ratio varied from Ti/C = 0 to Ti/C = 85. The alloy samples were kept for five hours in a tubular electric muffle furnace through which ammonia was allowed to circulate. The temperature range of treatment extended from 460 to 660° C (860 to 1220 ° F), and the degree of dissociation of ammonia was varied in a range of 24—92 per cent. The hardness distribution in the nitrided case was determined by means of a Zeiss Hanemann microhardness tester, on the polished and moderately-etched sections of the nitrided specimens.

Detailed data on the investigations and their results have already been published [2, 3].

A hardness distribution diagram, which was picked out as an example, is shown in Fig. 1. The treatment was performed at a temperature of 550° C

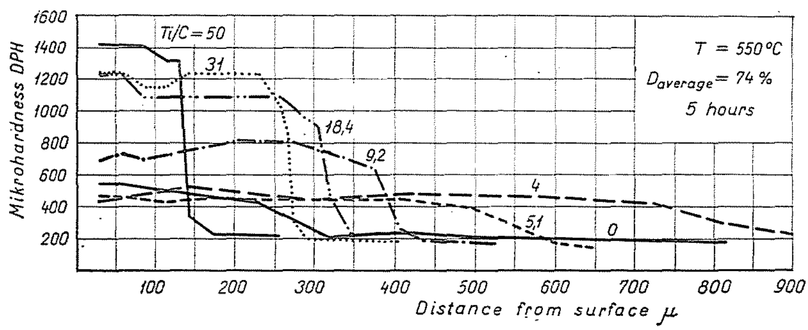

Fig. 1. Effect of titanium to carbon ratio on nitrided-case hardness of titanium-alloyed armco iron

(1022° F) during 5 hours with a degree of dissociation of 74 per cent, the titanium to carbon ratio varying from Ti/C = 0 to Ti/C = 50.

As it can well be seen from this unique series of selected diagrams, titanium has a considerable effect on the nitrided case of the iron. When alloys with low titanium content (Ti/C $\leq$ 4) were treated, approximately the same hardness was obtained as on pure armco iron, but the hardened case became deeper. Alloys with higher titanium content and increased titanium to carbon ratio (Ti/C > 4) resulted in a gradually-decreasing case depth, but greatly-increased case hardness. Consequently, by varying the titanium to carbon ratio a great variety in case properties could be realized.

Variation of the degree of dissociation from 24 to 74 per cent has no effect on the properties of the case.

Higher temperatures of treatment up to 600° C (1112° F) helped to increase the case hardness, and above this temperature a slight decrease was obtained. At the same time, the case depth continuously increased.

The typical case properties observed after five-hour experiments, appeared with a shallower case, even when the treatment lasted only one hour at a temperature of 550° C (1022° F). When the time of treatment was increased, after the third hour the maximum hardness failed to increase any longer. The depth of the case increased nearly in proportion to the time of treatment with a time interval of 1—7 hours.

From the point of view of hardness and depth of the nitrided case, the optimum temperature of treatment proved to be between 550 and 600° C (1022 and 1112° F). Maximum case depth was obtained in alloys with a titanium to carbon ratio between 4.0 and 5.1, and maximum case hardness appeared without any danger of brittleness when this ratio had a value of between 9 and 31.

As a final result, these experiments showed that at 460—660° C (860—1220° F) cases with DPH = 500—1420 kg/mm^2 microhardness (obtained by applying a 0.05-kg load) and 1.5—0.2 mm depth can be produced depending on the value of titanium to carbon ratio. It should be emphasized that these favourable case properties were obtained on the armco iron containing titanium with treatments lasting only 5 hours, which is an unusually short time in nitriding practice. Consequently, the use of iron or steel containing titanium seems to be very advantageous in nitriding technology.

The experiments were continued establishing the reasons responsible for the typical properties observed on the hardened case when armco iron with titanium content was nitrided. To approach this problem

1. diffusion studies and
2. X-ray microstructural investigations were made on the most typical of these alloys.

Diffusion studies being the main subject of this paper, they will be considered in detail in the following section. As far as the X-ray microstructure investigations are concerned, only the final conclusions will be summed up.

Diffusion studies

From the iron—nitrogen thermal—equilibrium diagram it is known that when nitriding is carried out at a temperature below eutectic point, first of all, the α-phase is saturated with nitrogen on the surface of the iron. A further increase of nitrogen content results in the appearance of γ'-phase, then after a narrow interval of pure γ' the ε-phase appears, so that, above 8.1—7.3 concentrations — this value depending on the temperature — only the ε-phase is present when an equilibrium state is attained.

The concentration distribution in the nitrided case presents sudden changes in concentrations due to the chemical compounds produced, therefore, a periodic distribution curve is obtained. The known solutions adequate for calculation purposes of FICK's second diffusion equation cannot be used when there is a periodic distribution. Therefore, absorption-velocity method [4] was used to determine the value of the diffusion coefficient.

