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## PHYSICAL CHANGES AND EQUILIBRIA IN SPECIAL STEELS.

By H. A. Dickie, B.Sc., Ph.D., A.R.T.C.

This thesis describes research work carried out by the author in the Metallurgical Department of the Royal Technical College, Glasgow during the six years from 1923 to 1929. The work has been directed largely to the elucidation of physical changes and equilibria in ternary and quaternary steels with a view to placing the knowledge of these steels on a more rational basis than hitherto. It is a noteworthy fact that the knowledge of the mechanical properties and heat-treatment of special steels has been for many years far in advance of the fundamental scientific knowledge of them. This is due partly to the fact that direct practical applications are the chief aim of most industrial and even some academic researches and partly to the laborious nature of fundamental research with metals, thus necessitating a considerable passage of time before results of any consequence can be produced.

The author has been fortunate in having the support of the Executive Committee of the Carnegie Trust for the Universities of Scotland by the award of a Research Scholarship and later a Research Fellowship for the prosecution of metallurgical research from the standpoint of pure science.

The first portion of the thesis describes work designed to find the physical changes underlying the production of temper-brittleness in steels. These changes are shown to be connected

with the solubility of carbide in ferrite and the research was developed to determine the solubility lines of carbon in ferrite in a wide range of steels. To complete the scheme the work was extended to include changes at higher temperatures with particular reference to reactions in the  $Ac_1$  range. The latter part of the work throws light on all critical changes in ternary and quaternary steels.

The data (with a few exceptions) used in this thesis have been published in the following four papers in the Journal of the Iron and Steel Institute: No.2, 1926, p.359, No.1, 1927, p.647, No.2, 1927, p.223, and No.2, 1929.

#### TEMPER-BRITTLENESS.

The term "temper-brittleness" refers to the low impact value produced in a notched-bar impact test-piece after the steel has been treated in certain ways, for example, by cooling slowly from a high tempering temperature or by reheating the water-tempered steel to about  $520^{\circ}C$ . The effect is particularly noticeable in certain nickel-chromium steels, the Izod impact value being reduced from about 80 foot-pounds in the water-tempered condition to about 10 foot-pounds in the brittle condition. This phenomenon attracted much attention during the war owing to the extensive use of nickel-chromium steels in connection with armaments, and it has remained for years one of the most puzzling problems in the metallurgy of steels.

The effect of variation of heat-treatment on the notched-bar impact value of steels susceptible to temper-brittleness is now well known, due to much practical work on the matter and to

many published researches, outstanding among which is the **exhaustive** work of Greaves and Jones. <sup>(1,2)</sup> The effect of variation <sup>in composition</sup> is also fairly well known as the result of work by these investigators and <sup>(3)</sup> by Andrew and Green, <sup>(4)</sup> Griffiths, <sup>(5)</sup> Honda and Yamada, <sup>(6)</sup> and Oberhoffer, Hochstein and Hessenbruch. <sup>(7)</sup> Attempts by many workers have, however, entirely failed to reveal the cause of the variations in impact value and no convincing explanation has been put forward by previous investigators.

Until the publication of the first portion of this work a few years ago it was generally accepted that whereas the impact value falls when a steel which is susceptible to temper-brittleness is cooled slowly from the tempering temperature, yet no appreciable change had been shown to take place in any other mechanical property (with the possible exception of a small change in elastic limit), in any physical property (with the possible exception of some magnetic properties), or in microstructure.

In consequence of the apparent absence of any physical changes in any way commensurate with the great change indicated by the arbitrary notched-bar impact tests, the value of all or any of the modifications of the latter test as a measure of the real toughness or brittleness of a material has naturally been questioned. From the work published by other workers it is easy to conclude that a minute and almost negligible change in the condition of a steel is magnified out of all proportion by a notched-bar impact test.

It is evident that the subject could never be placed on a satisfactory basis until the physical changes which produce the alteration in impact value were elucidated.

PHYSICAL DETERMINATIONS BY OTHER INVESTIGATORS.

Greaves and Jones<sup>(2)</sup> have compared the specific gravity, hardness, and specific resistance of tough and brittle specimens in which tempering effects have been equalised by a double heat-treatment. They found that the specific gravity of water-cooled tough steel was from 0.0004 to 0.0010 less than that of the brittle steel, but that when the tough steel was reheated to 200°C. this difference was greatly reduced. This rise in specific gravity on low temperature annealing they attributed to removal of a condition of strain in the water-quenched steel, and they concluded that "the difference in density due solely to the condition of toughness or brittleness appears to be at most 1 part in 20,000."

From Brinell hardness determinations on water-quenched and slowly cooled specimens they conclude: "These results show that when unequal tempering effects are eliminated in producing tough and brittle material, there is no appreciable difference in the hardness of the two varieties."

From determinations of specific resistance on similarly treated specimens they conclude that: "The resistivity at 0°C. of tough and brittle material was identical within the experimental error."

The same investigators found that in the majority of steels the elastic limit in the brittle condition was about 3 tons per square inch higher than that of the same steels in the quenched tough condition, but that when moderate rates of cooling were adopted, or when the quenched steel was subjected to low-temperature annealing, the elastic limits of the two conditions were

equalised.

Philpot<sup>(8)</sup> found no change in specific gravity on comparing steels in various conditions. His conclusions were supported by other observers.

Rogers<sup>(9)</sup> claimed that the brittle state was softer than the tough, but no attempt was made in his experiments to differentiate between the effect of "extra-tempering" in the slowly cooled specimens and the effect of the change to the brittle condition.

The softening effect observed in many cases has usually been attributed to "extra-tempering", and Greaves and Jones, as already stated, produced very good evidence to show that when tempering effects were equalised there was no softening in the brittle state.

Thermal curves taken by the differential method have been published by Rogers<sup>(9)</sup> and Greaves and Jones<sup>(2)</sup>. These point to the possibility of an absorption of heat on heating and an evolution on cooling through the "brittleness range".

Guillet<sup>(10)</sup> has carried out work on dilatation and thermo-electric power. His conclusions are as follows: "Dilatation experiments did not furnish any information," and "Thermo-electric tests gave equally no indication" of a physical change.

The magnetic properties of tough and brittle steel have been compared by Kayser.<sup>(11)</sup> He gave figures showing that the remanence of one steel, which was susceptible to brittleness, increased 40 per cent. on slow-cooling.

Figures given by Gebert<sup>(12)</sup> of magnetic tests on a nickel

and on a nickel-chromium steel, quenched and tempered at various temperatures, followed by air-cooling, showed that the residual induction in both steels increased very considerably after tempering at 425°C. and above. Gebert did not, however, compare specimens in the tough and brittle condition.

Similar experiments by Dowdell<sup>(13)</sup> on a number of carbon and special steels showed a similar rise to that observed by Gebert but only in a few steels was the rise at all pronounced, and the change was much greater in all his carbon steels than in any of the special steels examined. He did not compare brittle and tough steels

It is evident from the work of Dowdell that the rise in residual induction after tempering to 400°C. or 500°C. is very marked in steels which are not susceptible to temper-brittleness. Results published by other workers support this view<sup>(14, 15, 16)</sup>.

Honda and Yamada<sup>(6)</sup> have shown a difference of <sup>magnetisation in</sup> <sub>tough and</sub> brittle specimens. This difference is, however, also found in non-susceptible steels. These investigators also measured the change in resistivity after reheating to temperatures above 400°C. This change, however, <sup>is</sup> <sub>due to</sub> spheroidisation of carbide, as will be seen later in this thesis, and is not a measure of either temper-brittleness or carbide solubility. It is present in many steels which are not susceptible to brittleness.

Finally, many workers testify to the absence of any detectable change in microstructure.

It is clear that all the evidence published up to the present by other workers points to the absence of any substantial physical change associated with the change in impact value from



the tough to the brittle condition. There would appear to be no change in density, hardness, resistivity, thermo-electric power, or microstructure, and any changes which may take place in magnetic properties are common to all steels whether susceptible to temper-brittleness or not.

#### EXPERIMENTAL METHODS.

In order to have any chance of finding the changes producing temper-brittleness it was evidently essential, in view of the negative results produced by other workers in this field, to use more accurate methods than those previously in use and also to carry out the investigation in a more comprehensive and systematic manner. No clue existed in previous work as to the nature of the changes involved and it was therefore necessary to cover the whole physical field from the beginning, starting only with the knowledge of the variation in mechanical properties which had been very fully revealed by previous workers.

