

HYDROGEN IN STEEL

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IT is now generally accepted that hydrogen is largely responsible for a number of harmful phenomena in alloy steels, four of the most important being:

- (1) 'Wild' heats and blowhole formation,
- (2) Embrittlement,
- (3) Hairline cracks,
- (4) Hard zone cracking during welding.

The present paper will deal only with the first three of these and particularly with hairline cracks.

Fundamental Considerations

Solubility — Although quantitative data on commercial steels are somewhat meagre, it is established that the solubility of hydrogen in iron varies with temperature in the manner indicated in Fig. 1. There is a big drop in solubility as the metal solidifies and further discontinuities occur at the $\delta = \gamma$

and $\gamma = \alpha$ transformations. Below about 400°C. the solubility is very low indeed. Before it can dissolve in iron or steel, molecular hydrogen must be dissociated into the atomic form and this leads to Sievert's law. According to this law, the amount of hydrogen which will go into solution in a metal at a given temperature is proportional to the square root of the partial pressure of hydrogen surrounding the metal. The metal is in equilibrium with its surrounding atmosphere through the process $H_2 \rightleftharpoons 2H$ and the factor which directly determines the solubility is the concentration of atomic hydrogen on the surface. This is why iron and steel pick up hydrogen so rapidly during pickling or electrolysis, for both processes generate atomic hydrogen at the surface of the metal. Cathodic pickling at a current density of 1 amp./sq. cm. produces an equivalent hydrogen pressure on the surface of steel equal to 17,000 tons/sq. in. so that very high solubilities may result¹.

The recombination of atomic hydrogen to form molecules only occurs at a free surface of the metal and before it can escape from the metal, the hydrogen must diffuse in atomic form through the lattice to a free surface. This free surface may be external or it may be an internal free surface provided by a cavity or void in the metal. In either case hydrogen will continue to leave the metal until the partial pressure of hydrogen in the surrounding atmosphere is in equilibrium with the hydrogen retained in solution. If a specimen charged with hydrogen to the extent of A cc./100 g. is held at a temperature such that the solubility in equilibrium with one atmosphere of hydrogen is B cc./100 g. then, from Sievert's law, the equilibrium

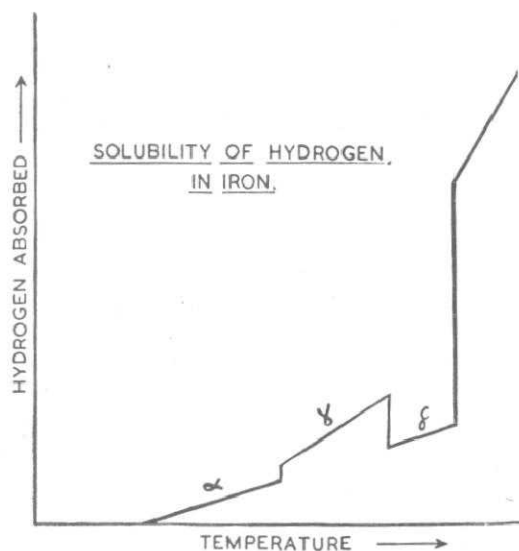


FIG. 1

pressure which will tend to be built up at any free surface will be P atmospheres given by

$$P = \left(\frac{A}{B}\right)^2 \dots \dots \dots (1)$$

This is the limiting pressure that can be built up within a cavity whose volume is small compared with that of the steel. For larger cavities, or for external surfaces, the pressure that can be attained will be less than this, depending upon the volume involved.

Diffusivity — Hydrogen in steel obeys Fick's law

$$\frac{dm}{dt} = -D \frac{dc}{dx} \dots \dots \dots (2)$$

where dm is the mass transferred across unit area in time dt when the concentration gradient is $\frac{dc}{dx}$ and D is the diffusion coefficient.

It has been shown for hydrogen in iron alloys that D is independent of concentration over a wide range².

