

THE EFFECTS OF HYDROGEN ON ALLOY STEEL PRODUCTION

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ONLY relatively recently has the presence of hydrogen in steel become the object of serious study, although over eighty years ago Thomas Graham, then Master of the Mint in London, observed that hydrogen formed a substantial part of the gases evolved when ferrous materials were heated in a vacuum [*Proc. Roy. Soc.* **15** (1866-67), 502-503].

As a result of work done in the last twenty years or so, it is now accepted that hydrogen can cause unsoundness in ingots in killed steel, with accompanying defects in the products of such ingots. It is reasonably established that hydrogen, if present in solid steel, can lead to reduction in the ductility. It is also fairly certain that hydrogen plays a very important part in the formation of hair-line cracks. Reduction in ductility and hair-line cracks are both extremely unwelcome to the producer of large forgings and he has to go to considerable lengths to avoid these ill-effects of hydrogen. To him, therefore, and to any producer of high quality steel, a clearer understanding of the effects of hydrogen in steel, together with an indication of the means which may be useful in preventing excessive amounts of hydrogen from entering the steel, is of great value.

The first problem which had to be solved was that of determining the hydrogen content of steel with a fair degree of accuracy. This was eventually solved by designing an apparatus in which steel samples could be heated to about 650°C. in vacuum and the evolved gases pumped off and analysed; it was found that it was unnecessary to melt the samples, although the first reliable figures for hydrogen had actually been obtained by

the vacuum fusion methods for the determination of oxygen in steel.

Having developed a reliable method for the determination of hydrogen in steel, attention was then turned to the possibility of determination of the hydrogen content of liquid steel in the furnace. The problem was, therefore, to develop a suitable method for sampling the liquid steel to produce a solid sample containing the whole of the hydrogen. Since the solubility of hydrogen in liquid steel is far greater than that of solid steel and since the solubility in solid steel decreases with temperature, it appeared likely that there would be loss of hydrogen on solidification and cooling of any sample taken from the steel bath. After careful comparison of several methods of sampling, including several types designed so that any gases evolved are collected and analysed, we are of the opinion that a notched pencil test produced by pouring the metal from a spoon into a split mould (FIG. 1), extracting the pencil as soon as solid and quenching in water and then storing in contact with solid carbon dioxide until it can be dealt with, is perfectly adequate as a method of sampling for this purpose. Provided the sample is treated in the spoon with aluminium if it is taken from a bath which is not fully killed, provided the sample obtained is free from slag and provided the quenching is efficiently done, this method of sampling can be claimed to be as accurate as any other yet proposed.

Using this type of sampling, it has been found possible to establish ranges of hydrogen contents which may be expected in various types of steel melted in the various types of steel-making furnaces. But it would be as well, before we go on to discuss these

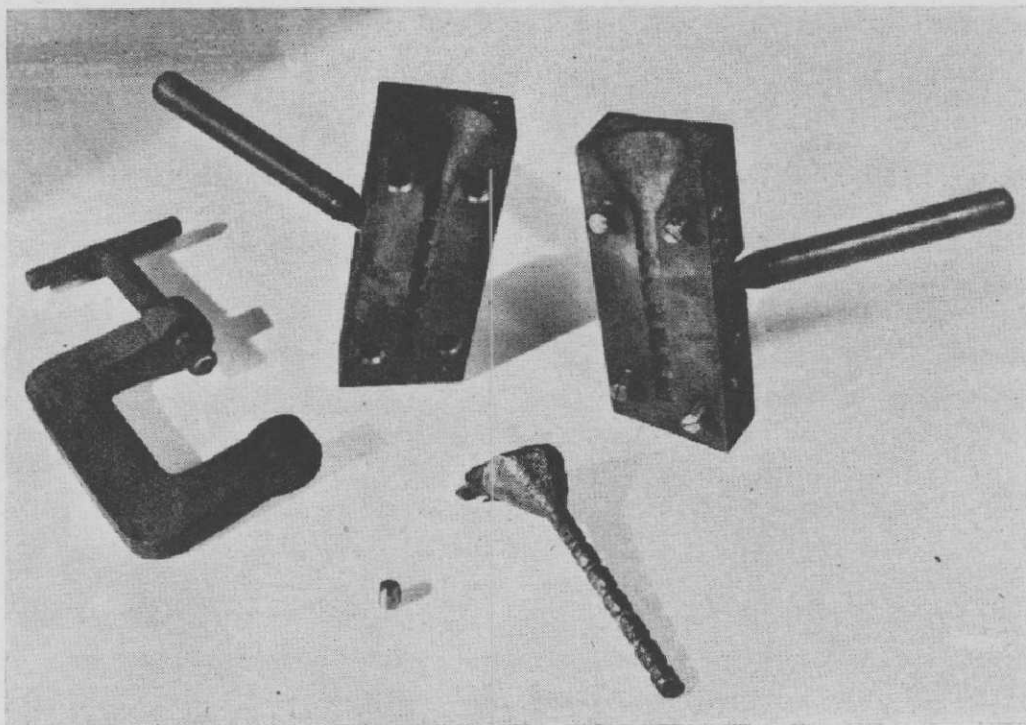


FIG. 1 — NOTCHED PENCIL TEST MOULD WITH CLAMP, ALSO SHOWING A CAST PENCIL AND A SAMPLE PREPARED FOR ANALYSIS

matters, to indicate the various systems in common use for expressing the hydrogen contents of steel. The usual method of expressing contents in weight per cent, whilst suitable for most of the impurities in ferrous materials, has the disadvantage that the contents likely to be met are so small that, on low-alloy steel, a content of 0.0006 per cent hydrogen is definitely on the high side. To overcome the inconvenience of so many decimal places, two other systems have appeared in the literature. The usual American practice is to consider the volume of hydrogen (at N.T.P.) extractable from unit volume of steel and a content of one 'Relative Volume' indicates that 1 ml. of hydrogen at N.T.P. is extractable from 1 ml. (or 7.8 g.) of steel. The British system is to report hydrogen contents in ml. (again at N.T.P.) per 100 g. of steel. Table 1 gives a comparison of the three systems for various hydrogen levels. Throughout this paper the contents will be quoted in ml. per 100 g.

TABLE 1—COMPARISON OF THE VARIOUS METHODS OF REPORTING HYDROGEN CONTENTS

Calculations are based on: (a) 2.016 g. of hydrogen occupy 22.4 litres (Gram Molecular Volume); (b) 7.8 g. per ml. as the mean density of steel

ML. PER 100 G.	WEIGHT, %	RELATIVE VOLUME
0.5	0.00005	0.04
1.0	0.00009	0.08
2.0	0.00018	0.16
3.0	0.00027	0.23
4.0	0.00036	0.31
5.0	0.00045	0.39
5.6	0.00050	0.44
6.0	0.00054	0.47
6.4	0.00058	0.50
7.0	0.00063	0.55
8.0	0.00072	0.62
9.0	0.00081	0.70
10.0	0.00090	0.78
11.2	0.00100	0.87
12.0	0.00108	0.94
12.8	0.00115	1.00
15.0	0.00135	1.17

Hydrogen Contents of Various Types of Steel

Examination of the results of hydrogen determinations at the Brown-Firth Research Laboratories on pencil tests derived from a large number of heats of steels of varying qualities has led to some very interesting conclusions.

The earliest survey of the hydrogen content of liquid steel was carried out on basic electric arc heats. It was found that the figures obtained just prior to tapping the furnace varied considerably from one heat to another. It was also found that the hydrogen content at the end of the boil was usually lower than that at the end of the heat, sometimes considerably so. The increment between the end of the boil and tapping the furnace was found to be lower when limestone was used for making the final slag rather than burnt lime; similarly, when burnt lime was used which had been stored for some time in the shop (and had presumably picked up moisture from the atmosphere), the finished heat was likely to have a higher hydrogen content.

These features have been reported by other workers throughout the world. It appears that during the boil the evolution of carbon monoxide from the bath, produced by the reaction of the iron oxide with the carbon:



sweeps out a considerable amount of hydrogen with it, provided the boil is sufficiently vigorous. In addition, since the bath of steel is then in a somewhat oxidized condition, that is, its content of iron oxide is relatively high, any likelihood of the reaction



followed by the solution of the atomic hydrogen in the liquid steel is largely prevented by the high oxide content, which tends to drive this reaction in the reverse direction. Thus the hydrogen content is

likely to be relatively low at the end of the boil.

Deoxidation of the steel bath by the addition of silicon, aluminium, etc., removes the ferrous oxide and replaces it with less reactive oxides. There is now no evolution of gas occurring to sweep out any further hydrogen, and there is opportunity for the reaction of the iron with any moisture added, according to the reaction already quoted. This accounts for the fact that the hydrogen content invariably rises towards the end of the heat.

When this was realized, it became obvious that care should be taken to prevent the addition of moisture with the final slag-making materials and with the alloys used to bring the metal to the desired composition. In the author's works this was effected by careful control of delivery and storage within the works of the burnt lime; in this way it was found possible to ensure that the lime charged contained on average only about 0.5 per cent of moisture. This step, together with the preheating of the alloys where these are relatively large in quantity, has enabled far more consistent results to be obtained from determinations of hydrogen content on tapping which are, on average, about 2.0 ml. per 100 g. lower than those originally obtained.

Typical figures for the hydrogen contents at tapping of various classes of steel melted in the basic electric arc furnace are given in Table 2. In all cases these are the mean values from at least forty determinations, while for some qualities the number of casts examined runs into several hundreds.