The measure<sup>ment</sup> of specific volume and Brinell hardness was selected at the outset as the most suitable method of attack. Specific volume may be said to be the most fundamental property of steels and a method for its very accurate measurement was adopted and developed. This property is most conveniently considered as specific volume and not as specific gravity since an increase in specific volume means expansion and a decrease contraction. The results are thus easier to interpret than if the specific gravity were used. Also, in almost all cases in steels increase in specific volume is accompanied by increase in hardness and vice

versa. The hardness can be conveniently taken on the same specimens as used for specific volume and thus a very good check on the results is obtained.

In regard to heat-treatment it was found that carrying this out in a vacuum was much preferable to heating in either coal gas or nitrogen. It will be shown later that specimens could be heated for lengthy periods without any appreciable decarbonisation or other alteration in the specimens.

Specimens of the steels about 25 grammes in weight were heat-treated in a wire-wound electric furnace having a transparent fused-silica tube. The vacuum was obtained by a Toepler mercury pump of large capacity. A solution of celluloid in amyl acetate was found to be very efficient in obtaining airtight joints on the furnace and pump.

As temperature indicator a platinum platinum-iridium<sup>couple</sup> was used in conjunction with a Cambridge and Paul Universal Test<sup>Set</sup>, a Siemens Temperature Indicator, or a Tinsley potentiometer and galvanometer. The latter was used in all cases when absolute accuracy of temperature was desired as, for example in treatments near to or in the  $Ac_1$  range. The calibration of the couple, which was done directly against steam and the freezing points of pure tin, lead, zinc, aluminium, sodium chloride and copper, was checked from time to time.

The specimens after heat-treatment were ground thoroughly all over, the entire surfaces being finally finished off with French paper. The specimens were washed perfectly clean, dried and placed in a desiccator for at least half-an-hour.

Brinell marks were invariably ground off between treatments.

For weighing, a specially sensitive balance was used, giving accurate weighings to one-tenth of a milligram. The weights were standardised before commencing the research and from time to time throughout. Each specimen was weighed in air lying on the balance pan, and a standard specimen of known specific gravity was also weighed. The specimens were then immersed in paraffin and left for over half-an-hour to allow the temperature to stabilise. A beaker of the same paraffin was used in which to weigh the specimens, these being suspended in the liquid in a cage made of platinum wire. The standard specimen was weighed before and after each specimen. The specific volume was then obtained by calculation using seven-figure logarithms.

There is a surprising number of points to be watched in carrying out this process with the greatest possible accuracy. These are only appreciated after some experience and practice.

#### Accuracy of the Specific Volume Method.

With a view to finding the accuracy of the method the following experiments were carried out:

Five pieces of Armco Iron were annealed by heating at 950°C. and cooling slowly. A short bar of a carbon steel was annealed similarly at 800°C. and five specimens were cut from the bar. A bar of a nickel-chromium steel was quenched in oil after half-an-hour at 850°C., tempered for two hours at 650°C., and slowly cooled at 0.5°C. per minute to 450°C. Six specimens were cut from the bar.

The specific volume of all these specimens was determined

TABLE O.

<u>Armco Iron.</u>	<u>1st. Determination.</u>	<u>2nd. Determination.</u>	<u>Difference.</u>
(1)	0.127164	0.127152	0.000012
(2)	0.127176	0.127153	0.000023
(3)	0.127183	0.127167	0.000016
(4)	0.127171	0.127179	0.000008
(5)	0.127168	0.127177	0.000009
Maximum Difference = 0.000031			

<u>0.71% C Steel,</u>			
<u>A4.</u>	<u>1st. Determination.</u>	<u>2nd. Determination.</u>	<u>Difference.</u>
(1)	0.127528	0.127518	0.000010
(2)	0.127517	0.127526	0.000009
(3)	0.127532	0.127515	0.000017
(4)	0.127519	0.127524	0.000005
(5)	0.127517	0.127515	0.000002
Maximum Difference = 0.000017			

<u>Nickel-Chrom-</u>			
<u>ium Steel, AH.</u>	<u>1st. Determination.</u>	<u>2nd. Determination.</u>	<u>Difference.</u>
(1)	0.127694	0.127684	0.000010
(2)	0.127652	0.127648	0.000004
(3)	0.127685	0.127660	0.000023
(4)	0.127704	0.127684	0.000020
(5)	0.127640	0.127652	0.000012
(6)	0.127674	0.127668	0.000006
Maximum Difference = 0.000064			

and then the process was entirely repeated. The two sets of results are shown in Table O. It will be seen that the difference on a repeat determination is practically the same in each of the materials used. From the figures shown the experimental error when the same specimen is used for the redetermination is a shade greater than  $\pm 0.00001$ . When different specimens of the same material are compared, however, the maximum difference is considerably raised although the specimens were subjected to the same treatment. The carbon steel is an exception. The nickel-chromium steel shows relatively large variations between specimens. This must be due to heterogeneity. It is thus very advisable to use the same specimen throughout a series of experiments. Differences due to variation of composition or soundness of the steel are consequently practically excluded from the results. This precaution was invariably adopted throughout the research.

The standard specimen used was a piece of annealed 0.48 per cent. carbon steel. Its true specific gravity was determined as follows: (1) Determination of the specific gravity of ~~the~~ oil by specific gravity bottle method at an exact temperature of  $15^{\circ}\text{C}$ . (2) Determination of the specific gravity of the standard specimen in the oil at the same exact temperature. (measured by Beckmann thermometer).

By the above method variations due to the alteration of temperature of the oil are automatically allowed for.

The Brinell hardness was taken on an Alpha machine using a load of 1500 kilograms. A special ball was kept for use in this research and its diameter did not vary even after years of use.

Other experimental methods are described later in connection with the experiments to which they refer.

#### EXPERIMENTS TO DETERMINE THE EFFECTS OF SLOW COOLING.

The five steels shown in Table 1 were selected for this first series of experiments. NP1 and NP5 are two of the steels used by Andrew and Green<sup>(4)</sup> in their work on the effect of phosphorus on the notched-bar impact value. NP1 has a very low susceptibility to temper-brittleness, whereas NP5 has a high susceptibility. AW22 and AW23 were available in very small quantity only and impact tests could not be carried out on them. They were the only nickel-chromium steels available at the time. They are of compositions known to develop temper-brittleness to a considerable degree. The carbon steel was included for purposes of comparison.

Two sets of specific volume specimens of these five steels were treated as follows:

First Set - Oil-quenched from 850°C. and tempered for three hours at various temperatures from 450°C. upwards and quenched in water after each treatment.

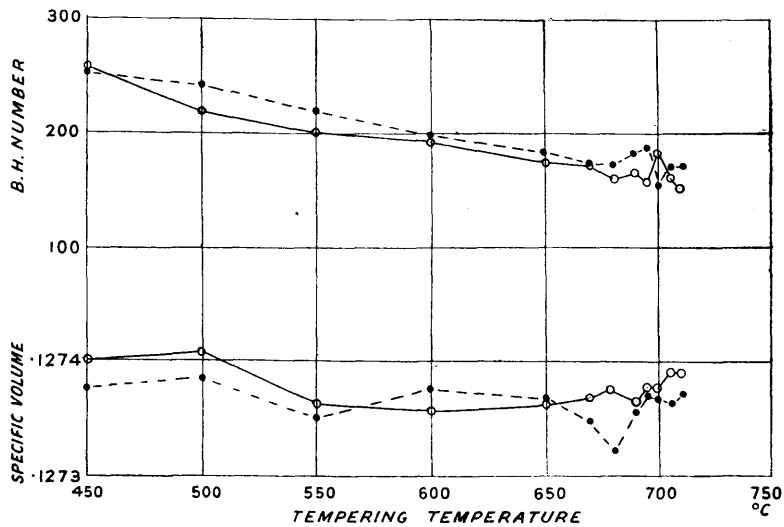
Second Set - The same treatment except that tempering was followed by slow cooling at a rate of 2°C. per minute instead of water-quenching. This rate of cooling was controlled as exactly as possible. It is not sufficiently slow<sup>to produce</sup> much if any brittleness in the steels but it was thought to be sufficiently slow to produce some change in the steels and it was a convenient rate for carrying out a number of experiments with great accuracy.