The diffusion coefficient for a given phase is related to temperature by the relationship

$$D = D_0 e^{-E/RT} \dots \dots \dots (3)$$

There is an abrupt drop in the diffusion coefficient as iron solidifies, a further drop at the δ - γ change and an increase at the γ to α change. In other words, the diffusivity of hydrogen in austenite is *less* than in ferrite at the same temperature. Chang and Bennett² found that nickel and molybdenum had little effect upon the diffusion of hydrogen through binary iron alloys containing up to 10 per cent of the second element. Chromium had little effect on diffusion in the γ phase, but greatly reduced diffusion in the α phase. At temperatures near the melting point diffusion is so rapid that it is rarely the rate-controlling process, but at lower temperatures and, particularly with large masses of steel, diffusion becomes increasingly important.

Phenomena Caused by Hydrogen

'Wild' Heats — Wild heats which rise in the moulds and give ingots full of well-developed blowholes (see FIG. 2) are frequently caused by high hydrogen contents. Sykes, Burton and Gegg³ have reported 'wild' heats resulting from hydrogen contents in the molten state ranging from 9 cc./100 g. for a 3¼ per cent nickel steel to 16.6 cc./100 g. for a 13 per cent chrome stainless iron. It will be appreciated from Fig. 1 that as a result of the very big drop in solubility on solidification, the residual molten steel will become increasingly rich in hydrogen as solidification proceeds and may become saturated although the original melt was not. Hydrogen causes wildness in heats of ferritic, martensitic and austenitic steels and there is good reason to believe that movement of the hydrogen-filled blowholes accentuates the segregation of sulphur.

Hydrogen Embrittlement — It has been known for a long time that hydrogen picked up as a result of pickling or electrolysis causes embrittlement. The same is true of hydrogen remaining in the steel from the steel-making process and of hydrogen deliberately introduced into the solid steel, whether this is done by soaking in hydrogen

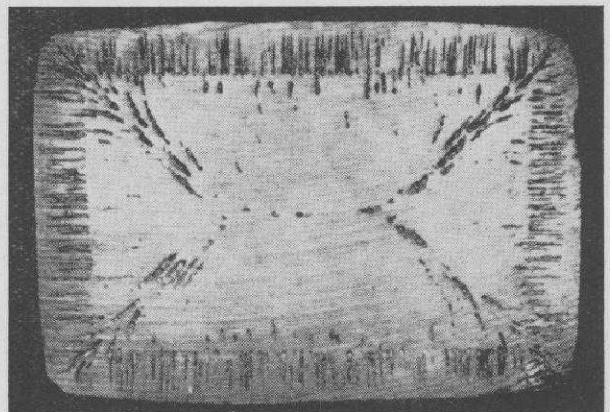


FIG. 2 — TRANSVERSE SECTION OF A WILD INGOT OF AUSTENITIC STAINLESS STEEL WHICH CONTAINED ABOUT 14 ML. HYDROGEN PER 100 G. PRIOR TO CASTING (Courtesy of BARRACLOUGH, Murex Welding Review, 1)

at atmospheric pressure at hardening temperature or by hydrogen treatment at high pressure at tempering temperatures. It is characteristic of this type of embrittlement that it disappears if the hydrogen is removed by ageing or by heating *in vacuo* or in an inert atmosphere. The yield point and maximum stress in the conventional tensile are not affected by hydrogen, but as shown in Table 1 the elongation and more particularly the reduction of area are progressively lowered as the hydrogen content is increased⁴.

TABLE 1 — EFFECT OF HYDROGEN UPON MECHANICAL PROPERTIES OF 3 PER CENT Cr-Mo STEEL

HYDROGEN CONTENT, cc./100 g.	YIELD POINT, tons/sq. in.	MAX. STRESS, tons/sq. in.	ELONGATION, %	REDUCTION IN AREA, %
< 0.1	44.3	53.3	23.5	70.5
5.4	46.3	53.3	17.5	49.0
9.0	45.3	54.0	16.5	37.0