It will be seen that the carbon steels, in general, are lowest in hydrogen, with the low-alloy steels containing slightly more; the chromium-molybdenum steels seem capable of holding rather more hydrogen than the other low-alloy steels. Turning to stainless steels, the straight chromium ferritic types (13-20 per cent chromium) carry considerably more hydrogen than the low-alloy steels, while the austenitic stainless steels (18 per

TABLE 2 — AVERAGE VALUES FOR THE HYDROGEN CONTENT OF VARIOUS STEELS AT TAPPING WHEN PRODUCED BY VARIOUS STEEL-MAKING PROCESSES

QUALITY OF STEEL	HYDROGEN CONTENT, ml. per 100 g.		
	Basic Electric Arc Process	Acid Open-Hearth Process	Basic High-Frequency Process
Carbon steel	4.6	4.1	(4.6)
1.3% Ni steel	4.7	4.1	—
Ni-Cr-Mo steel	4.7	4.1	—
1% Cr-Mo steel	4.8	4.2	—
3% Cr-Mo steel	5.5	4.6	(5.0)
13% Cr stainless	8.2	—	7.4
18% Cr - 8% Ni stainless, etc.	10.3	—	8.8

cent chromium-8 per cent nickel, etc.) have the highest hydrogen contents of any of the steels so far studied.

Some heats melted in basic lined high-frequency induction furnaces have been examined. From such limited data as are available it would seem that the figures for carbon and low-alloy steels are approximately the same as would be obtained in the basic electric arc furnace. With stainless steels, however, the basic high-frequency furnace is capable of producing heats with lower hydrogen contents than the arc furnace, as will be seen by further reference to Table 2. Since the lining material and the slag ingredients are essentially the same for both types of furnace, it may be that the atomization of atmospheric moisture by the arc is responsible for this extra hydrogen. The figures, which are given in brackets for the high-frequency furnace in Table 2, are mean figures from relatively few heats.

Turning now to the acid open-hearth process, it has been found that the hydrogen contents usually met here are about 0.5 ml. per 100 g. less than those likely to be encountered in the basic processes. Typical

figures can again be found in Table 2. This might be expected when it is remembered that the process consists of a long boiling period followed by only a short quiescent period in the furnace prior to tapping. On the other hand, it can be argued that the furnace atmosphere contains burnt hydrogen, that is water vapour, which is only separated from the metal by a layer of slag, and that there should, therefore, be some equilibrium between the two, leading to a tendency for the metal to pick up hydrogen. This tendency would appear to be counteracted by the amount of iron oxide present in the liquid metal, since, when intentionally wet materials were on one occasion charged to the acid open-hearth furnace, the hydrogen fell during the boil to a normal level and remained so. It is of interest to note, however, that some German investigations lead to the suggestion that a vigorous boil, such that 0.30 per cent carbon is removed per hour, is necessary to prevent hydrogen increment in the acid open-hearth furnace [H. WENTRUP, H. FUCKE & O. RIEF, *Stahl und Eisen*, **69** (1949), 117 et seq.]; the corresponding figure quoted for the basic open-hearth furnace is 0.50 per cent per hour.

The author has no experience of the last-quoted type of furnace. From published data, however, it would appear that steel melted in the basic open-hearth furnace is likely to contain somewhat higher hydrogen contents than would be expected from the basic electric arc furnace for comparable qualities.

When the steel leaves the furnace, the liquid metal presents a large surface area to the atmosphere; oxidation presumably occurs and it is possible that one of the elements undergoing oxidation is hydrogen. This would explain one feature which has been noticed repeatedly: that the hydrogen content of the metal in the ladle is lower than it was when it left the furnace. The difference in hydrogen content is usually of the order of 0.3-0.8 ml. per 100 g. of steel

(it appears that this figure is likely to be less in acid open-hearth steel than in basic electric steel). On some occasions it must be admitted that the reverse occurs, sometimes giving an increment of as much as 2.0 ml. per 100 g. It is usually found, however, that cases of a major increment can be traced to the use of a newly bricked or newly patched ladle which has not been thoroughly dried out, and it must be assumed that the moisture present has reacted with the steel.

The question of the hydrogen content of the slag itself is of importance, since this is in intimate contact with the metal. It is possible that slags also contain combined moisture, in spite of their high temperature. Little work has been carried out on the slags, but there would appear to be considerable differences in the capacity of acid and basic slags for carrying hydrogen and water, basic slags having much higher contents. This may account for the greater ease with which basic melted steel picks up hydrogen after deoxidation; it may also have some bearing on the apparently lower decrease in hydrogen content noted on tapping the acid melted steel.

Typical hydrogen histories of various heats will probably be of interest at this stage. Fig. 2 relates to two basic electric furnace heats of 2.5 per cent nickel-chromium-molybdenum steel, melted under standard conditions, but showing the effect of moisture content of the lime used for making the final slag. Fig. 3 shows a plot of a heat of semi-killed steel made in a large American basic open-hearth furnace [R. M. SCAIFE, *Trans. A.I.M.E.*, **162** (1945) 375-381]. The effect of adding hydrogen-bearing material (in the form of powdered coal) to the ladle and also the increment when the vigour of the boil diminishes, as shown by the slow fall in carbon around the middle of the heat, are clearly seen. (The hydrogen figures reported here are lower than any which the author has personally observed; it is felt that the figures quoted are all probably low by a consistent amount throughout.)

The steps which can be taken to ensure that a heat of steel has as low a hydrogen content as possible may be summarized as follows:

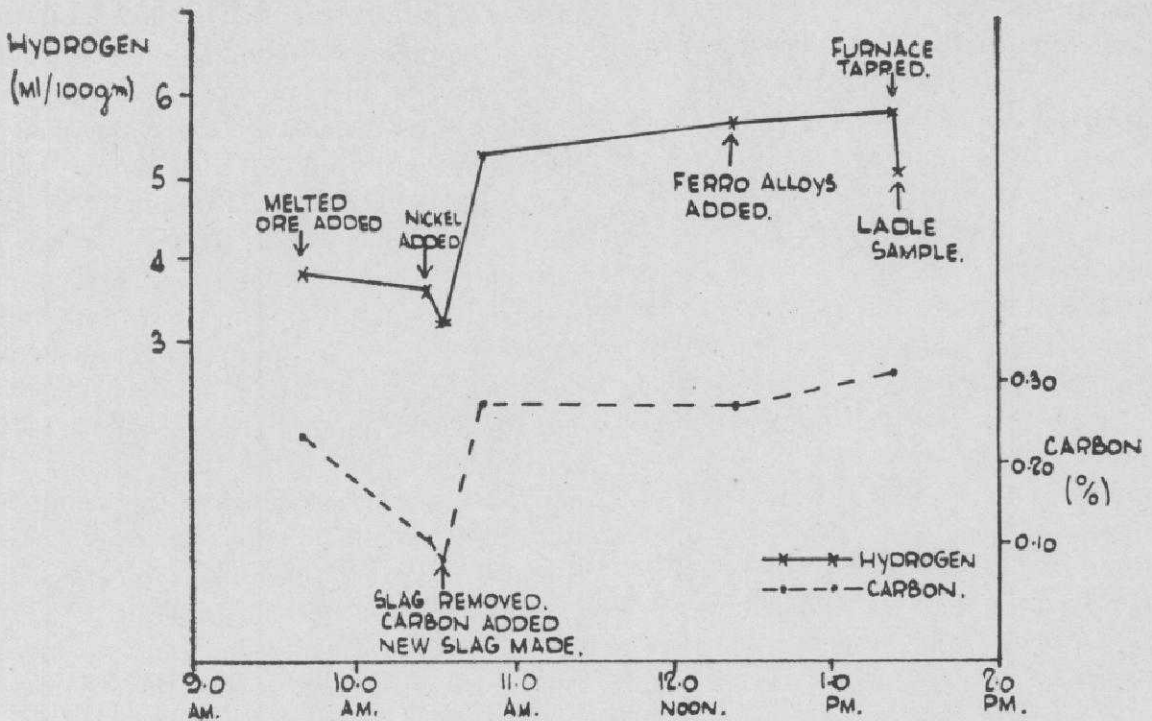
- (1) Charge as little moisture to the furnace as possible, particularly during the period when the steel is deoxidized; this applies particularly to slag-making materials in the later stages of basic furnace practices.
- (2) Ensure that the boil is as vigorous as possible by having a reasonably high carbon at melt and an active oxidizing slag.
- (3) Make sure that the launder, the ladle, the nozzle, runner bricks, moulds, etc., are thoroughly dry.

There would appear to be little else which can be done which has any bearing on the final content of hydrogen.

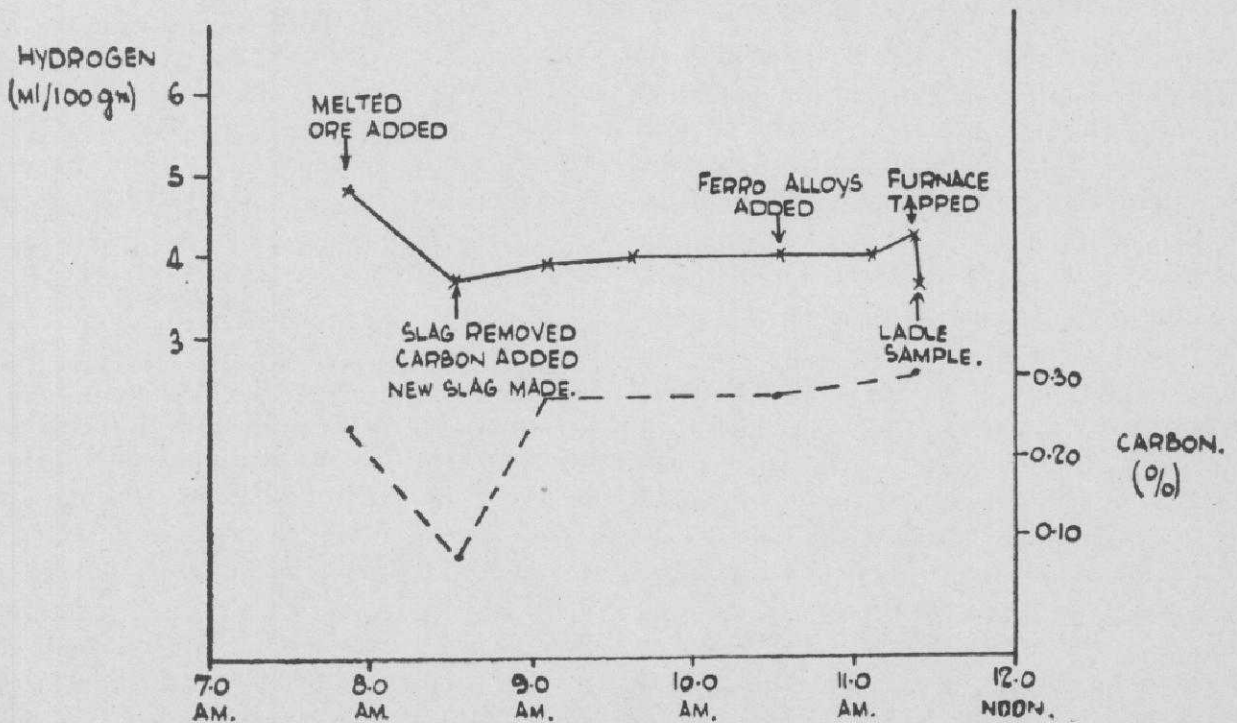
The Effect of Hydrogen on the Solidification of Liquid Steel

The most important part of any discussion of hydrogen in steel relates to its effect on the steel. This discussion can conveniently be divided into two sections, dealing with the effects of hydrogen on the solidification of liquid steel and those on the properties of solid steel.