Quenching in oil after half-an-hour at 850°C. preceded

*Analysis of Steels.*

Steel.	C. %	Mn. %	Si. %	P. %	S. %	Ni. %	Cr. %	Description.
A22	0.48	0.18	0.11	...	...	...	...	Plain carbon Nickel, low phosphorus
NP1	0.31	0.75	0.112	0.013	0.029	3.64	...	
NP5	0.33	0.70	0.065	0.098	...	3.66	...	Nickel, high phosphorus Nickel- chromium
AW22	0.33	0.52	0.177	0.016	0.014	3.48	0.76	
AW23	0.37	0.54	0.149	0.013	0.012	4.55	1.14	

**TABLE 1.**



**FIG. 1.—Carbon Steel, A22.**

Full line.—Specimen quenched in water.  
Dotted line.—Specimen slowly cooled at 2° C. per minute.

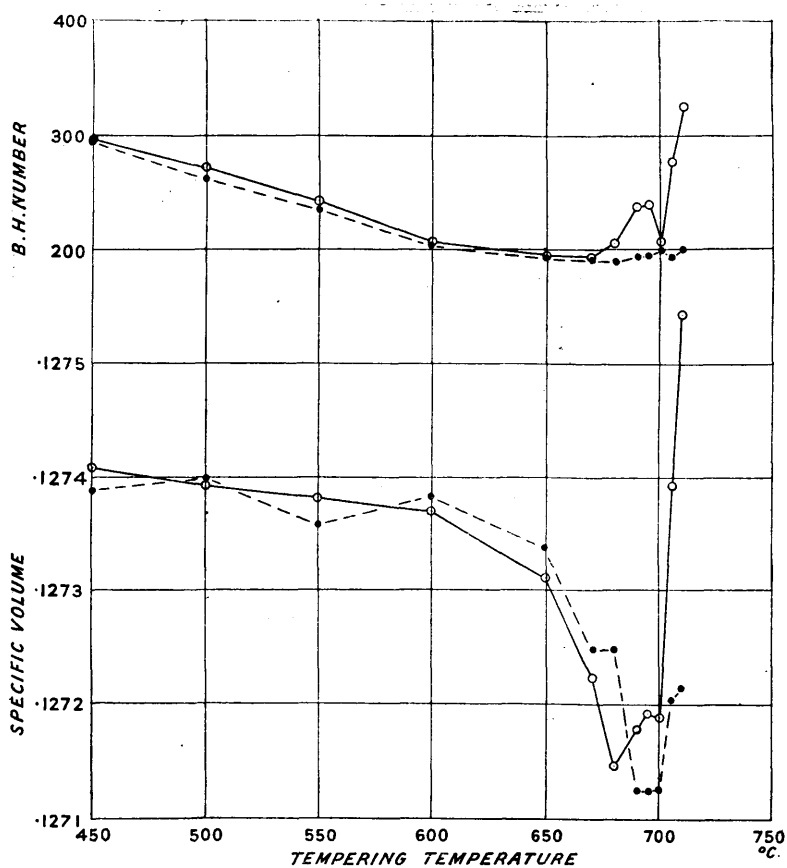


FIG. 2.—Nickel Steel (Low Phosphorus), NP1.  
 Full line.—Specimen quenched in water.  
 Dotted line.—Specimen slowly cooled at 2° C. per minute.

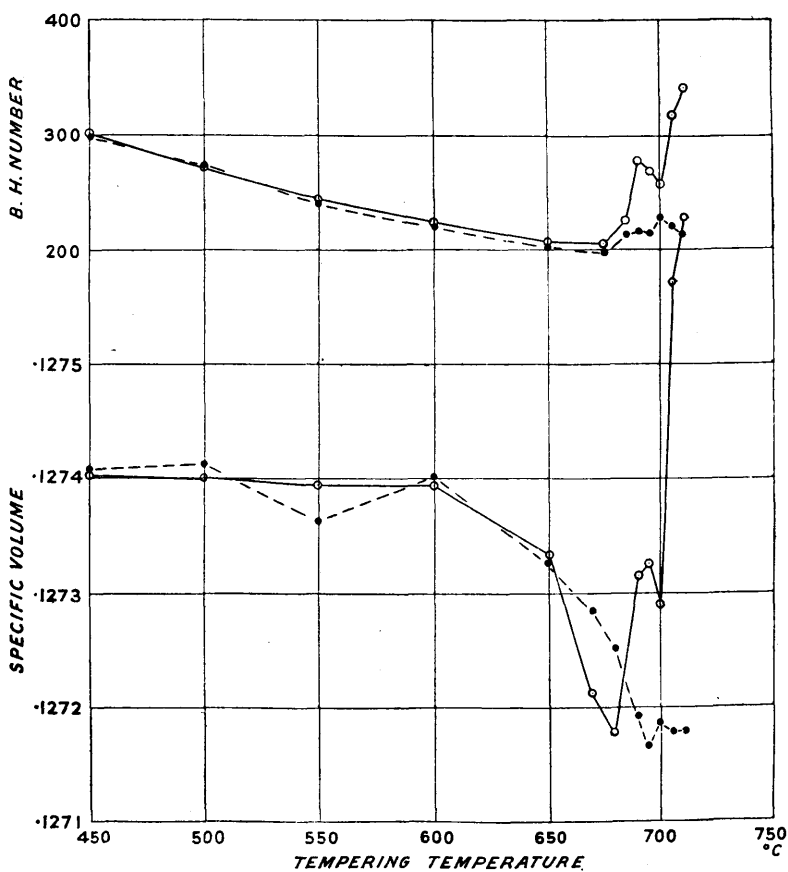


FIG. 3.—Nickel Steel (High Phosphorus), NP5.  
 Full line.—Specimen quenched in water.  
 Dotted line.—Specimen slowly cooled at 2° C. per minute.



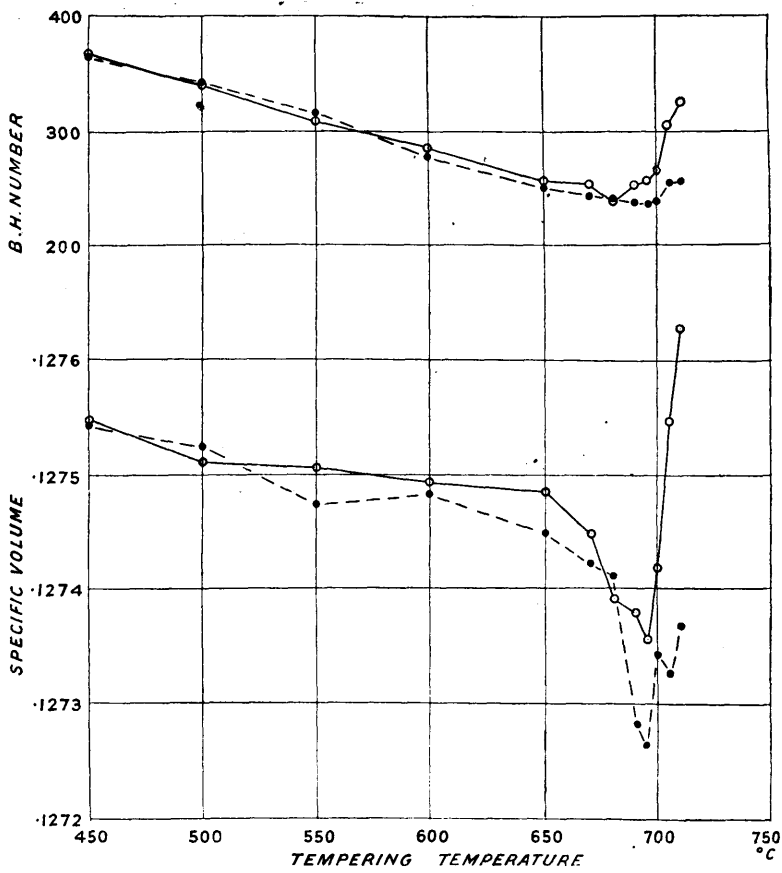


FIG. 4.—Nickel-Chromium Steel, AW22.