Hydrogen had been introduced into these specimens by soaking in hydrogen at high pressure at 600°C. Earlier, Andrew *et al.*⁵ had shown similar effects with a variety of steels containing about 1.2 cc. hydrogen per 100 g. of steel introduced by soaking at atmospheric pressure at 850°C. followed by air-cooling. In some steels the embrittling effect of hydrogen was more marked than indicated in Table 1. Thus with a steel containing 1.07 per cent chromium, 0.23 per cent molybdenum and 0.45 per cent carbon the normal reduction of area of 30 per cent was reduced to 3 per cent by 1.26 cc. of hydrogen/100 g. whilst elongation was reduced from 11.5 to 0.5 per cent. The same workers showed that the impact test was less sensitive than the tensile test to the effects of hydrogen. Thus in the normalized condition, a hydrogen content that was sufficient to reduce the reduction of area from 56 to 7.0 per

cent caused a reduction of Izod value only from 46 ft.-lb. to 39 ft.-lb. For a given hydrogen content the embrittlement depends upon the microstructure. Thus, a 3 per cent Cr-Mo steel isothermally transformed at 350°C. is much more severely embrittled than after transformation at 700°C.¹⁵ A similar steel containing 4 cc. hydrogen/100 g. hardened to 50 tons/sq. in. has a reduction of area of 60 per cent, but the ductility falls as the tensile strength is increased so that at 93 tons/sq. in. the reduction of area is only 2 per cent⁴.

Zapffe and his colleagues regarded hydrogen embrittlement as 'ageing by a gaseous precipitate'. They envisaged the hydrogen diffusing to the mosaic boundaries of the substructure and building up a pressure approaching the equilibrium value given by equation (1). The pressure thus developed would eventually exceed the 'elastic strength' of the steel and the mosaic blocks would be 'sprung apart'. One reason why this explanation was not generally accepted is that ten years ago the nature of the substructure in metals was less well understood than it is today. Another is that the mechanism involved the formation of molecular hydrogen at the substructure boundaries and it was difficult to see how this could diffuse out to leave the structure mechanically unimpaired.

The concept of substructure is now generally accepted and the boundaries between adjacent crystal blocks of slightly different orientations are regarded as dislocation walls. There are reasons for believing that some solute atoms will migrate to these walls and so affect their chemical activity¹⁶ and it has also been shown⁷ that the amount of hydrogen absorbed by armco iron increases nearly tenfold if the metal is cold-drawn 70 per cent. In view of the role played by dislocations in deformation, the possibility that such solute atoms will also affect the mechanical properties cannot be ruled out. Any such effect would not depend upon the

formation of molecular hydrogen, but only upon the interaction of dislocations with hydrogen atoms. One sees, therefore, that a modern version of Zapffe's general theory is possible and need not suffer from some of the defects of its predecessor.

Petch and Stables⁸ have shown that in the tensile test the degree of embrittlement for a given hydrogen content is dependent upon the duration of loading, the slower the test, the greater the degree of embrittlement. Petch⁹ considers that the hydrogen embrittlement of steel resembles the effect of air upon the delayed fracture of glass. On this basis the strength σ_c of a rapidly loaded specimen, of Young's Modulus E , is given by the Griffith relationship

$$\sigma_c = \sqrt{\frac{2ES_c}{\pi C}}$$

where S_c is the surface energy of the clean surface resulting from extension of the crack of width $2C$. If this surface can be covered by adsorbed atoms as soon as it forms, the strength will have a lower value given by replacing S_c by S_a , the energy of the surface when covered by the adsorbed layer. At stresses intermediate between σ_c and σ_a the Griffith cracks will be unstable and an increment of unclean surface will form as and when foreign atoms are available to be adsorbed on the exposed surface. Gradual extension will be replaced by sudden fracture when the crack has grown to the point at which a clean surface can be propagated by the applied stress. As Petch points out, embrittlement of steel differs from the delayed fracture of glass in that the adsorbed atoms are supplied from solution. There will be a tendency for the hydrogen atoms to migrate to the region of stress concentration not only because by doing so they may relieve elastic strain energy but also because the equilibrium pressure of hydrogen given by equation (1) will tend to be built up at the free surface by the process of diffusion and reassociation of hydrogen atoms already described. The pressure effect is not likely

to be important unless loads are maintained for considerable periods.

A completely satisfactory theory of hydrogen embrittlement, supported by quantitative evidence, is not possible at present. It can be stated, however, that

- (1) some degree of embrittlement occurs in constructional alloy steels whenever the hydrogen concentration is more than 1 cc./100 g.;
- (2) the effect of hydrogen is completely removed if the metal is freed from hydrogen;
- (3) the severity of the embrittlement for a given steel depends upon the microstructure.