The solubility of hydrogen in liquid steel is greater than that in solid steel at the melting point (*see* Electric Furnace Conference Proceedings, 1948, A.I.M.E.). This will lead to the assumption that, should a bath of liquid iron contain more than a certain amount of hydrogen, the amount of hydrogen in excess of this will be released on solidification. Such a state of affairs will be found to exist in some heats of steel, and the liberation of gas during the solidification will cause the metal to 'rise' in the mould and the heat is said to be 'wild'. Similar effects may be observed if a heat is not sufficiently deoxidized or killed. In this case the evolution of gas is due to the iron oxide-carbon reaction;



(a) HEAT MADE PRIOR TO PRECAUTIONS BEING TAKEN TO ENSURE MINIMUM MOISTURE CONTENT IN THE LIME.



(b) HEAT MADE WITH LOW MOISTURE LIME AND PREHEATED ALLOY ADDITIONS.

FIG. 2 — Hydrogen histories of two heats of 2.5 per cent nickel-chrome-molybdenum steel from a 25-ton basic electric arc furnace (a) with no special precautions, (b) with specially dried lime and preheated ferro-alloy additions

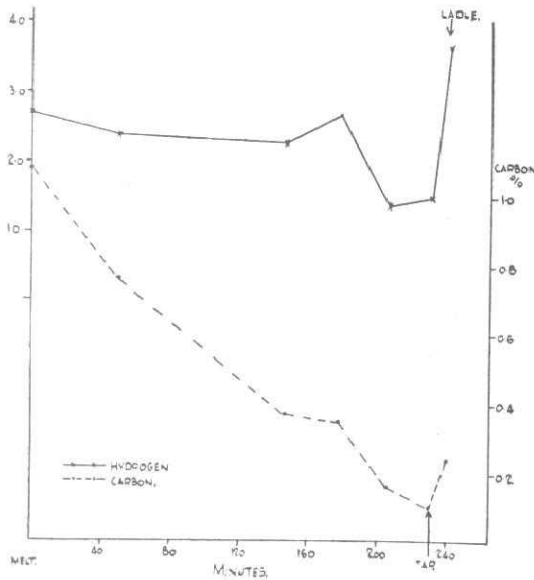


FIG. 3 — HYDROGEN HISTORY OF A HEAT OF SEMI-KILLED STEEL MADE IN A LARGE AMERICAN OPEN-HEARTH FURNACE [R. M. SCAIFE, *Trans. A.I.M.E.*, **162** (1945), 375-381]

such evolution of gas can be prevented by the addition of a small amount of aluminium or other suitable deoxidant capable of producing an oxide which will not react with the carbon. Another similar case may be met with high-chromium steels treated with nitrogen; if the nitrogen content is too high, the excess nitrogen will be liberated on solidification. The effect in all three cases is essentially similar. The metal at first settles down in the mould and may even show signs of sinking in the head. Then after a few seconds a slight oozing of liquid metal shows itself at the top of the ingot and the reaction quickly gathers speed. In bad cases liquid metal rises up and pours over the sides of the head box.

When the hydrogen content is lower than the critical amount necessary to cause wildness but is still too high for complete solubility, the ingots may appear to freeze normally. On further examination of the ingots, by taking chippings from the surfaces, it will be found, however, that pinholes are

present under the skin, particularly near the top of the ingots. Sectioning of such ingots in a transverse direction will reveal a pattern of small holes distributed below the skin of the ingot, with usually some larger holes along the crystallization axes and in the centre. Such ingots are termed porous.

From information obtained on such porous and wild ingots, it appears that, with fully killed steel, there are limiting hydrogen contents for the production of sound ingots; with somewhat more hydrogen, porosity will be encountered and, when the hydrogen content rises to still higher levels, the metal will rise in the moulds. Approximate hydrogen contents for such conditions are given for various types of steel in Table 3.

One very important point must be stressed in this connection: if the hydrogen content of a heat is within the range which should give sound ingots, it may still be found to produce porous, or even wild, ingots if other conditions are favourable to this. This can be illustrated by two actual examples.

The first example concerns a heat of acid open-hearth steel. This was a heat of 0.20 per cent carbon steel which came somewhat low in silicon, only 0.16 per cent being

TABLE 3 — APPROXIMATE HYDROGEN CONTENTS IN LIQUID STEEL EXPECTED TO PRODUCE POROSITY AND WILDNESS ON CASTING IN BASIC ELECTRIC ARC PRACTICE

TYPE OF STEEL	HYDROGEN CONTENT, ml. per 100 g.		
	Sound ingots	Porous ingots	Wild ingots
Carbon and low alloy	Up to 7.0	7.0- 9.0	Over 9.0
Chromium stainless	Up to 10.0	10.0-12.0	Over 12.0
Austenitic stainless	Up to 12.0	12.0-14.0	Over 14.0

present. The first ingots were seen to rise slightly; subsequently a small addition of aluminium was made to the moulds and the ingots were quite sound, while without the aluminium the ingots were subsequently scrapped on account of porosity. The addition of aluminium obviously prevented the reaction of oxides with the carbon, thus supplementing the somewhat low silicon content. It was felt, however, that the addition of aluminium should not have been necessary, since other heats with this silicon content had behaved quite normally. It was subsequently found that the hydrogen content was somewhat high for this type of steel, the figure obtained being 5.5 ml. per 100 g.; although this was within the limit for sound ingots in the ordinary way, the combination of the low silicon content (and thus the tendency towards the production of carbon monoxide) with the high hydrogen content had been sufficient to give gas evolution. When the tendency for the production of carbon monoxide had been removed by the addition of the aluminium, the hydrogen could be held in solution.

The second example concerns a heat of 18 per cent chromium-8 per cent nickel steel which gave rising ingots. Somewhat surprisingly it was found that the addition of aluminium to the liquid metal prevented the metal from rising and gave perfectly normal ingots. The steel in this case could in no way be considered as being insufficiently deoxidized, since it contained almost 1 per cent of silicon together with the deoxidizing effect of the large amount of chromium present. The hydrogen content of the steel was found to be just under 12.0 ml. per 100 g., which was high but should not have caused undue trouble. The explanation was given by a nitrogen determination, which showed over 0.06 per cent of this element. This, in conjunction with the rather high hydrogen content, was sufficient to give evolution of gas during solidification; when the aluminium was added, however, the nitrogen was com-

bined as nitride, and the hydrogen alone was not sufficiently high to give any trouble.

In both these cases, therefore, the liberation of gas during solidification was not solely due to hydrogen. It has been shown that the gas liberated from ingots of this type during solidification is never purely one gas. In the production of rimming steel, where gas evolution is deliberately produced by casting metal which is not fully killed, so that the iron oxide-carbide reaction will occur, it has been shown that the gas liberated is a mixture of carbon monoxide (up to 90 per cent), nitrogen (5.8 per cent) and hydrogen (3.6 per cent) together with small amounts of other gases. With reference to Table 3, therefore, if the steel is not fully killed or if it contains excessive amounts of nitrogen, the figures for hydrogen necessary to produce porosity and wildness will have to be reduced.

The type of structure obtained from wild ingots can be seen in Figs. 4-6. Fig. 4 is a section of a rectangular ingot of an austenitic stainless steel which rose in the mould. The steel in this case contained about 14 ml. hydrogen per 100 g. Fig. 5 shows a transverse macro-section from an ingot of a 3 per cent nickel steel which contained around 10 ml. hydrogen per 100 g.