Full line.—Specimen quenched in water.  
Dotted line.—Specimen slowly cooled at 2° C. per minute.

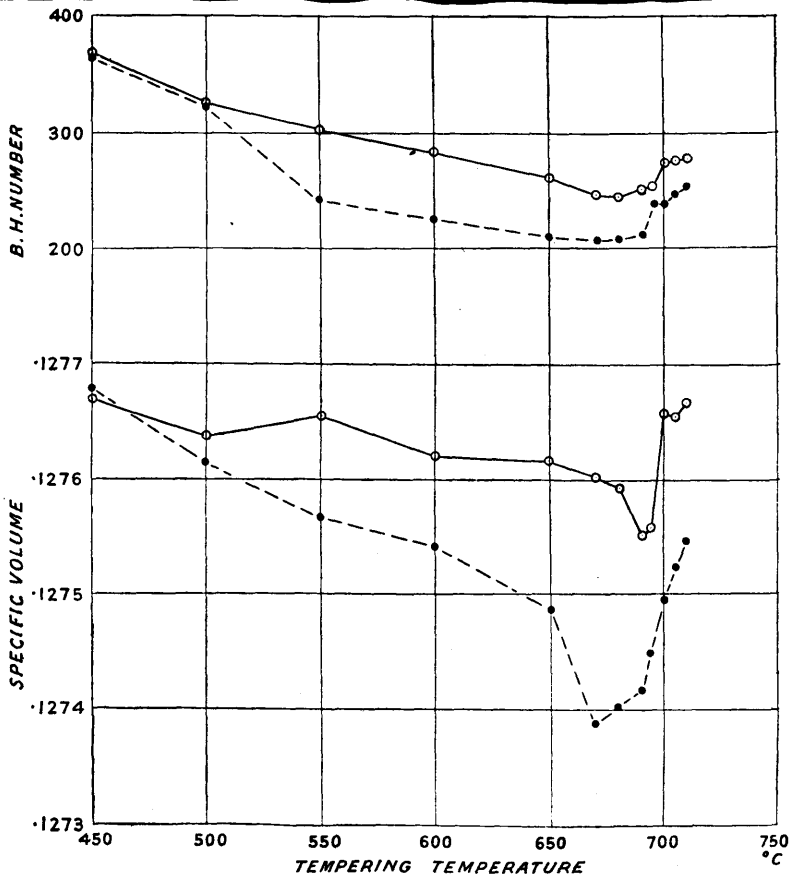


FIG. 5.—Nickel-Chromium Steel, AW23.

Full line.—Specimen quenched in water.  
Dotted line.—Specimen slowly cooled at 2° C. per minute.

each tempering treatment.

The specific volume and Brinell hardness results are plotted in Figs. 1, 2, 3, 4, and 5.

Steel AW23 (Fig. 5), which contains the most nickel and chromium, shows a very marked and consistent change from 550°C. upwards in both specific volume and hardness. The change in specific volume gets steadily greater as the temperature is raised. The changes only become apparent when the "brittleness range" is reached. Of the other steels AW22 shows indications of a similar change in specific volume but the remainder point to no physical change taking place. No change is evident between the quenched and slowly cooled specimens of steel NP5 which has been shown to be highly susceptible to temper-brittleness. The possibility that a strain effect induced by quenching is alone responsible for the very marked changes in specific volume and hardness in steel AW23 is completely discountenanced by the entire absence of any such change in the carbon steel or in the nickel steels, as well as <sup>by</sup> the very magnitude of the changes in steel AW23 itself. In each of the nickel and nickel-chromium steels there is a sharp reversal of direction of the curves for the quenched specimens at temperatures coinciding with the commencement of the  $Ac_1$  range in each steel. These changes will be gone into very fully <sup>later</sup> in the thesis. It is interesting to notice here that this reversal of direction is also noticed in the curve for the slow cooled specimens of steel AW23. This is due <sup>to</sup> the fact that the portions of  $\gamma$ -iron solid solution formed at the high temperature have an air-hardening and expansion effect on slow cooling. This only partially masks the changes taking place in the

Steel.	Original Treatment. Tempered Three Hours at 450° C.			Repeat at End of Experiments. Tempered Three Hours at 450° C.		
		Specific Volume.	Brinell Hardness.		Specific Volume.	Brinell Hardness.
A22	Quenched	0·127401	258	Quenched	0·127381	258
	Slowly cooled	0·127374	256	„	0·127418	256
NP1	Quenched	0·127407	298	„	0·127397	289
	Slowly cooled	0·127387	299	„	0·127416	287
NP5	Quenched	0·127430	302	„	0·127448	300
	Slowly cooled	0·127407	300	„	0·127432	298
AW22	Quenched	0·127548	365	„	0·127551	356
	Slowly cooled	0·127543	364	„	0·127552	361
AW23	Quenched	0·127666	369	„	0·127679	365
	Slowly cooled	0·127677	367	„	0·127678	367

Steel.	Original Treatment. Tempered Three Hours at 670° C.			Repeat Treatment. Tempered Six Hours at 670° C.		
		Specific Volume.	Brinell Hardness.		Specific Volume.	Brinell Hardness.
AW23	Quenched	0·127602	248	Quenched	0·127580	240
	Slowly cooled	0·127388	209	„	0·127615	240

TABLE 2.

ferrite portions of the steel.

In order to find whether the extra heating received by the slowly cooled specimens had produced any relative difference between them and the quenched specimens, the ten specimens were re-subjected, at the end of the series of experiments, to the original tempering treatment of three hours at 450°C. All the specimens were quenched from this temperature. The results after this treatment are given in Table 2. The two specimens of steel AW23 were then also resubjected to a six hours' treatment at 670°C., both specimens being quenched from this temperature. These results are also shown in Table 2.

The results of these experiments clearly prove that no appreciable alteration had taken place in any of the specimens throughout the course of treatments. This definitely excluded the possibility that decarbonisation or other alteration in composition had affected the course of the curves in any way, and also showed the excellence of the method of heat-treatment in an efficient vacuum when accurate physical work is being carried out.

The extra three hours' tempering at 670°C. given to the specimens of steel AW23 shows that the effect of extra-tempering on slow cooling was very small in the case of these experiments. Three hours extra tempering at the high temperature has given a drop of only 8 Brinell and 0.000022 in the specific volume. If a shorter period of heating had been used, however, in each treatment extra-tempering would probably have made its appearance in the results. It is thus essential in such experiments to use a long period of tempering in order that all tempering reactions be brought

as nearly as possible to completion at each temperature.

Other experiments will be described which also show that extra-tempering could not be made to explain the marked difference obtained on cooling steel AW23. The conclusion that this difference in specific volume and hardness was due to a radical physical change in the steel was thus well substantiated.

This contraction and softening of the steel on slow cooling is what one would expect from the separation of a solute which had been in solid solution at the tempering temperature and which is retained in the latter condition on quenching the steel in water. This will be more fully discussed after further experiments are described below.

It will be seen from the curves in Figs. 2 and 3 that the specific volume falls very considerably as the temperature is raised, and that this decrease increases rapidly at the higher temperatures. Benedicks<sup>(17)</sup> has given figures to show that troostite and pearlite have the same specific volume but it does not follow that the state of division of the carbide has no effect on this property. Indeed a great deal of evidence has been found in the course of this research which shows that the state of division, as well as the state of distribution, of the carbide has a very considerable influence. Globularisation of carbide in the nickel steels is rapid as compared with carbon steels, and the effect of aggregation of the carbide particles into globules leads evidently to the closest packing arrangement of the mixture of carbon and ferrite. Any solubility of the carbide in ferrite would oppose the observed fall in specific volume. The rapid change in the rate of

globularisation with slight variation in tempering temperature above 600°C. is probably responsible for the variable impact figures obtained in nickel steels which has been noted by Griffiths<sup>(5)</sup>. Similar changes are to be seen in the nickel-chromium steels in Figs. 4 and 5 but they are not so great, in all probability due to the different composition of the carbide.

#### "Extra-Tempering" Experiments.

It was thought advisable to find out fully the effect of extra-tempering on the specific volume and hardness of nickel-chromium steels in order to know to what degree this could affect the results in any heat-treatment.