Hairline Cracks — 'Wildness' and embrittlement are observed whenever certain critical hydrogen contents are exceeded. Hairline cracks, on the other hand, although they may be expected if the hydrogen content is 4-6 cc. per 100 g. and do not occur in the absence of hydrogen, may nevertheless be formed when only 2 cc./100 g. are present, and absent when the content is 6 cc./100 g. It is clear from this that although hydrogen is a prerequisite for hairline crack formation, the presence of hydrogen is not sufficient in itself. Before discussing the other factors that are important it may be well to review the characteristics of hairline cracks.

The hairline cracks observed commercially are usually arranged at random and there is a peripheral zone in which no cracks occur (FIG. 3). The cracks are shown up by magnetic etching, or deep etching, whilst ultrasonic testing reveals that the cracks are in fact discontinuities in the steel. If a billet containing hairline cracks is heat-treated to refine the structure of the matrix and then fractured, the hairline cracks are revealed as bright crystalline areas approximately circular in form. Their appearance explains why the term 'flakes' or 'snowflakes' is sometimes used to describe the phenomenon (FIG. 4). Hairline cracks are

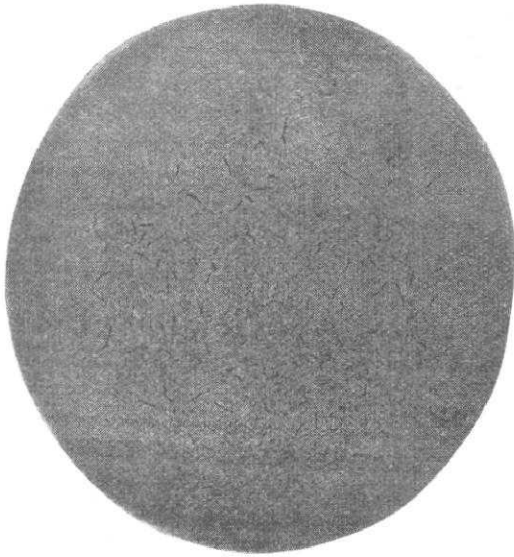


FIG. 3—HAIRLINE CRACKS IN Ni-Cr-Mo STEEL 4S11 PRODUCED BY SOAKING IN HYDROGEN AT 950°C. AND AIR-COOLING (DEEP-ETCHED. $\times \frac{2}{3}$)

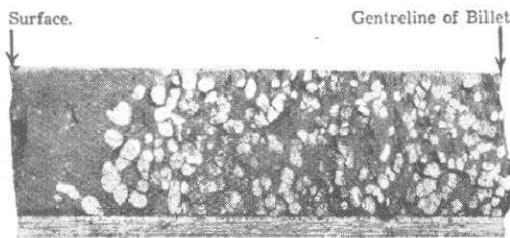


FIG. 4—SNOWFLAKES EXPOSED ON FRACTURING Ni-Cr-Mo STEEL BILLET CONTAINING HAIRLINE CRACKS (FULL SIZE)

not observed in plain carbon or austenitic steels. In construction alloy steels the cracks are less likely to occur if the wrought product has been slowly cooled. Large sections are more liable to the defect than smaller ones. The commercial treatments that were developed empirically to minimize hairline crack formation were such as to reduce both hydrogen content and internal stresses. One of the most effective treatments is to cool slowly to 300°C. and then reheat to 650°C. and hold at that temperature for a period determined by the ruling section. Bearing in mind the depression of

the transformation that occurs in alloy steels on cooling, it will be seen that this treatment involves heating at the highest temperature possible in the alpha range giving a combination of low solubility and high diffusivity and, therefore, maximum hydrogen removal. At the same time there will be maximum relief of stress.

Hairline cracks can be produced in the laboratory by soaking in hydrogen at a high temperature and cooling at a suitable rate. Under such conditions the cracks are usually associated with hydrogen contents of about 4-6 cc./100 g. If the steel is quenched the cracks are radial, but air-cooling produces random, deep-seated cracks that are quite undistinguishable from those observed in commercial steels (FIG. 3). Quenched specimens give off hydrogen at room temperature and this can be collected over paraffin or mercury. With some steels the evolution is at first slow and then, after a period of time varying from a few hours to a few days, there is a sudden large rush of gas, followed by evolution at a slower and diminishing rate. In such steels no hairline cracks are observed until after the sudden evolution. Other steels do not show such a well-defined incubation period; instead the evolution curves show a succession of smaller steps and hairline crack formation takes place over a period.