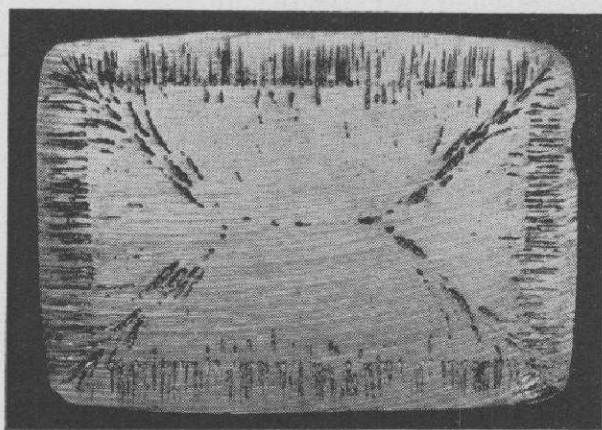


FIG. 4 — TRANSVERSE SECTION OF A WILD INGOT OF AUSTENITIC STAINLESS STEEL WHICH CONTAINED ABOUT 14 ML. HYDROGEN PER 100 G. PRIOR TO CASTING

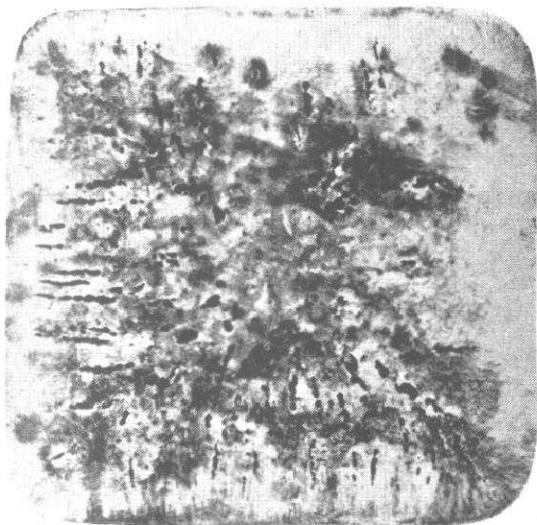


FIG. 5—ETCHED TRANSVERSE SECTION OF A WILD INGOT OF 3 PER CENT NICKEL STEEL WHICH CONTAINED ABOUT 10 ML. HYDROGEN PER 100 G. PRIOR TO CASTING

A longitudinal section was cut from a further ingot from this cast and was sulphur-printed, with the result shown in Fig. 6(a), which should be compared with Fig. 6(b), showing a similar print from a normal ingot in the same material. The sulphur print of the wild ingot is interesting in that streaks of high sulphur concentration follow the lines of the gas bubbles; it would appear that bubbles push sulphides and other inclusions in front of them, only depositing them when the liquid becomes too pasty to allow free passage to the bubbles.

Such wild ingots will forge or roll down and give apparently sound slabs or billets, unless the porosity is so close to the surface of the ingot that oxidation during heating for hot-working penetrates into them; in this case the surface of the resultant product will be extremely rough, with deep defects running into the body of the steel. Unless the holes are oxidized, however, they can be welded up by rolling or forging. On careful examination, however, some defects will still be found. Inclusion stringers can almost always be detected in such material;

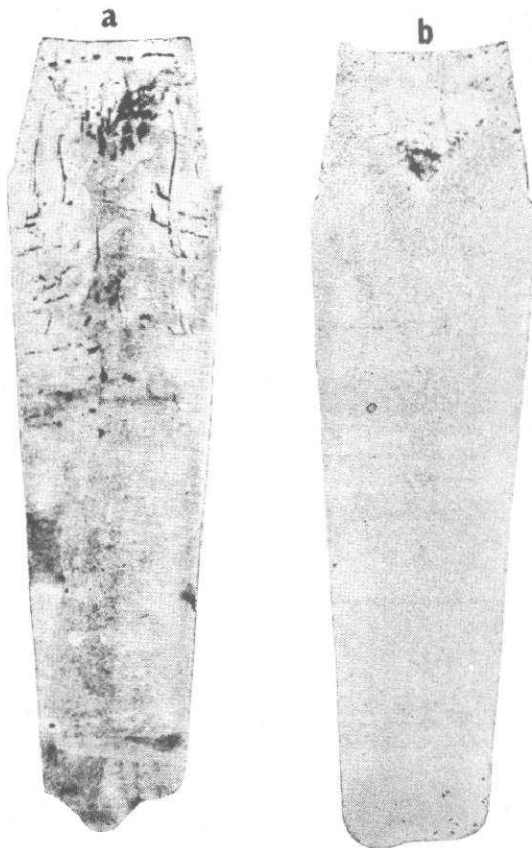


FIG. 6—SULPHUR PRINTS OF LONGITUDINAL SECTIONS OF TWO INGOTS IN 3 PER CENT NICKEL STEEL. (a) A WILD INGOT FROM THE SAME CAST AS THE SECTION SHOWN IN FIG. 5, (b) A NORMAL CAST

such were found in slab produced from the wild austenitic stainless ingot. On rolling this slab down, curious patterns could be seen on the hot-rolled 16-gauge sheet and blisters developed during the annealing of the 22-gauge cold-rolled sheet. These blisters can be seen in Fig. 7. Incidentally, analysis of the gas in the blisters showed it to be almost entirely nitrogen, and it must be assumed that this was the residue of the gas which originally occupied the blowholes in the ingot; this would originally be mostly hydrogen plus a small amount of nitrogen, but the hydrogen would diffuse out preferentially during the hot-working operations in the production of sheet. Some ingots from

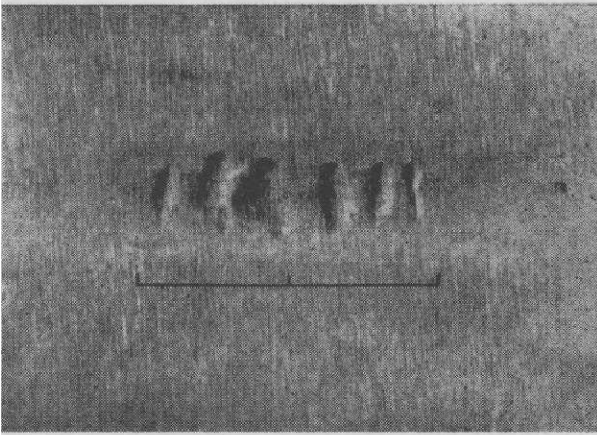


FIG. 7 — BLISTERS ON SHEET PRODUCED FROM THE WILD INGOT OF STAINLESS STEEL SHOWN IN FIG. 3 (Each division equals 1 in. on original sheet)

the wild 3 per cent nickel steel cast were rolled down to billet; these billets produced exceptionally bad transverse sulphur prints with gross segregation such as can be seen in Fig. 8.

If porous or wild ingots are encountered in killed steel production, it appears that it

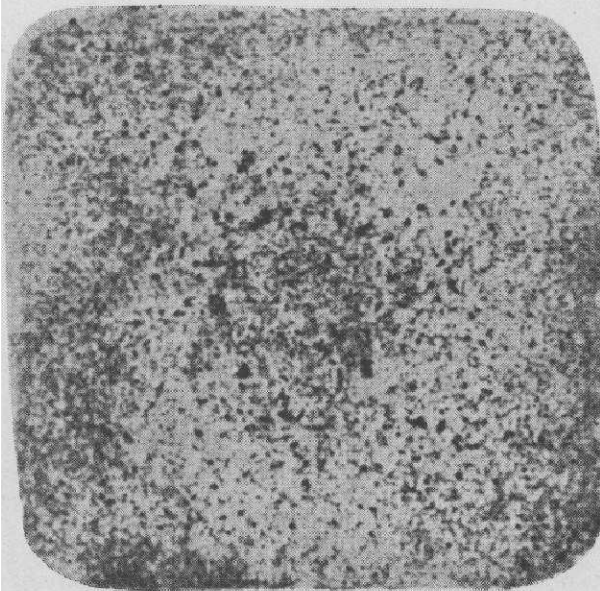


FIG. 8 — SULPHUR PRINT OF A TRANSVERSE SECTION FROM A 3 IN. BILLET PRODUCED FROM THE SAME WILD CAST OF 3 PER CENT NICKEL STEEL AS SHOWN IN FIGS. 4 AND 5

is always preferable to scrap them rather than roll them down to inferior products. When such heats are produced, however, there is usually a fairly obvious cause. The austenitic steel quoted above, for example, was produced using a supply of lime for the finishing slag which had a much higher moisture content than is normally met; due to a temporary shortage of burnt lime an emergency supply was obtained from an outside source, and this was subsequently found to contain as much as 5 per cent of moisture. The 3 per cent nickel steel heat was made with an experimental aluminous slag, and the bauxite used was decidedly damp. A similar heat was encountered when, during a period of wintry weather, transport was held up and a load of ferro-chromium, which arrived wet, was used immediately in the production of a heat of 13 per cent chromium steel. This heat, on tapping, gave a pencil test which contained 16.7 ml. per 100 g., the highest hydrogen content ever met at the Brown-Firth Research Laboratories. The metal, on casting, not only rose in the moulds: it lifted the head boxes off the moulds and ran out in quantity over the tops of the moulds. The following heat, of the same quality, was made in precisely the same manner, but the ferro-chromium in this instance was preheated. At tapping, this heat contained only 8 ml. hydrogen per 100 g.

Two other points in connection with unsoundness in ingots should be mentioned.

It is normal practice, in the production of ingots in killed steel, to coat the insides of the moulds with tar or some other dressing prior to casting, to produce a better ingot surface by creating a slight pressure away from the mould walls during the casting of the liquid metal. This procedure may give rise to some trouble if care is not exercised in the application of the tar; if the tar contains moisture, or if the mould is cold and an excessive layer of tar is applied, the action of the hot metal on coming into contact with the tar will be to create a rapid evolution of

gas rich in hydrogen, which may cause local segregation of hydrogen in the vicinity of the skin of the rapidly freezing ingot. Any hydrogen trapped in this way will give rise to a series of very small blowholes or pinholes just below the surface of the ingot. When the ingot is subsequently rolled, these will behave similarly to the blowholes near the skin in a wild or porous ingot, except that the effect will be on a smaller scale. The resulting billet will be covered with a mass of fine lines, such as those shown in Fig. 9, which is a photograph of a slice of a billet which has been etched to show up these defects, which are known as 'seams'. Normally seams are of little consequence unless they are exceptionally deep; if, however, the billet is to be used for the production of forgings, the presence of seams can give rise to considerable trouble, an example of which can be seen in the partly finished drop stamping shown in Fig. 10. Ingots showing this trouble can be detected by examination with a chipping hammer. On removal of the skin small blowholes can be found, which, however, are removed by taking a further cut, thus differentiating them from truly porous ingots, where the effect becomes more marked on cutting deeper. Localized porosity may also be

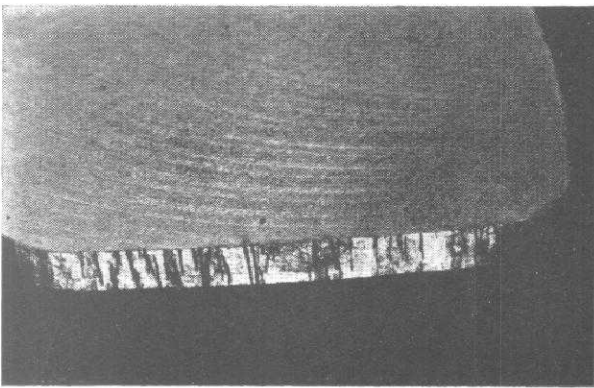


FIG. 9 — VIEW OF A TRANSVERSE SECTION OF A BILLET, SHOWING SEAMS



FIG. 10 — VIEW OF A PARTLY FINISHED DROP STAMPING, SHOWING THE EFFECT OF SEAMS IN THE BILLET FROM WHICH IT WAS FORGED

found in ingots which show patches of slag attached to the ingot faces; on chipping in these areas pinholes can often be found, but these again can be cleared by cutting slightly deeper into the ingot. Here, apparently, the slag is high in hydrogen, giving a localized concentration of hydrogen during solidification; alternatively, it may be postulated that the slag, being rich in oxides of iron and manganese, increases the tendency for formation of carbon monoxide in a local area by neutralizing the effect of the deoxidants present in the steel and then the combined effect of the hydrogen and the carbon monoxide produces the porosity.