The steels shown in Table 3 were used in these experiments. The three new nickel-chromium steels, AH, NJ, and NR3, were obtained, through the kindness of Dr McCance, of the Clyde Alloy Steel Co., Motherwell, in sufficient quantity to allow of impact testing to correlate with the physical determinations.

Specimens of these steels were tempered (after oil-quenching from 850°C.) at 650°C. for two hours and quenched in water. They were then retempered at 650°C. for additional periods of six hours each and quenched in water after each treatment. The specific volume and the hardness were measured after each treatment, and the results are plotted in Fig. 6.

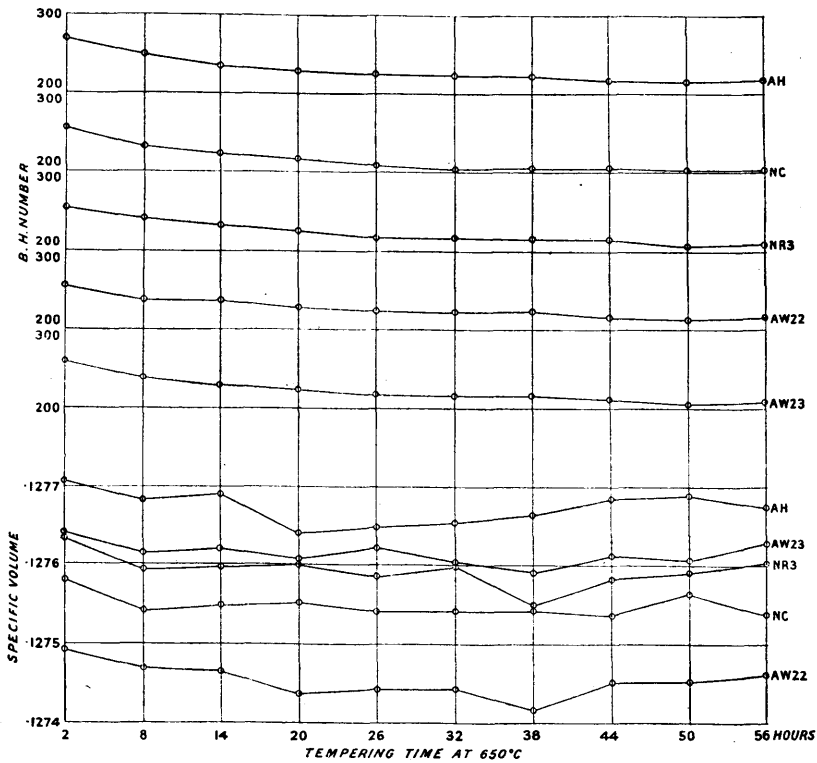
The fall in specific <sup>volume</sup> and in hardness is small in all the steels for short periods of extra-tempering. Six hours of extra-tempering at 650°C. produce only a difference of approximately 20 Brinell and 0.00004 in the specific volume. It is certain that

*Analysis.*

Steel.	C. %	Mn. %	Si. %	P. %	S. %	Ni. %	Cr. %
AH	0.31	0.47	0.310	0.015	0.021	4.46	1.41
NC	0.31	0.57	0.145	0.026	0.029	3.20	0.83
NR3	0.36	0.34	0.275	0.016	0.021	1.90	1.15
AW22	0.33	0.52	0.177	0.016	0.014	3.48	0.76
AW23	0.37	0.54	0.149	0.013	0.012	4.55	1.14

As in First Series

**TABLE 3.**



**FIG. 6.—Five Nickel-Chromium Steels.**

the effect of extra-tempering at 650°C. (see Figs. 4 and 5) <sup>is greater</sup> than at lower temperatures during slow cooling and thus it is apparent that any marked contraction or softening which is observed in slowly cooled nickel-chromium steels cannot be attributed to this factor. The curve for steel AW23 shows conclusively that the change observed on slow cooling in the earlier experiments (Fig. 5) is not due to the effect of extra-tempering, but must be due to a physical change which takes place during cooling.

This series of experiments was carried much further than originally intended, owing to an apparent very slight rise in specific volume after the specimens had been tempered for a considerable period. After this rise was first noticed each succeeding tempering treatment merely seemed to accentuate it, except in steel NC, which shows an increase in one treatment only. The hardness dropped slightly but continuously in all the steels until the last treatment, when it rose very slightly in each case. The hardness results throughout show that the rise in specific volume is not due to graphitisation of the carbide, and it is possible that a very small separation of carbide at the grain-boundaries on each reheating was responsible for the slight rise in values. Whiteley<sup>(18)</sup> has found such an effect in Armco iron and carbon steels by microscopical methods. The present experiments were carried out before Whiteley's observations were made known.

#### Izod Impact Experiments.

A number of experiments were carried out on the new steels AH, NC, and NR3 to find their susceptibility to temper-brittleness.



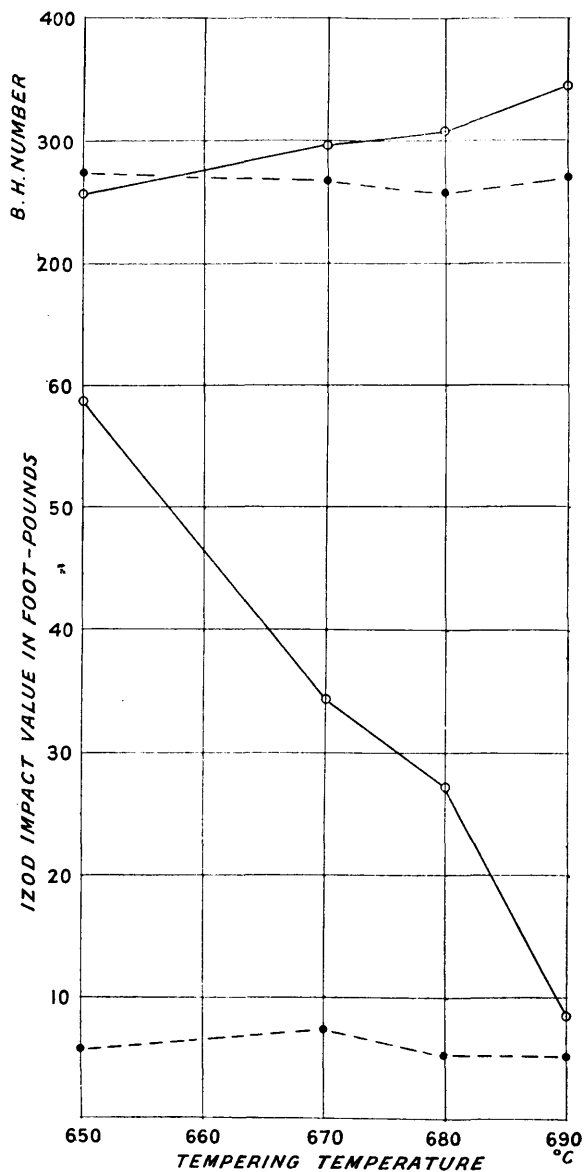


FIG. 7.—Nickel-Chromium Steel, AH.

Full line.—Bars quenched in water.  
Dotted line.—Bars slowly cooled at 0.3° C. per minute.

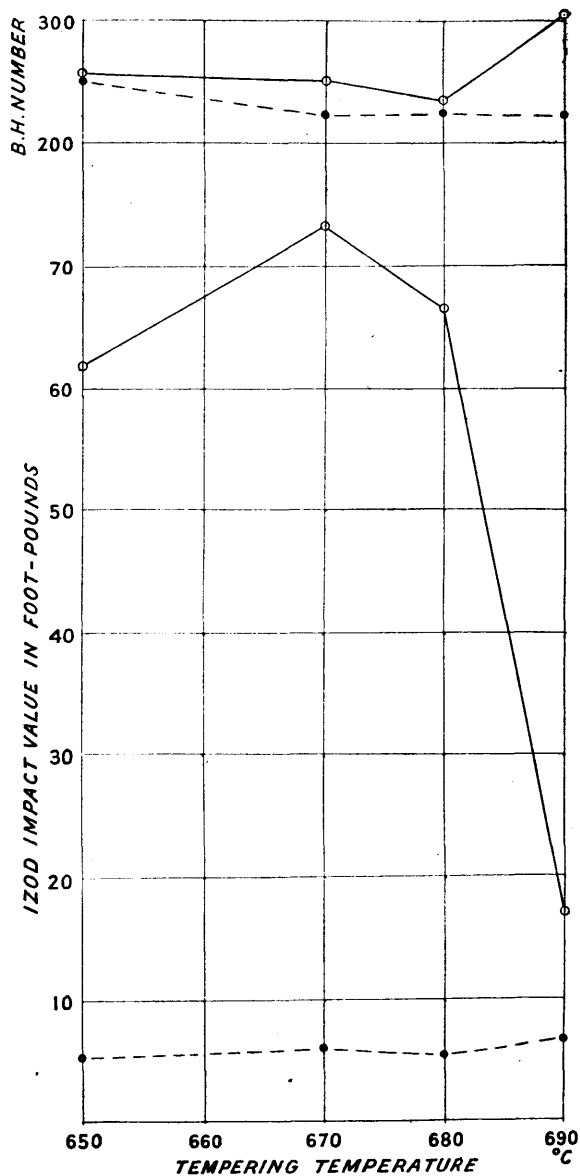


FIG. 8.—Nickel-Chromium Steel, NC.