Experiments such as these focus attention on the *movement* of hydrogen during hairline crack formation, but it was before such experiments had been made and, indeed, before there was any widespread belief in the importance of hydrogen that Honda¹⁰ put forward his pressure theory. He attributed hairline cracks to the movement of hydrogen out of solution into tiny voids in the steel where very high pressures of molecular hydrogen were built up. Essentially the theory was based on equation (1) and Honda calculated that pressures sufficient to disrupt the steel could be built up as a result of the decrease in solubility of hydrogen as the

temperature fell. In his mathematical treatment of crack formation by hydrogen pressure, Honda came to the conclusion that cracks could not be formed above 580°C. or below 200°C. This aspect of the theory was realized to be wrong when it was found that cracks frequently formed at room temperature and that an incubation period was necessary for their formation. Nor was it possible on Honda's theory to explain the sudden evolution of hydrogen that occurred in some steels at the end of the incubation period. To overcome this difficulty and to explain their own observations Andrew and his colleagues¹¹ postulated that a hydrogen-rich constituent was formed during cooling. Hairline cracks were believed to form when this constituent subsequently broke down at a lower temperature with the liberation of hydrogen.

Many workers have found difficulty in accepting the pressure theory, with or without the hydrogen-rich constituent. Instead they have considered that crack formation may be adequately explained in terms of hydrogen embrittlement and the stresses due to cooling and transformation. Quite recently Troiano and his colleagues¹² have taken this view and have attributed the major role in hairline crack formation to stresses due to the transformation of austenite; they did not observe flakes in the absence of transformation stresses. Much earlier, however, Andrew *et al.*⁵ had shown that transformation stresses were *not* necessary for crack formation and two of their experiments are worthy of mention. Both concerned a nickel-chrome-molybdenum steel 4S11 (4.2 per cent Ni, 0.7 per cent Cr, 0.23 per cent Mo and 0.33 per cent C). In the first experiment cylindrical specimens were quenched to a temperature in the range 250°-600°C., held for varying times and then quenched into brine. After ageing at room temperature the specimens were examined for cracks. Whether cracks were observed or not depended upon the length of time in the isothermal bath, but not upon the transformation that

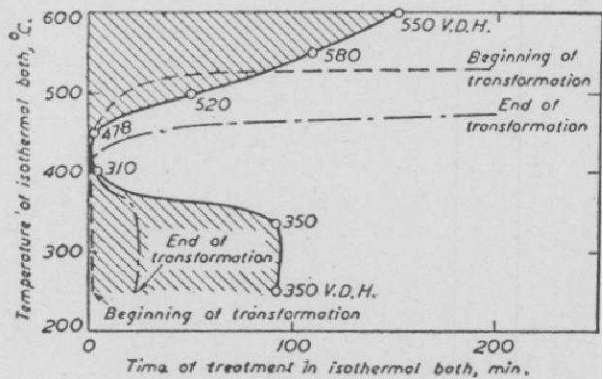


FIG. 5 — RELATION BETWEEN CRACK FORMATION AND TRANSFORMATION CHARACTERISTICS OF 4S11

had occurred before quenching (see FIG. 5). From 525° to 600°C. no transformation occurred in the bath and the stresses in the quenched specimens were, therefore, a maximum. Cracks occurred for holding times less than 100 min., but not if the times were greater than 150 min., On the other hand, cracks were observed in specimens quenched from the range 250°-375°C. even when transformation was completed in the isothermal bath before quenching into brine. Within this lower temperature range transformation was completed in 24 min., but deep-seated and random cracks were observed in specimens held for over 90 min.