The other factor which can produce local unsoundness in an ingot is the use of damp head boxes on the top of moulds or even failure to dry out the cement used to fix the head box on the mould. In this case reaction between the steel and the moisture in the head will occur and there will arise a localized high concentration of hydrogen sufficient to produce unsoundness. The most disturbing feature, however, is that the porosity is not confined to the head, where it would be of little consequence, but that it strikes back into the metal which is still

liquid when the metal first reacts with the moisture. Cases have been found where metal has been rendered unsound over a foot below the head joints, thus causing the rejection of a considerable quantity of otherwise good material. It is often found that only one or two ingots per cast are affected in this manner, if any at all. This is an indication that damp heads (or at any rate, conditions peculiar to those moulds) are responsible; it also means that all ingots in any suspected cast must be examined by chipping.

It will be appreciated that the lower the hydrogen content of the steel in the ladle, the more hydrogen must be picked up to produce the level of hydrogen necessary to give porosity. It has been found that the control of the hydrogen as far as possible in the furnace has reduced the tendency for these localized porosities to occur.

In the production of castings the same effects occur as in ingot production. Normal practice is to add a liberal amount of aluminium or other strong deoxidant before casting into green-sand moulds to ensure that no evolution of carbon monoxide will occur to give a porous casting. Even so, blowholes near the skin do occur; with control of hydrogen during melting as far as possible it is found that the tendency for such defects to occur is greatly reduced or eliminated. Conversely, the addition of aluminium can be reduced, with beneficial effects on the fluidity of the liquid metal.

The Effects of Hydrogen on Solid Steel

It remains now to discuss the effects of hydrogen on solid steel. As far as can be ascertained, provided an ingot free from porosity is obtained, very little effect due to hydrogen can be detected in stainless steels, either the austenitic steels or the plain chromium steels. It is quite common, for instance, for billets of 18 per cent chromium-8 per cent nickel steel to contain between 6.0 and 8.0 ml. hydrogen per 100 g. without

any noticeable effect on the properties of the steel. In the case of the low-alloy and carbon steels, however, the effect of hydrogen in the solid steel cannot be so easily dismissed.

It has long been known that the presence of hydrogen has the effect of lowering the ductility of low-alloy steel. Typical test results obtained on core tests from rotor shaft forgings in 3 per cent chromium-molybdenum steel, which illustrate this point, can be seen in Table 4.

TABLE 4 — CORE TESTS ON 3 PER CENT Cr-Mo ROTOR SHAFTS

BODY DIA., in.	HEAT TREATMENT	MAX. STRESS, tons/sq.in.	REDN.OF AREA, %	HYDROGEN CONTENT, ml./100 g.
Acid Open-Hearth Steel				
28.25	HT 670°C.	45.2	15	5.7
	HT 670°C. + SR 630°C.	45.2	56	0.3
31.00	HT 675°C.	46.8	42	2.8
	HT 675°C. + SR 700°C.	41.0	67	0.4
Basic Electric Arc Steel				
31.00	HT 640°C.	50.4	30	4.5
	HT 640°C. + T 620°C.	50.8	55	0.1
28.00	HT 640°C.	45.8	21	3.4
	HT 640°C. + T 620°C.	46.4	71	0.2

HT = hardened and tempered; SR = stress relieved; T = tempered in testpiece form.

A detailed investigation of the effect of hydrogen on the ductility of low-alloy steel has recently been reported [J. D. HOBSON & C. SYKES, *J. Iron & Steel Inst.*, **169** (1951), 209-220]. Previous experiments on hydrogenated test specimens had relied on impregnation with hydrogen, either by electrolysis or by heating in the gas at

elevated temperatures. The first method is extremely erratic, while the second method alters the microstructure and hydrogen is lost on any subsequent tempering. The recent work relied on the introduction of hydrogen by heating the steel samples (usually in the form of tensile testpieces) in hydrogen under pressure at temperatures below the change point of the steel. In this way the effect of hydrogen on steel, heat-treated to any particular tensile strength, could be observed. The percentage reduction of area from the tensile tests, plotted against the hydrogen contents, can be seen in Fig. 11. This shows that the results obtainable by the method are reproducible for the same class of material and also indicates a linear drop in the reduction of area with increase in hydrogen content.

These factors have also been indicated by work carried out in America. Fig. 12 is taken from an American paper (S. MARSHALL, T. M. GARVEY & D. S. LLEWELYN, *Proc.*

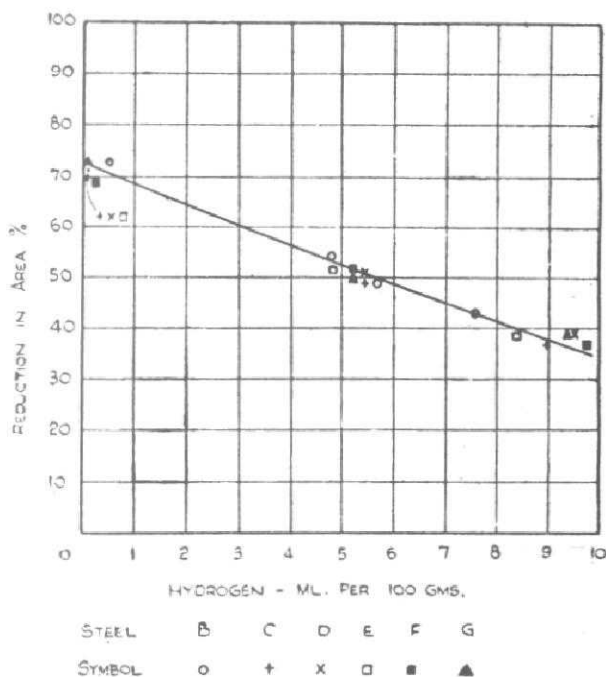


FIG. 11 — EFFECT OF HYDROGEN ON THE DUCTILITY OF BARS FROM SIX CASTS OF 3 PER CENT CHROMIUM-MOLYBDENUM STEEL

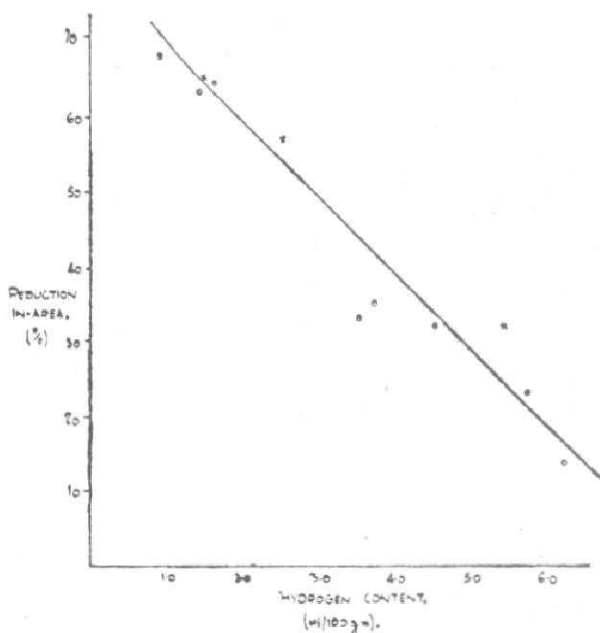


FIG. 12 — EFFECT OF HYDROGEN ON THE DUCTILITY OF 0.10 PER CENT CARBON STEEL (SHADBURN MARSHALL AND CO-WORKERS, *Electric Furnace Conference, A.I.M.E., 1948*) (The results are derived from two casts, denoted by circles and crosses respectively)

Electric Furnace Conference, A.I.M.E., 1948) and shows data from two casts of 0.10 per cent carbon steel, tested some months apart; the crosses and circles represent the two different casts.