Full line.—Bars quenched in water.  
Dotted line.—Bars slowly cooled at 0.3° C. per minute.

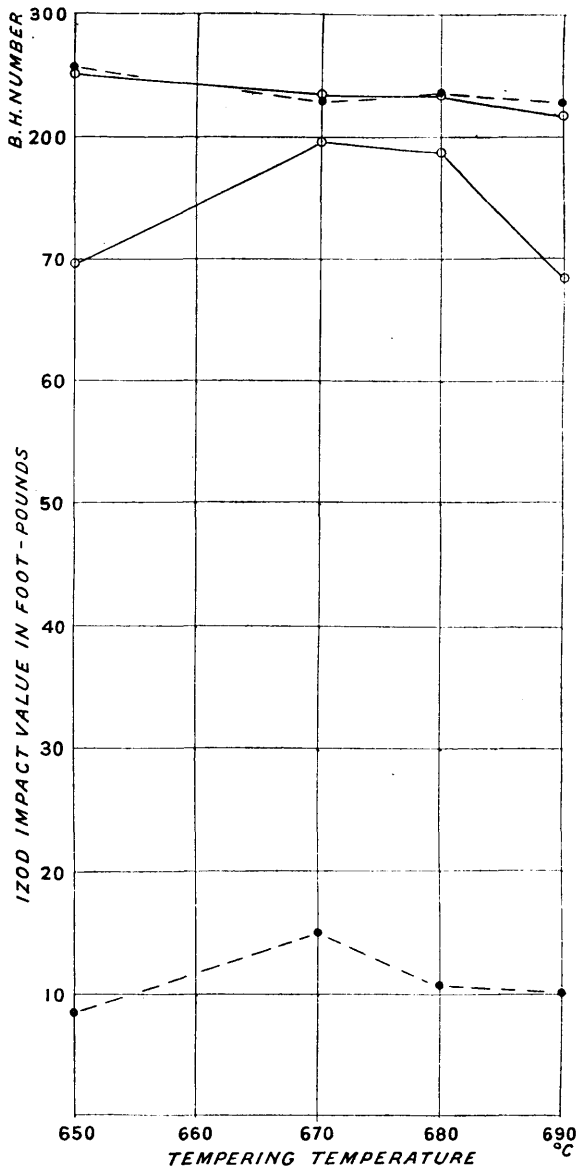


FIG. 9.—Nickel-Chromium Steel, NR3.

Full line.—Bars quenched in water.

Dotted line.—Bars slowly cooled at 0.3° C. per minute.

(as measured by the standard Izod test), and also to show the effect of temperatures above the normal generally used in such tests.

Bars of the steels were first oil-quenched from 850°C. and then tempered for two hours at 650°C., 670°C., 680°C., and 690°C. The treatments were carried out in a large electric tube furnace having an effective heating length of about two feet and wound so as to give as even a temperature as possible from end to end. The five-inch bars, which were placed in the centre of the furnace, were thus very evenly heated throughout their length, and tests showed that the variation in temperature did not exceed a few degrees. Bars of each steel were quenched in water from each tempering temperature, and other bars were cooled at a very slow rate (0.5°C. per minute) in order to produce the maximum brittleness. Izod test-pieces were then machined from the bars, impact tests carried out, and the Brinell hardness taken near each fracture on the impact pieces.

The mean results are plotted in Figs. 7, 8, and 9.

Each of the steels is very susceptible to brittleness. The most interesting feature of the results is the rise in the impact value of the bars water-quenched above 650°C. in steels NC and NR3 (AH falls at 670°C., but might be expected to rise between 650°C. and 670°C.). This rise in impact value is accompanied by a fall in hardness due to the increased tempering effect as the temperature is raised (see Figs. 4 and 5). These experiments show that the higher the tempering temperature (provided the  $A_{c1}$  range is not reached) the higher the impact value of the tough steel. This appears to be due to increase of spheroidisation of carbide with temperature. Whenever the start of the allotropic change is reached, however,

the impact figure again falls, and this fall is accompanied by a rise in hardness, showing that some solution of carbide in  $\gamma$ -iron has taken place at the tempering temperature, with subsequent formation of some martensite on quenching.

DETERMINATION OF THE PHYSICAL EFFECTS OF  
VERY SLOW COOLING.

The ten steels shown in Table 4 were used in this series of experiments.

Specimens of these steels were treated with a view to producing the maximum amount of brittleness in order to obtain the maximum physical change. In each experiment the rate of cooling was  $0.3^{\circ}\text{C}$ . per minute.

Various tempering treatments were given before slow cooling was commenced. Steel G2 was quenched in oil from  $1100^{\circ}\text{C}$ . and the others from  $850^{\circ}\text{C}$  before each treatment. The treatments and results are given in Table 5, together with figures for the same steels quenched from a tempering temperature of  $650^{\circ}\text{C}$ . The results cannot all be presented graphically but a few have been plotted in Figs. 11, 12, and 13.

The results of experiments (2), (3), and (4) (Table 5) were at first very puzzling and disappointing in view of the absence of a substantial change in any of the steels. Steel AW23 showed no change in specific volume of the nature found in earlier experiments although the hardness fell appreciably.

Consideration of the results after several failures to produce a decrease in specific volume or hardness with very slow cooling led to the conclusion that an intermediate rate of cooling

Five nickel-chromium, AH, NC, NR3, AW22, AW23 }  
 One plain carbon, A22 } As in previous series.  
 Two nickel, low and high phosphorus, NP1 and NP5 }  
 One chromium, AAX (C, 0.32; Mn, 0.91; Si, 0.145; P, 0.026; S, 0.027;  
 Cr, 0.97 per cent.).  
 One high carbon, nickel-chromium, G2 (C, 1.50; Mn, 0.26; Ni, 3.46; Cr, 1.80  
 per cent.).

**TABLE 4.**

Steel.	(1) Oil-hardened and Tempered 650° C. for Two Hours and Water-Quenched.		(2) Oil-hardened and Tempered 650° C. for Two Hours and Cooled at 0.3° C. per Minute.		(3) Oil-hardened and Tempered 670° C. for 2½ Hours and Cooled at 0.3° C. per Minute.		(4) (3) Retempered 550° C. for Three Hours and Cooled at 0.3° C. per Minute.		(5) Oil-hardened and Tempered 670° C. for Three Hours and Cooled at 2° C. per Minute.	
	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.
AH	0.127694	278	0.127698	267	0.127693	266	0.127716	266	0.127577	252
NC	0.127556	264	0.127617	242	0.127559	256	0.127565	254	0.127524	235
NR3	0.127611	266	0.127602	263	0.127630	269	0.127596	270	0.127543	245
AW22	0.127490	257	0.127466	247	0.127481	252	0.127487	249	0.127337	235
AW23	0.127619	265	0.127592	230	0.127591	238	0.127613	235	0.127492	238
									0.127482	238
									0.127490	239
A22	0.127364	177	0.127368	170	0.127361	168	0.127361	170	0.127351	165
NP1	0.127330	198	0.127363	195	0.127296	192	0.127318	190	0.127153	196
NP5	0.127353	211	0.127288	201	0.127264	196	0.127303	196	0.127249	211
AAX	0.127625	261	0.127569	257	0.127631	215	0.127650	215	0.127620	228
G2	...	...	0.128120	401	0.128109	364	0.128063	331	0.128004	284

**TABLE 5.**

would show up a change in properties, whereas very slow rates would not.