In the second experiment Andrew and his colleagues soaked a specimen of 4S11 in hydrogen for 48 hr. at 1100°C. and then allowed it to cool in air until a sensitive dilatometer showed that the expansion at the transformation was completed. It was then quenched in water and immediately cut half-way through on the mid-transverse section and half-way longitudinally, so that a quarter of the specimen was removed. The remainder of the specimen was allowed to age at room temperature for two days after which the longitudinal cut was completed and the whole longitudinal section was etched to reveal cracks. As Fig. 6 shows quite clearly the first longitudinal saw cut must have been completed before the

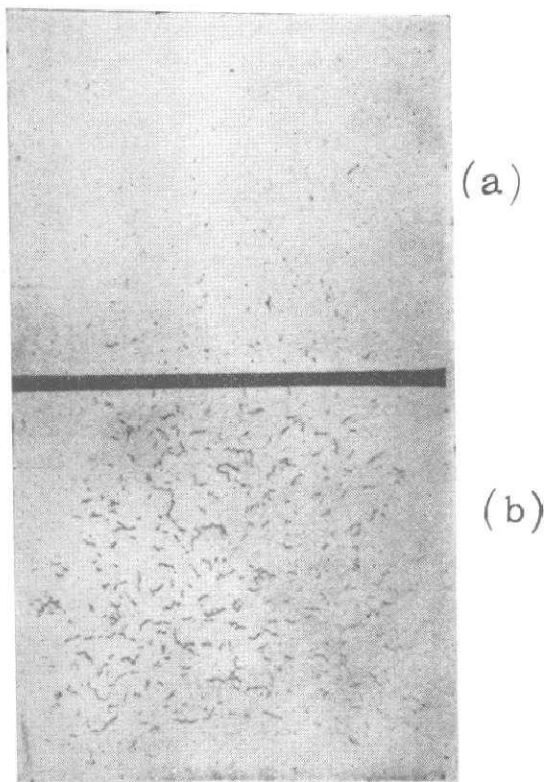


FIG. 6 — STEEL 4S11, HYDROGEN-SOAKED AND WATER-QUENCHED FROM JUST BELOW A_1 POINT. (a) SECTIONING BEGUN BEFORE END OF INCUBATION. (b) SECTIONED AFTER INCUBATION HAD ENDED

incubation period was over, but the last half-inch or so coincided with the first stages of crack formation. Ageing for two days at room temperature gave ample opportunity for numerous cracks to be formed in the lower half of the specimen. The appearance of the cracks in Fig. 5 and the difference between the top and bottom halves give the impression that the cracks are not formed suddenly as one might expect if it were merely a matter of the resultant stresses being locally sufficient to rupture the hydrogen-embrittled steel. Rather it seems that tiny cracks are first formed and that these then extend with time until they are clearly visible to the naked eye.

Referring back to that part of the work of Troiano and his colleagues which appears

to conflict with the earlier work by Andrew, it is perhaps worth mentioning that the critical specimens of the nickel-chrome-molybdenum steel 4340 that had been isothermally treated at 325°C . are both reported as containing the same amount of hydrogen. This in spite of the fact that one specimen had been in the isothermal bath five times as long as the other at a temperature which is known to promote rapid removal of hydrogen.

The Effect of Hydrogen Upon Transformation

Some ten years ago it was shown that hydrogen retarded transformation in 4S11 above 450°C . but had little, if any, effect in the range 330° - 450°C .⁵ More recently Cottrell¹³ observed that the effect of hydrogen in a manganese-molybdenum steel was to reduce the transformation occurring on cooling to the M_s temperature and to retard subsequent martensite formation. In hitherto unpublished work at Sheffield it has been shown that hydrogen has no effect upon the M_s temperature, but in four of the five alloy steels examined has retarded the martensite reaction. The effect does not appear until about 40 per cent of the austenite has transformed and then becomes increasingly marked as the transformation proceeds. As determined by metallographic methods the M_f temperature is depressed by as much as 50°C ., but the last traces of martensite may be more persistent than this figure suggests.

Although much work remains to be done, it is clear that any theory of hairline crack formation must take into account the stabilizing effect of hydrogen upon austenite.

The Mechanism of Hairline Crack Formation

The mechanism of hairline crack formation is a complex one in which many factors play a part and it is not at present possible to assess their relative importance. There

is every reason to believe that hairline cracks do not occur in the absence of hydrogen. Due account must, therefore, be taken of the following effects of hydrogen:

- (1) hydrogen embrittlement — when cracks are developed the steel generally contains far more hydrogen than is necessary for marked embrittlement;
- (2) the diffusion of atomic hydrogen into internal cavities and the building-up of pressures of molecular hydrogen — this process must go on, but it is not possible to say whether the pressure developed in a particular case will be large or small, only that the limiting pressure *may* be high compared with the strength of the steel;
- (3) the stabilization of austenite and its retention to lower temperatures.