The effect of maximum stress on susceptibility to hydrogen embrittlement was then studied. Various treatments were used to vary the maximum stress on bars of 3 per cent chromium-molybdenum steel, the bars being treated at 1 in. diameter and subsequently machined to testpieces. The relationship between maximum stress, reduction of area and hydrogen content for tensile strengths down to 51.5 tons/sq. in. is given in Fig. 13(a) and for tensile strengths of 51.5 tons/sq. in. and under is given in Fig. 13(b). The interesting features here are the increase in the embrittlement effect with increasing departure from a tensile strength of 51.5 tons/sq. in., either upwards or downwards, as well as with increasing hydrogen content, thus indicating that there

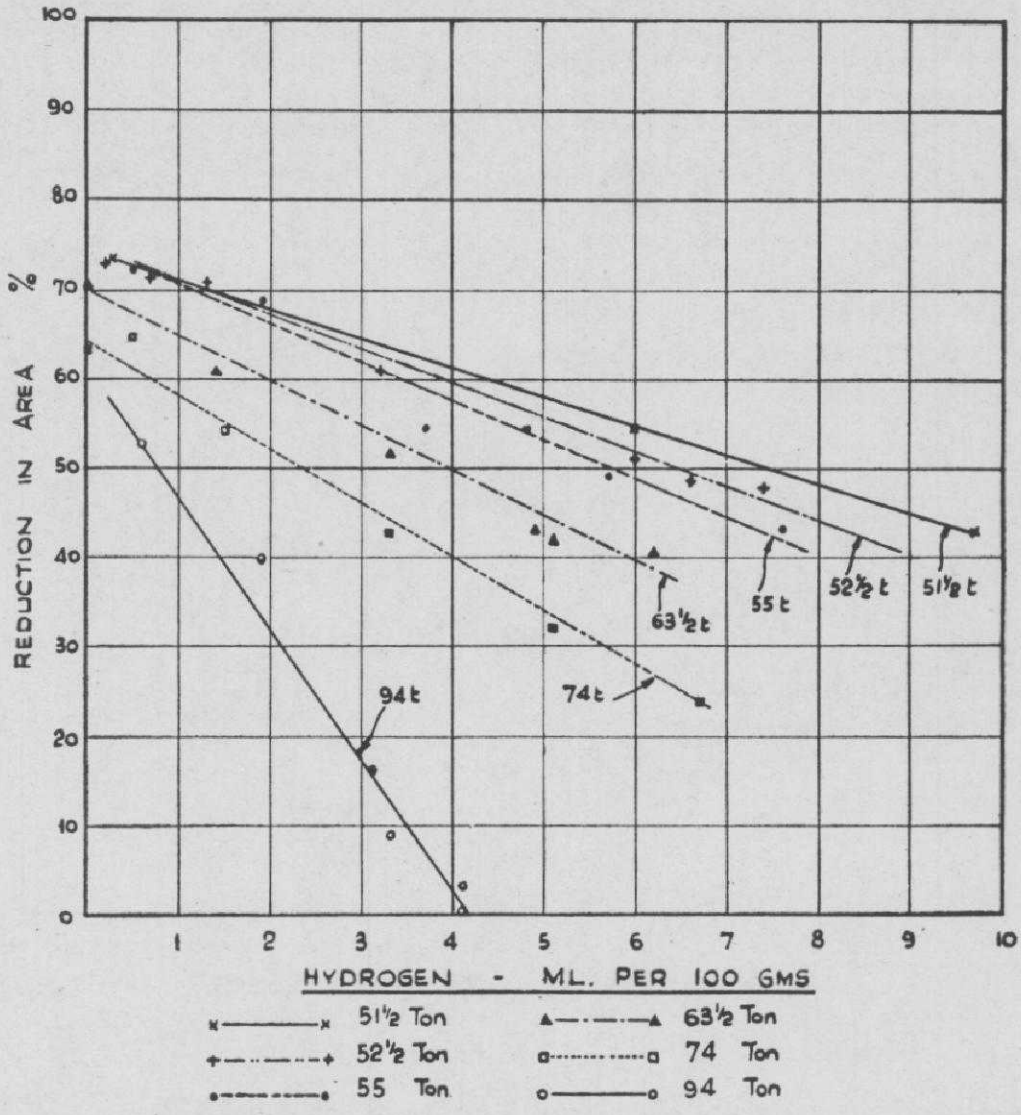


FIG. 13(a) — EFFECT OF HYDROGEN AND TENSILE STRENGTH ON DUCTILITY OF 3½ PER CENT CHROMIUM-MOLYBDENUM STEEL, FOR TENSILE STRENGTHS OF 51.5 TONS/SQ. IN. UPWARDS

is an optimum tempering temperature at which the susceptibility to hydrogen embrittlement is at a minimum. In this particular case the tempering temperature appears to be 670°C. Prolonged tempering above this temperature shows spheroidization in the microstructure of the steel; this appears to be a significant factor in the resistance to embrittlement at lower tensile strengths. The effect of optimum temperature can probably be shown more clearly by plotting reduction of area against tensile strength for

varying hydrogen contents; this has been done in Fig. 14.

The effect of the method of production of the bar was studied by comparing the results obtained on radial, transverse and longitudinal test bars derived from a forging produced from a 50-ton ingot and also on a transverse test bar from a 95-ton ingot, both in 3 per cent chromium-molybdenum steel. The bars were oil-quenched from 900°C. and then tempered at 660°C. to give a tensile strength of approximately 55 tons/sq. in.

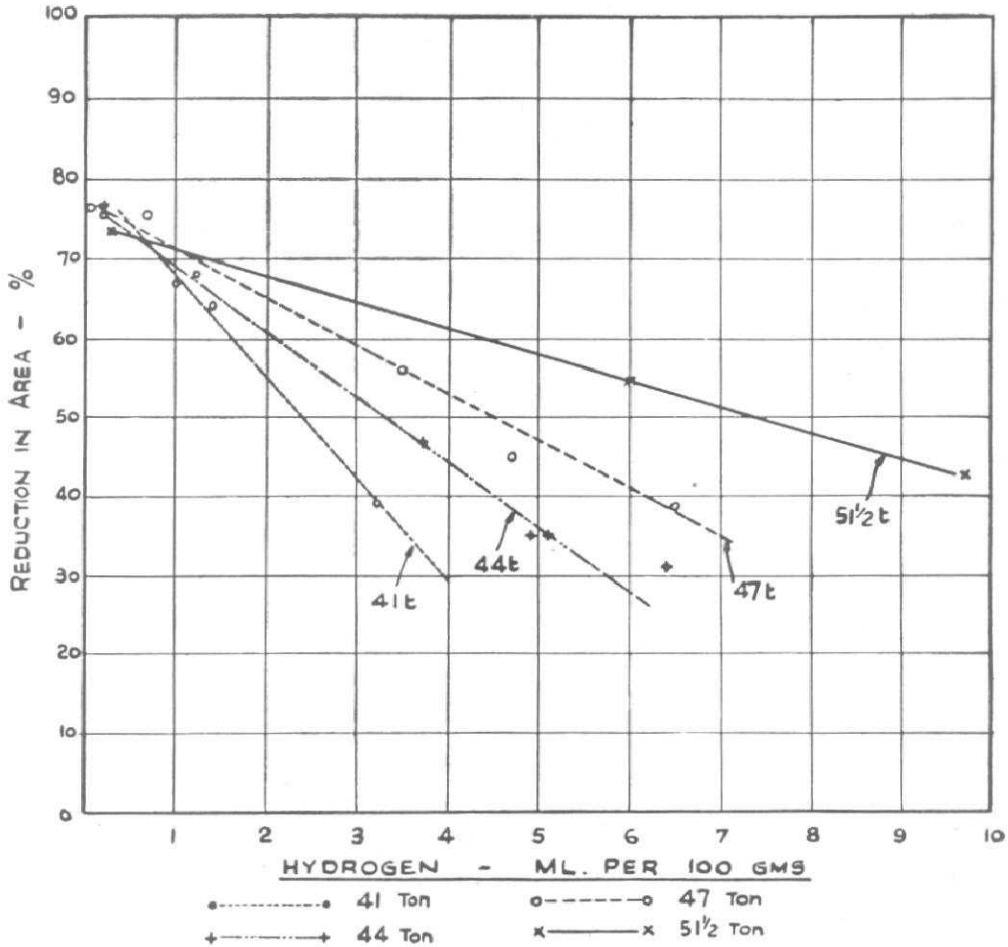


FIG. 13(b) — EFFECT OF HYDROGEN AND TENSILE STRENGTH ON DUCTILITY OF $3\frac{1}{2}$ PER CENT CHROMIUM-MOLYBDENUM STEEL, FOR TENSILE STRENGTHS OF 51.5 TONS/SQ. IN. DOWNWARDS

Tensile testpieces were then prepared and hydrogenated to different levels. The results of these tests can be seen in Fig. 15. The results from the longitudinal tests show little difference from the results obtained on rolled bar previously. Transverse and radial tests, however, show lower ductility without hydrogen present than do the longitudinal tests and are also subject to hydrogen embrittlement, although the slopes of the curves are somewhat flatter than those for the longitudinal tests. The radial and transverse tests from large forgings, however, are considered as an important indication of the suitability of the

forgings for service in many cases; it would appear, therefore, that steps should be taken to reduce the hydrogen content at the centre of forgings to below 2.0 ml. per 100 g. if the transverse and radial tests are not to be adversely affected.

Further tests were carried out, this time with 3 per cent nickel steel, to determine whether any difference in susceptibility to hydrogen embrittlement could be detected in forged and rolled material. Bars, forged and rolled from the same cast, were normalized from 850°C. and then tempered at 650°C. to give a tensile strength of about

50 tons/sq. in. Both materials, hydrogenated to different levels in the form of tensile testpieces, showed a similar embrittlement effect; the results are shown in Fig. 16.

Several other tests were carried out on a variety of steels. These confirmed the conclusions already put forward. Fig. 17 is of interest in that it shows the embrittling

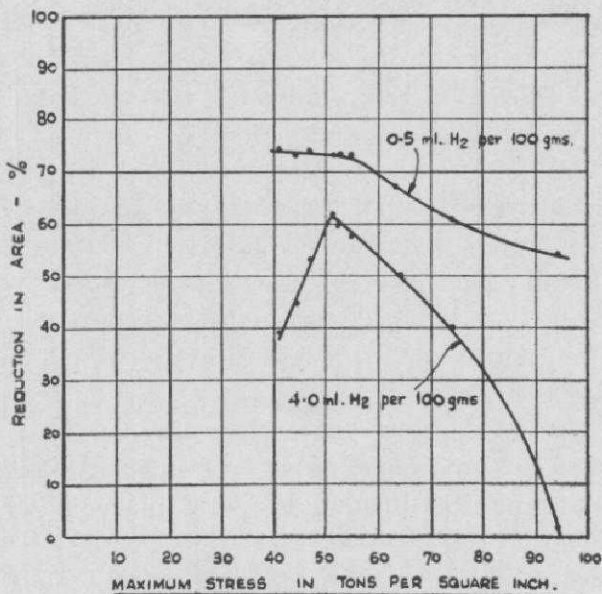


FIG. 14 — VARIATION OF REDUCTION IN AREA WITH TENSILE STRENGTH FOR 3.5 PER CENT CHROMIUM-MOLYBDENUM STEEL CONTAINING (a) 0.5 ML. HYDROGEN PER 100 G., (b) 4.0 ML. HYDROGEN PER 100 G.