Another experiment (5) (Table 5) was carried out with the series of ten steels at a rate of cooling of  $2^{\circ}\text{C}$ . per minute, and the results fully confirmed this conclusion. A marked change was not only produced in steel AW23 but in all the nickel-chromium steels. Three specimens of steel AW23 were used in this experiment, and the results for the three agree remarkably. (Two of these three specimens were the identical ones used for the experiments in Fig. 5.) The fall in specific volume in each case is very pronounced, i.e. in steel AW23, but the hardness figure has not altered. This must have been due to slight solution of carbide in  $\gamma$ -iron at the soaking temperature. Cooling curves have shown that when slight solution is induced at the commencement of the critical range in a steel of this composition a critical point on cooling is produced at about  $100^{\circ}\text{C}$ . This results in a hardening of the steel. It seemed remarkable that the changes in hardness with variation of cooling rate had not been noticed by previous investigators, but a search of the published work showed that no hardness determinations had been made in experiments in which the effect of various rates of cooling on the impact value of steels had been carried out. Later it was found that the changes in hardness are, in many cases, not so conspicuous when tempering temperatures of  $650^{\circ}\text{C}$ . or less are used, and that the changes are often somewhat masked by the softening effect of extra-tempering.

In view of the well-established fact that the amount of brittleness is more or less directly proportional to the rate of

cooling, it has previously been assumed that the physical change which produces the change in impact value would also be proportional to the rate of cooling. It now became evident from the present work that two changes giving opposite effects, depending on the rate of cooling, may take place in slowly cooled steels.

Also the fact that no appreciable change is, as a rule, revealed in density or in hardness when the tough state is compared with the fully brittle state has led, naturally enough, to the false assumption that no change would be observable when intermediate rates of cooling were used.

The present work makes it apparent that the similarity in most cases in density and in hardness of the tough and the brittle states is merely accidental, and that in fact a considerable transformation takes place in the physical condition of the steels on slow cooling.

It is now clear that many of the results which have been attributed to the softening effect of extra-tempering must have been due, in part at least, to the change taking place in the "brittleness range" with intermediate rates of cooling. For example, Rogers<sup>(9)</sup>, using a rate of cooling of  $1^{\circ}\text{C}$ . per minute, obtained a softening in all his steels. When his results are compared with those in the present research on the effect of extra-tempering it is clear that the decrease in hardness obtained by him is considerably more in some cases than could be explained by this factor. Greaves and Jones<sup>(2)</sup>, using a rate of cooling of  $0.3^{\circ}\text{C}$ . per minute and equalising the tempering effects, found that there was no difference in hardness between the water-quenched and the fully brittle

condition. These results, which have previously appeared to be incompatible with each other, are now shown to be due to the difference in the rate of cooling employed, and the experimental results of these investigators agree in general with the observations made in the present investigation.

While it is true that the specific volume and hardness of the tough (water-quenched) and the brittle conditions are in many cases very similar yet this is by no means invariably the case. Several instances will be seen among the results where the properties of the two varieties are noticeably different.

#### DETERMINATION OF THE EFFECTS OF VARIOUS COOLING RATES.

The seven steels shown in Table 6 were treated to find the effect of various cooling rates on the hardness and specific volume. AW23, which had shown such a marked physical change in previous experiments, had unfortunately to be omitted from this series, together with AW22 and NP1, as sufficient of the steel was not available for all the experiments. NP1 was replaced by a fairly low phosphorus nickel steel N3.

Five sets of these seven steels were treated, after a preliminary oil-quenching from 850°C., as follows:

<u>First Set.</u>	Tempered 2 hours at 650°C. and quenched in water.
<u>Second Set.</u>	do. slow-cooled at 3°C/min.
<u>Third Set.</u>	do. do. 2°C/min.
<u>Fourth Set.</u>	do. do. 1°C/min.
<u>Fifth Set.</u>	do. do. 0.6°C/min.

All the steels except N3 had been previously treated at a cooling rate of 0.3°C. per minute. The results are plotted in Figs. 10 to 16.



Three nickel-chromium, AH, NC, and NR3.

One plain carbon, A22.

Two nickel, low and high phosphorus, N3 (C, 0.29; Mn, 0.65; Si, 0.113; P, 0.036; S, 0.032; Ni, 3.22 per cent.), and NP5.

One chromium, AAX.

**TABLE 6.**

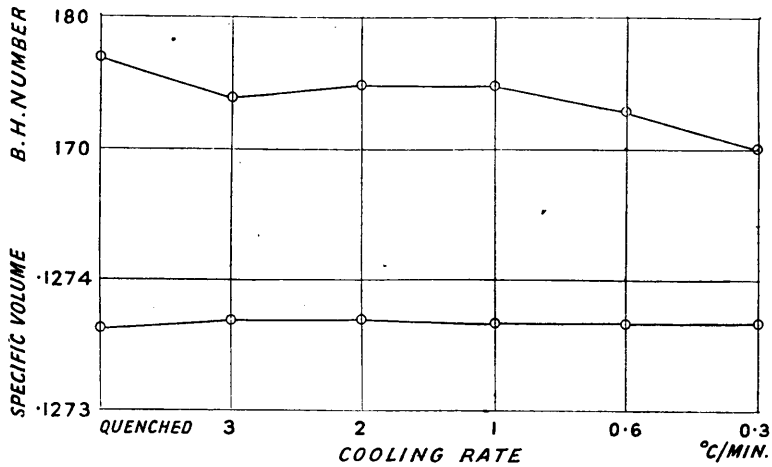


FIG. 10.—Carbon Steel, A22.

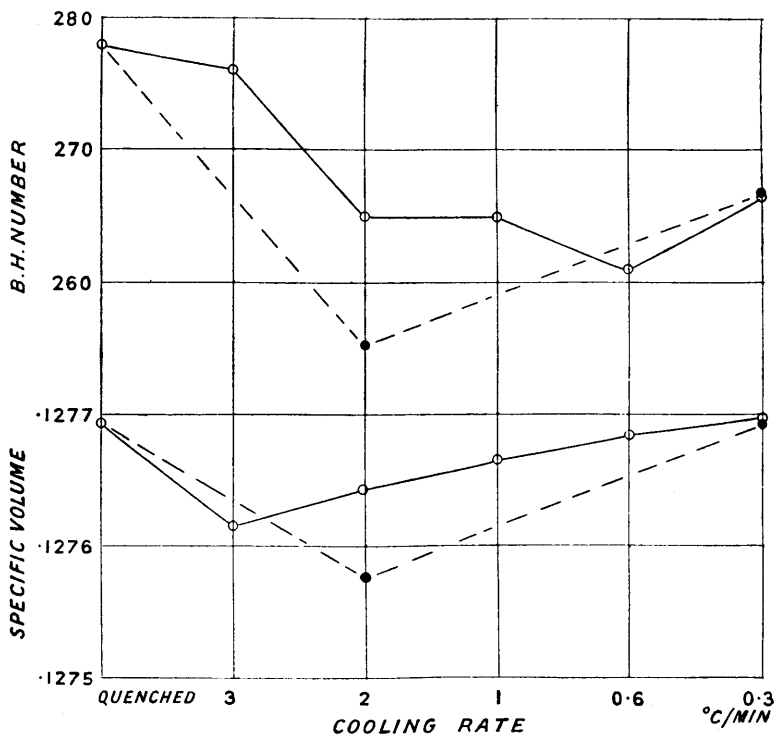


FIG. 11.—Nickel-Chromium Steel, AH.

Full line.—Specimens tempered at 650° C.  
Dotted line.—Specimens tempered at 670° C.