When a cylindrical wire having a diffusion element concentration C_a is maintained during a time t at a temperature at which diffusion coefficient of the gas or element in the metal is D and the final equilibrium concentration in ammonia gas after $t = \infty$ would be C_e, the mean concentration of the gas or element C in the metal as a function of time is given by

$$\frac{C - C_e}{C_a - C_e} = \sum_{\nu=1}^{\nu=\infty} \frac{4}{\xi_\nu^2} e^{-\xi_\nu^2 \frac{Dt}{R^2}} \tag{1}$$

where ξ_ν denotes the abscissas of the zero points of the Bessel function of zero order ($\xi_\nu = 2.405, 5.520, 8.654, 11.792, \ldots$) and R is the wire radius.

With large t values the sum in equation (1) can be replaced, with a good approximation, by the value of the first term

$$\frac{C - C_e}{C_a - C_e} = \frac{4}{2.405^2} e^{t/\tau''} \tag{2}$$

where τ'' is the so-called characteristic time expressed as

$$\tau'' = \frac{R^2}{2.405^2 \times D} . \tag{3}$$

To facilitate the computations, equation (2) is written in the more convenient logarithmic form

$$\log \frac{C - C_e}{C_a - C_e} = \log \frac{4}{2.405^2} - 0.434 \frac{t}{\tau''} = 0.160 - 0.434 \frac{t}{\tau''} \tag{4}$$

For $t < \tau''/3$, *i. e.*

$$\log \frac{C - C_e}{C_a - C_e} < - 0.3 \tag{5}$$

equation (4) gives satisfactory results, but it is also valid for shorter times, taking into account that equation (1) involves a rapidly-convergent series.

By plotting values of log $[(C - C_e)/(C_a - C_e)]$ as a function of time, a straight line is obtained when the velocity of the process is determined by diffusion. The slope of this straight line gives the characteristic time τ'' (equation (4)), and from this value, by using equation (3), diffusion coefficient D may be determined.

From the series of alloys with different titanium to carbon ratio three typical alloys were selected : those with Ti/C = 4 (characterizing group Ti/C $\leq$ 4), Ti/C = 31 (characterizing group Ti/C > 4) and Ti/C = 0 (pure armco iron as a reference).

From the selected alloys three wires with a diameter of 1.08 mm were drawn and then heated for 10 minutes in a vacuum of order 10^{-6} mm of mercury at 930° C (1706° F).

These wires were treated together for 1, 2.5, 5, 10, 14 and 20 hours, respectively, in an ammonia current at 600° C (1112° F). The degree of dissociation varied between 52 and 68 per cent.

The wires were analyzed in a Parnass—Wagner apparatus using a damp chemical procedure to determine the N_2 content, these measurements yielding the values of C.

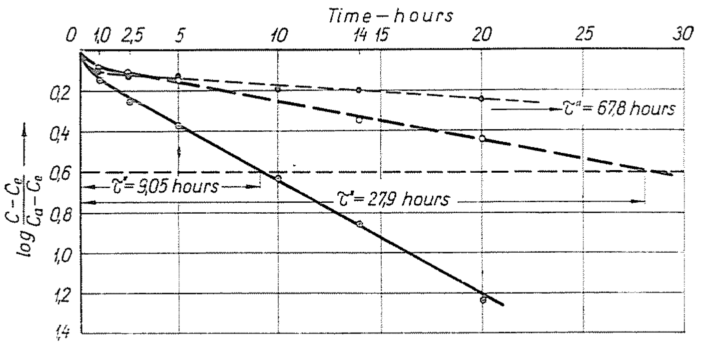

Fig. 2. Variation of log $[(C - C_e)/(C_a - C_e)]$ with the time treatment

The C_a values obtained for the three alloys were 0.007, 0.004 and 0.006 per cent, respectively, but taking the low accuracy in the calculations and construction into account, C in each case can be regarded as equal to zero.

From the result of a treatment lasting over a long period of time, and on the basis of other considerations a value of 8.1 per cent was taken as a final concentration value for C_e. The connected values of log $[(C - C_e)/(C_a - C_e)]$ and time were calculated and plotted in a diagram shown in Fig. 2.

On determining the times τ'' from this diagram the following values for the diffusion coefficients at 600° C (1112° F) were obtained :

Armco iron $D_N = 1.545 \cdot 10^{-8}$ cm^2 sec^{-1}

Armco iron with Ti/C = 4 titanium content $D_N = 0.501 \cdot 10^{-8}$ cm^2 sec^{-1}

Armco iron with Ti/C = 31 titanium content $D_N = 0.204 \cdot 10^{-8}$ cm^2 sec^{-1}

From the results obtained by diffusion investigations, it can be seen that the addition of titanium unambiguously decreases the diffusion coefficient of nitrogen in iron.

X-ray diffraction studies

Investigations were made on nitrided and unnitrided wires drawn from four different materials, using the Debye—Scherrer method. These materials were as follows :

1. Unalloyed armco iron
2. Armco iron with Ti/C = 4 titanium content
3. Armco iron with Ti/C = 31 titanium content
4. Iodide titanium made by using the modified van Arkel process

For all the nitrided wires the lines of $Fe_4N(\gamma)$, $FeN(Fe_2N - Fe_3N)$ (ε) and Fe_3N, an intermediate phase, unambiguously appeared on the Debye—Scherrer records.