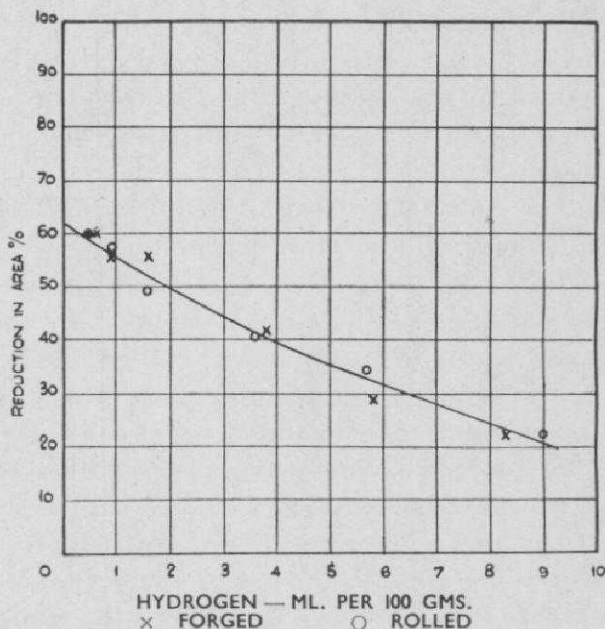


FIG. 16 — EFFECT OF HYDROGEN ON THE DUCTILITY OF FORGED AND ROLLED BARS DERIVED FROM ONE CAST OF 3 PER CENT NICKEL STEEL

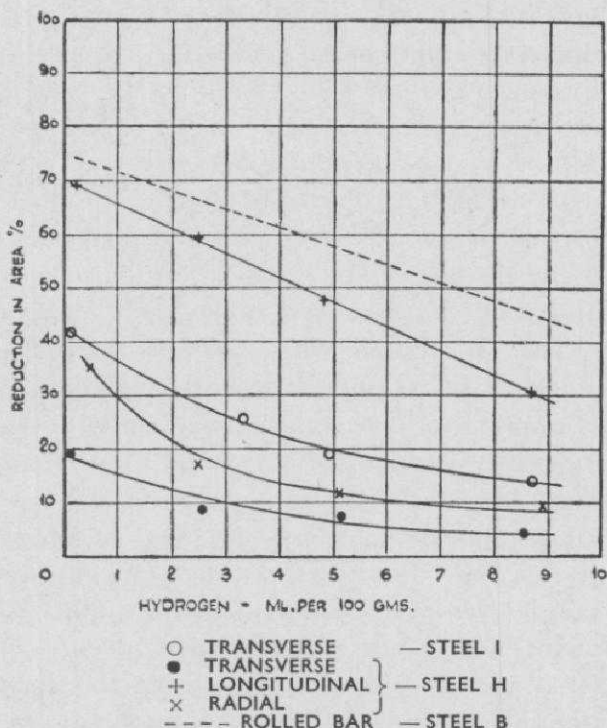


FIG. 15 — EFFECT OF HYDROGEN ON THE DUCTILITY OF SAMPLES DERIVED FROM FORGINGS IN 3 PER CENT CHROMIUM-MOLYBDENUM STEEL

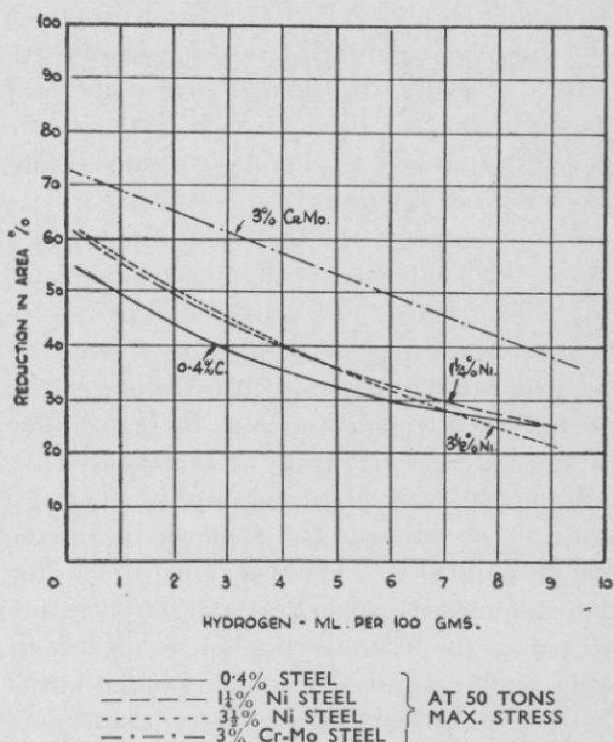


FIG. 17 — EFFECT OF HYDROGEN ON THE DUCTILITY OF VARIOUS ALLOY STEEL BARS

effect of hydrogen on various steel compositions treated to a tensile strength of about 50 tons/sq. in. It will be seen that all the four steels show a similar effect; the carbon steel, if anything, shows less effect than the chromium-molybdenum steel, while the nickel steels are slightly more susceptible, as judged by the slopes of the curves. This is a statement to which reference will be made later.

The embrittling effect of hydrogen in steel together with the tendency of hydrogen to diffuse out from steel, explains a phenomenon which has been remarked upon several times in the literature: if a forging or billet is tested some considerable time after its production, the ductility will always be found to have improved. The diffusion of hydrogen from steel is a complex process. It has already been mentioned that temperature has a considerable effect on the rate of evolution of hydrogen; we have also found that the diffusion of hydrogen from austenite is slower than from ferrite at the same temperature. In addition, the size of the piece of steel has a great effect on the rate at which the hydrogen content decreases: in fact, with a bar of twice the diameter it takes four times as long for the hydrogen at the centre to fall to the same level under the same conditions. Now diffusion is the only means we know of reducing the hydrogen content of a piece of solid steel. It appears obvious, therefore, that to remove the hydrogen content as rapidly as possible we shall heat the mass of steel to a temperature where it will remain ferritic but which at the same time is as high a temperature as possible. This, in general, with alloy engineering forgings, will be a temperature somewhere in the region of 650°C. The time for which the forging must be soaked at this temperature to reduce the hydrogen content to an acceptable limit depends, of course, on the initial hydrogen content, on the rate of diffusion, and particularly on the size. Various complex calculations have been made in

this connection, but the period allowed for the treatment still appears to be a matter of trial and error. With large-diameter forgings, however, it is clear that the time allowed at 650°C. is of necessity a long one; one calculation [C. SYKES, H. H. BURTON & C. C. GEGG, *J. Iron & Steel Inst.*, **156** (1947), 155-180] indicates that to reduce the hydrogen content of the centre of a forging 50 in. in diameter to half its previous level would take 625 hr. or, assuming an original uniform hydrogen content of 8 ml. per 100 g., the time required at 650°C. to reduce the hydrogen content of the centre to 1 ml. per 100 g. would be 2500 hr.

It will thus be quite clear that any steps which can be taken to prevent hydrogen entering the steel in the first place in the melting furnace will be well worth while where large forgings are concerned.

The embrittling effect of hydrogen, by and large, is not significant on bars up to about 6 in. in diameter or of similar cross-section. This is because the normal metallurgical operations in the manufacture of such products are sufficient, in general, to reduce the hydrogen content below 2 ml. per 100 g. and often to a figure much smaller than this. This does not mean, however, that hydrogen may not have a deleterious effect on products of such sizes, as a further problem remains to be discussed which can affect both large and small forgings and billets.

The formation of so-called 'hairline cracks' still requires adequate explanation. It appears to have some connection with the hydrogen content of the steel, but there must be some other factors, at present unknown precisely, which are also involved. In any case, however, hairline crack formation is even more serious than the embrittlement effect, since embrittlement, if encountered, can often be overcome by further heat treatment, while hairline cracks can cause rejection of the material. Illustrations of typical hairline cracks can be seen in

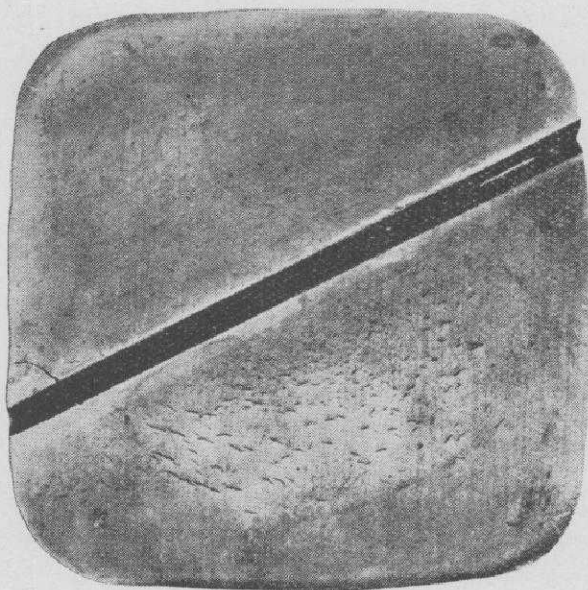


FIG. 18 — SECTION OF A 5 IN. BILLET IN 3 PER CENT NICKEL STEEL, SHOWING HAIRLINE CRACKS. THE BILLET HAS BEEN NICKED AND FRACTURED ON A DIAGONAL LINE; *see* FIG. 20

Figs. 18-22. Fig. 18 represents a section through a 5 in. billet produced from the wild/nickel steel cast which has been mentioned previously. The billet was rolled from the ingot and subsequently held for 4 hr. at 650°C. and water-quenched. The hairline cracks produced can be seen quite clearly. The hydrogen content at the centre of this billet was found