At the same time, the steel will be subject to the various stresses developed during its manufacture and particularly whilst cooling after hot-working. These stresses will include:

- (4) body stresses due to temperature difference during cooling;
- (5) transformation stresses;
- (6) stresses due to the presence of inclusions and segregates.

To these stresses should probably be added another due directly to (3), namely

- (7) stresses resulting from the breakdown of traces of austenite that have been stabilized to a lower temperature by hydrogen. Breakdown of traces of austenite at relatively low temperature would produce tensile stresses in the surrounding matrix.

It could be that this last effect is the one that triggers off crack formation, for the local resultant of all the stresses operating could be high and there would be a high local hydrogen concentration and corresponding embrittlement of the steel. Once a crack has been initiated the hydrogen pressure mechanism must operate to greater or lesser

extent and this may be the cause of the gradual extension of the cracks.

The Prevention of Hairline Cracks

Until a completely satisfactory theory of hairline cracks has been developed, remedial measures must be aimed at minimizing hydrogen pick-up during steel-making and at the removal of as much hydrogen as possible during the hot-working process and subsequent cooling.

As far as the steel-making process itself is concerned there is reason to believe that even with best melting shop practice hydrogen contents below 4 cc./100 g. cannot be systematically produced. Such hydrogen contents correspond to equilibrium with the gas phase having a hydrogen partial pressure of about 18 mm. of mercury and it may be that the lower limit for hydrogen in the steel bath may be imposed by atmospheric humidity. Precautions must be taken if the hydrogen is to be kept down to this level, however, for hydrogen may easily be added to the melt as:

- (1) Moisture contained in lime or limestone additions — if it is all transferred to the steel, the moisture in one pound of completely slaked lime will give a hydrogen content of about 11 cc./100 g. to one ton of steel.
- (2) Rust on the scrap — light scrap is more dangerous than heavy scrap in this respect. Scrap may contain 16-50 cc. H_2 /100 g.¹⁴
- (3) Hydrogen in alloy additions — should be minimized by heat treatment in air prior to use.

Fresh nickel has been reported as containing 85-93 cc. H_2 /100 g., but this is reduced to 2 cc./100 g. by heating in air for one hour at 850°C.¹⁴

Ferro-manganese (80 per cent) may contain over 100 cc. H_2 /100 g., whilst 70 per cent ferro-chrome contains from 2 to 21 cc./100 g.¹⁴

Hydrogen may also be picked up from the ladle or the feeder head if damp refractories are used; 'wild' ingots can sometimes be traced to this cause. With good practice, however, there may be a drop of about 0.5 cc. H_2 /100 g. between furnace and ladle, presumably due to the large effective surface exposed to air by the stream of molten steel.

It is generally believed that the 'boil' helps to remove hydrogen and the passage of bubbles of carbon monoxide through the bath should certainly have this effect, but Sykes, Burton and Gegg³ have found no systematic effect. The hydrogen content at the end of the boil was sometimes greater and sometimes less than at melt-down.

Once the steel has solidified, hydrogen can only be removed by heat treatment. For smaller sizes of billets up to say 6 in., it is frequently sufficient to stack hot from the forge in cooling pits, but for larger sections more elaborate treatment is necessary. Hydrogen removal is a diffusion process and, as mentioned earlier, the most effective treatment is one which gives the optimum conditions for diffusion, namely heating at 650°C., high in the alpha range. The time necessary will depend upon the ruling section, varying as the square of the linear dimension. For really large forgings the time may be impracticable except for special products. Thus if with 2 in. bar the hydrogen content can be reduced from 6 cc./100 g. to 1 cc./100 g. in 5 hr., the time required for a forging of 24 in. ruling section will be 30 days.

It follows from this that in normal production hydrogen is not eliminated from the steel

but is reduced to as low a level as practicable. Heat treatments that are satisfactory with billets or forgings made from ingots of low hydrogen content may be inadequate with casts containing much hydrogen. Close co-operation is, therefore, called for at all stages from raw material to finished product if hairline cracks are to be avoided.

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