Even the most definite lines of TiN did not appear in the nitrided titanium-alloyed irons, and their presence could not be established by the spectrum lines even in the nitrided titanium wire.

On the other hand, the results obtained by the simultaneously accomplished microhardness measurements suggest the presence of TiN in some form, because other phases could not give rise to the surface hardening observed on the titanium wire and the considerable degree of hardening, $DPH = 1410$ kg/mm^2, of the Ti/C = 31 iron wire as compared to the much lower 442 and 458 kg/mm^2 values on wires with Ti/C = 4 and Ti/C = 0, respectively. In the meantime, the presence of TiN was also proved in a publication by Norén and Kindbom [5] on electron microscope records.

A partial solution to the problem was given by the systematic line displacement observed on records concerning nitrided titanium wires. From data obtained on Debye records, a and c parameters of the hexagonal crystal lattice of titanium α were calculated using relation

$$\sin^2 \Theta_{hkl} = \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2} l^2 . \tag{6}$$

These parameter values for untreated and nitrided conditions are as follows :

Untreated α	$a = 2.9516$ Å
	$c = 4.6931$ Å
Nitrided α (hardened case)	$a = 2.9752$ Å
	$c = 4.7603$ Å

By a comparison made between the obtained values and Ehrlich's data [6], it can be seen that as a result of the nitrogen enrichment a series of TiN_x phases appeared in the nitrided case of the titanium wire, the upper limit of nitrogen concentration in this series can be proved as corresponding to at least $TiN_{0.33}$.

Taking into account these facts and the observations made by Norén and Kindbom, it can be presumed that the series of TiN_x phases extend to nitrides of higher order including $TiN_{1.0}$ — $TiN_{1.16}$ and appears with considerable dispersity even in the nitrided case of the Ti/C = 31 alloy, giving rise to the unusual case hardness of this alloy.

Evaluation of the experimental results

On the basis of the diffusion studies and X-ray microstructure investigations, and considering the known properties of TiN [7], the typical qualities of nitrided cases obtained on irons with titanium contents can be explained as follows :

Group of alloys with Ti/C > *4.* These alloys contain free Ti. Titanium nitrides in different compositions are formed in the hardened case even during a short nitriding process. Nitrides are very quickly produced at the surface and have a high dispersion, so that hardness is greatly increased. However, titanium nitrides appearing on the surface layer mechanically reduce the dispersion section, the quantity of the penetrating nitrogen continuously decreases, and a very slow increase in case depth is obtained.

The higher the titanium content, the more and the higher nitrides are produced, therefore, the hardness continuously increases and the depth of the case — because of the stronger blocking effect — continuously decreases.

In the *group of alloys with* Ti/C = 4 titanium content an apparent contradiction is seen between the increase of case depth towards the Ti/C = = 4 alloy and the lower diffusion constant in this alloy, as compared to that in pure iron. This contradiction may be solved by a proposed explanation, which is an *assumption*, because sufficient measurement results of our own and of published data are unavailable. There is no free titanium in the alloys, theoretically all titanium content being bound as TiC. However, titanium has a high affinity to nitrogen, so that at the appearance of nitrogen this TiC is presumably decomposed and TiN_x nitrides are produced. This assumption is supported by the results obtained by Comstock [8] who found that titanium even with Ti/C = 2—4 ratios reduces the quantity of nitrogen dissolved in steel to the same extent (from 0.012 to 0.002) as when Ti/C > 4.

As the formation of titanium nitrides takes place very rapidly and efficient hardening is attained, alloys with titanium contents of Ti/C = 2—4 present deeper hardened cases in spite of their lower diffusion coefficients. However, due to the small quantities of TiN nitrides, the hardness cannot be higher than that obtained on the unalloyed iron after nitriding. A considerable increase in hardness can be observed only when the quantity of free titanium and, therefore, that of the titanium nitrides, is increased ; *i. e.* in $Ti/C > 4$ alloys. A definite limit cannot be established, the transition being continuous.

Summary

Nitriding experiments on titanium-alloyed armco iron were performed using samples containing 0 to 4.25 per cent titanium with titanium to carbon ratios between 0 and 85.

By treatments at 460—660 °C (860—1220 F°) lasting only five hours, which is an unusually short time of treatment in nitriding practice, nitrited cases of DPH = 500—1420 kg/mm^2 microhardness and 1.5—0.2 mm depth were obtained, these values depending on the titanium to carbon ratio.

Diffusion coefficients of three typical alloys were determined at a temperature of 600 °C (1112 °F) by the absorption velocity method.

The results of X-ray microstructure tests and diffusion measurements showed that these favourable case properties were caused by dispersed TiN compounds which appeared in the hardened case in different quantities depending on the titanium to carbon ratio, and not by improving the diffusion conditions.

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