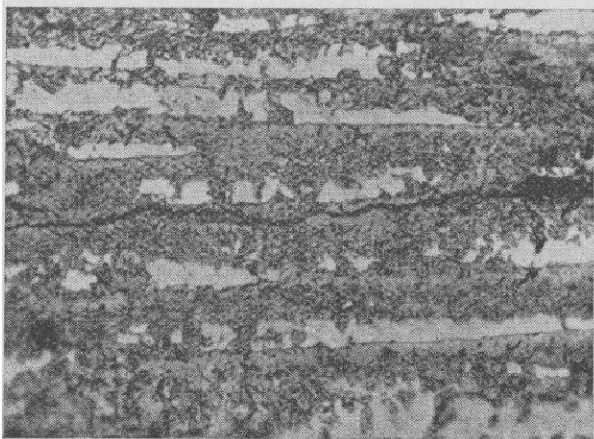


FIG. 19 — PHOTOMICROGRAPH ($\times 50$) OF AN AREA FROM FIG. 18, SHOWING A HAIRLINE CRACK

to be in the region of 10.0 ml. per 100 g. Fig. 19 gives an enlarged view of the area round one of these cracks. Fig. 20 shows a fracture through a transverse slice of a similar billet; the brightness of the fracture in the hairline crack can be clearly seen, explaining the use of the term 'snowflake' or 'flake' as an alternative to hairline crack. Fig. 21 shows a fracture in a 10 in. diameter shaft in nickel-chromium-molybdenum steel which failed in service. The fracture was initiated by fatigue, at the top of the section; as the crack spread, however, it met hairline cracks, whose effect on subsequent fracturing can be clearly seen.

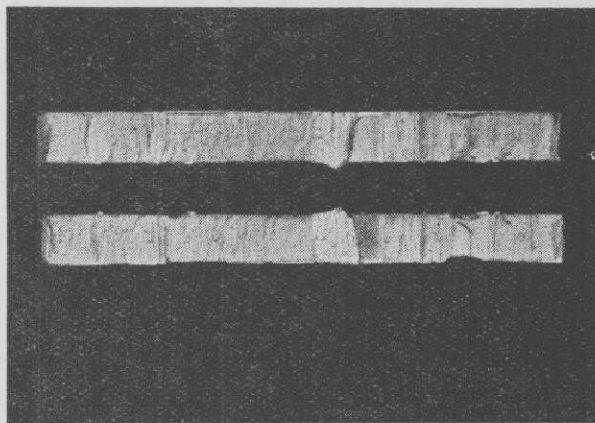


FIG. 20 — FRACTURE OF A TRANSVERSE SLICE OF A BILLET IN NICKEL-CHROMIUM STEEL, SHOWING THE EFFECT OF HAIRLINE CRACKS

Hairline cracks can occur not only in forgings and rolled billets but also in ingots; Fig. 22 gives a magnetic etch print of a transverse slice from an ingot of 4 per cent nickel-chromium case-hardening steel and shows the presence of cracks distributed along the crystal boundaries.

The occurrence of hairline cracks is far more prevalent in alloy steels than in carbon steels; nickel steels are among the most susceptible to this trouble, with chromium-molybdenum steels less susceptible than nickel steels but more so than carbon steels. It will be remembered it was mentioned

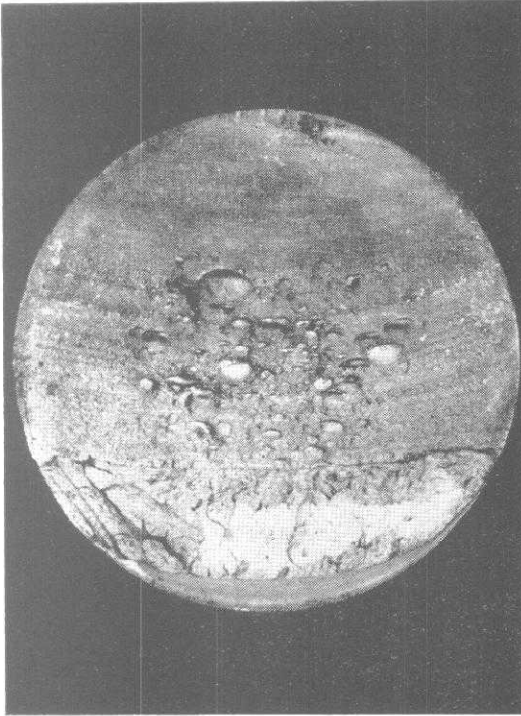


FIG. 21 — VIEW OF A FATIGUE FRACTURE IN A 10 IN. NICKEL-CHROMIUM-MOLYBDENUM SHAFT, SHOWING THE EFFECT OF HAIRLINE CRACKS

earlier that it appeared, the susceptibility to hydrogen embrittlement appeared to be greatest with nickel steels and least with carbon steels, with chromium-molybdenum steels in an intermediate position. This correlation appears significant until it is realized that, with hydrogen contents as high as 8.0-10.0 ml. per 100 g., which is far more than is usually found, even at the centres of large forgings, reductions of area over 20 per cent are obtained with 50-60 tons/sq. in. tensile strength. This ductility should be sufficient to prevent the completely brittle fracture typical of hairline crack formation, and it would seem that hydrogen embrittlement is not the whole cause of hairline crack formation. In addition, the remarkably constant effect of hydrogen on embrittlement is in complete contrast with the erratic nature of hairline crack formation.

That hydrogen does have some part in hairline crack formation is generally accepted. It is well known that larger sections are far more likely to suffer from hairline cracks than are smaller ones, and the heat-treatment experts will treat larger forgings for a much longer period of time at 650°C. to prevent hairline crack formation. Whatever else this treatment does, it certainly removes hydrogen. Again, it is also well known that acid open-hearth steel is less prone to suffer from hairline cracks than is basic electric steel of the same composition; we have already seen that the acid steel is lower, in general, in hydrogen contents. In addition, since steps have been taken to control the hydrogen content of basic electric steel as far as possible, it has been found that the incidence of hairline cracks has been somewhat lower.

Normal practice in the author's works when rolling billets up to 6 in. in diameter in 3 per cent nickel steel is to slow-cool them by stacking them hot in cooling pits; this is found to be sufficient to prevent them from

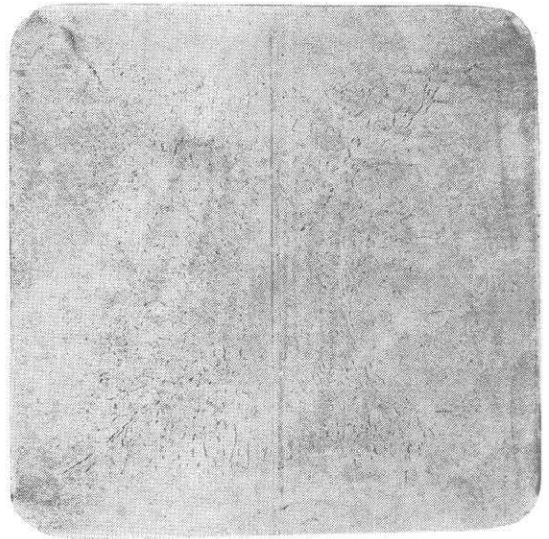


FIG. 22 — MAGNETIC ETCH PRINT OF A TRANSVERSE SECTION OF AN INGOT IN 4 PER CENT NICKEL-CHROMIUM CASE-HARDENING STEEL, SHOWING HAIRLINE CRACKS

suffering from hairline cracks subsequently. Referring back to the wild cast, a billet from which produced hairline cracks as shown on Fig. 18, pit-cooling of the billets in this case was not sufficient to prevent the formation of hairline cracks, this could conceivably be due to the high hydrogen content of about 10.0 ml. per 100 g. One ingot from the wild cast, however, was given a long-term annealing treatment prior to rolling to 5 in. billet; portions of the resulting billet were pit-cooled, floor-cooled, oil-quenched or water-quenched, and in no case was a hairline crack produced; the hydrogen content of these billets was under 1.0 ml. per 100 g. This is of considerable interest, since normal 3 per cent nickel steel ingots, which as cast contain about 4.0-5.0 ml. hydrogen per 100 g., might be expected to give billets containing 1.5-2.5 ml. hydrogen per 100 g., which will tend to show hairline cracks unless they are pit-cooled. Thus we have further support for the contention that hydrogen is responsible for hairline crack formation.

Further experiments with the 3 per cent nickel steel billets, however, showed that suitable heat treatment, namely transformation at 450°C. followed by a full softening treatment at 650°C., produced a billet which, although containing a large quantity of hydrogen, could be quenched or air-cooled without any hairline crack formation. [Details of all these experiments are to be found in the paper by C. Sykes, H. H. Burton and C. C. Gegg, *J. Iron & Steel Inst.*, **156** (1947), 155-180, from which Table 5 is reproduced.]

Thus the question of hairline crack formation remains an unanswered one; the most

TABLE 5 — RESULTS OBTAINED ON 5 IN. BILLETS DERIVED FROM A WILD 3 PER CENT Ni STEEL CAST

TREATMENT AFTER ROLLING	MAGNETIC TEST	HYDROGEN CONTENT, ml. per 100 g.
A. Air-cooled	Badly cracked	8.3
do	do	9.1
B. Pit-cooled	A few cracks	5.4
do	do	15.4
C. 2 hr. at 450°C.; reheated to 650°C. in 2 hr.; held 4 hr. at 650°C.; water-quenched	Sound	11.2
do	do	10.9
do	do	9.5
D. As C, but air-cooled from 650°C.	Sound	12.1
do	do	11.3
do	do	7.2
E. As C, but cooled from 650°C. to 400°C. in 5 hr., held 30 min. and air-cooled	Sound	10.6
F. As E to 400°C., then transferred to furnace at 850°C., levelled for 45 min., held 30 min., and air-cooled	Sound	9.3
do	do	9.2

that can be said at the present time is that it is in some way related to the hydrogen content of the material, but that other factors, as yet unknown, have a significant effect also.