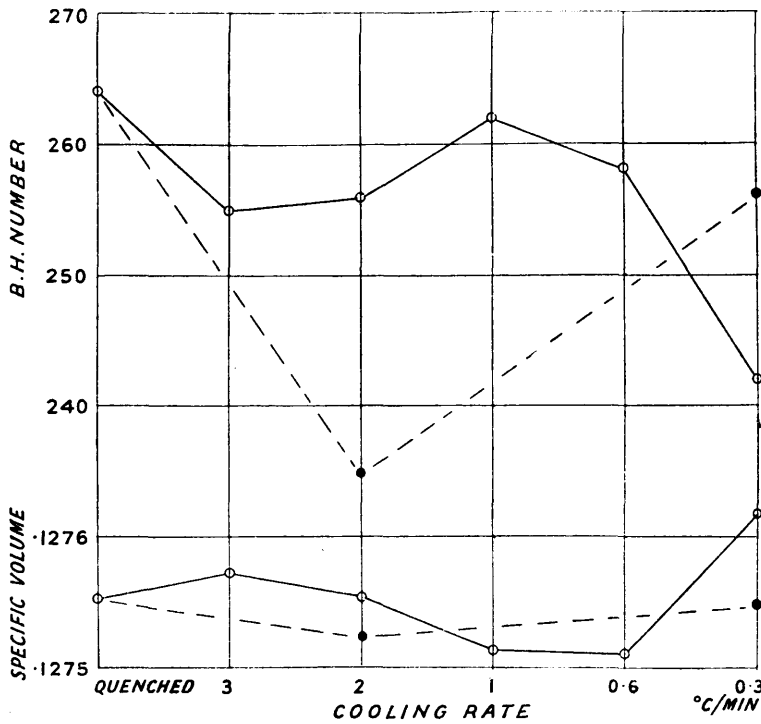


FIG. 12.—Nickel-Chromium Steel, NC.  
 Full line.—Specimens tempered at 650° C.  
 Dotted line.—Specimens tempered at 670° C.

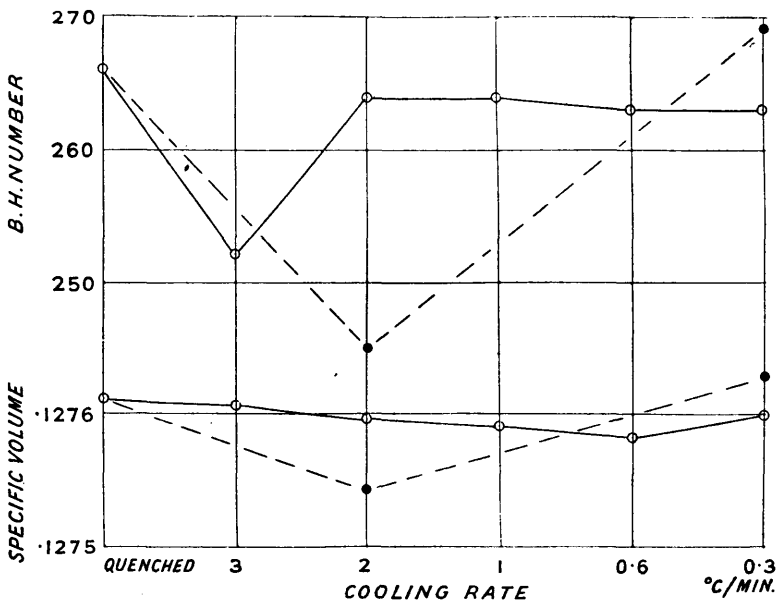


FIG. 13.—Nickel-Chromium Steel, NR3.  
 Full line.—Specimens tempered at 650° C.  
 Dotted line.—Specimens tempered at 670° C.

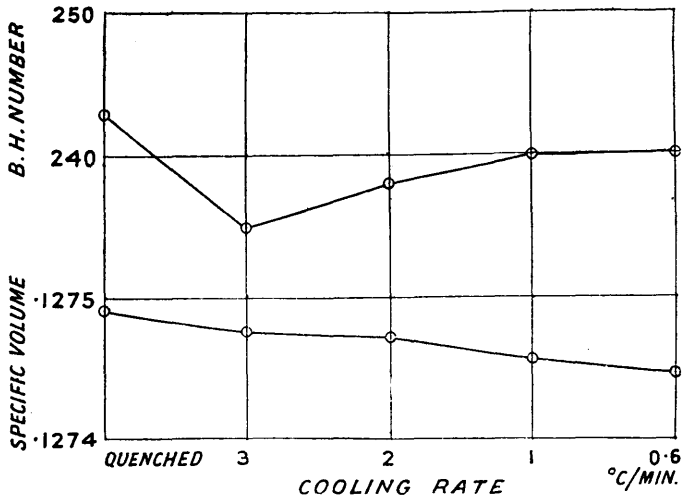


FIG. 14.—Nickel Steel, N3.

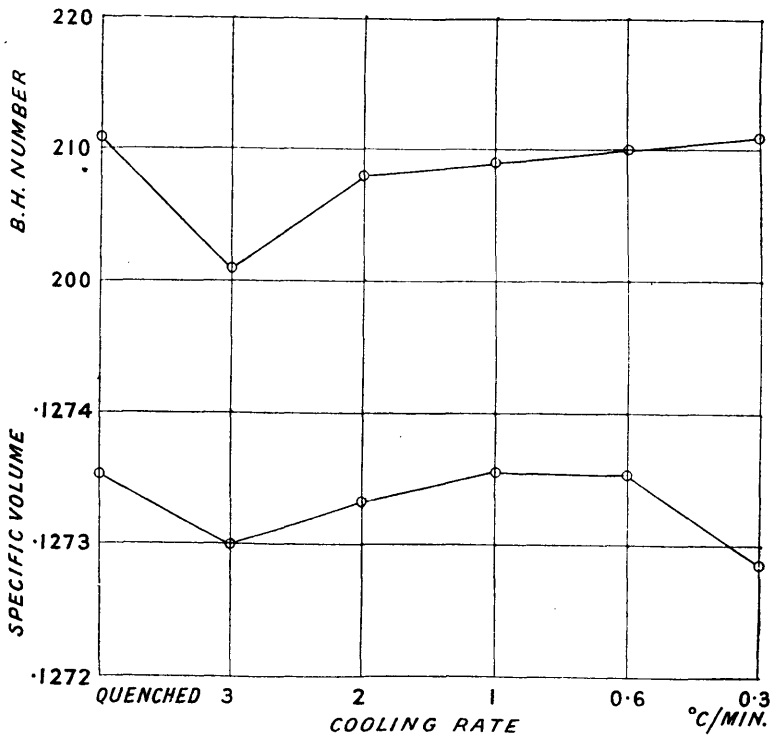


FIG. 15.—Nickel Steel (High Phosphorus), NP5.

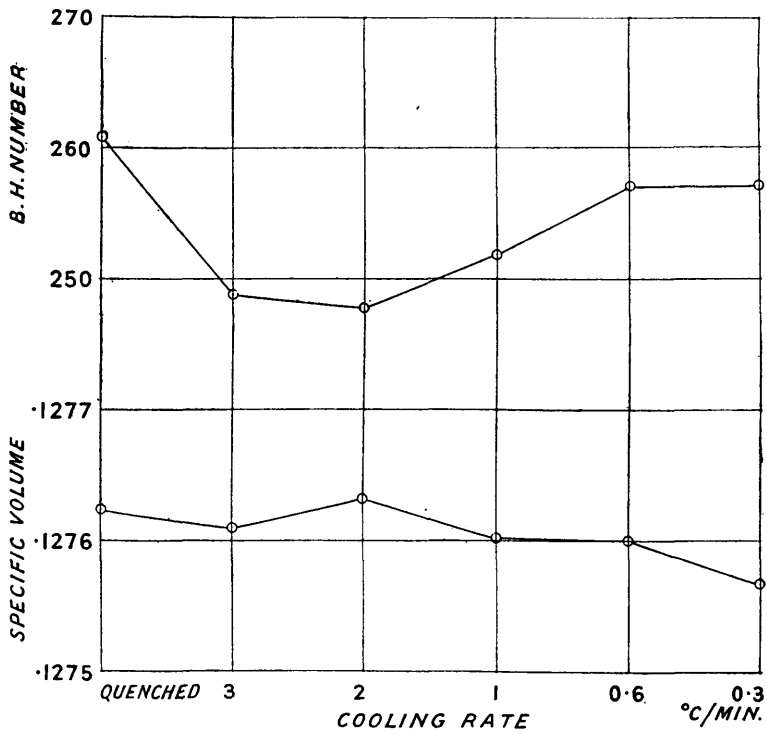


Fig. 16.—Chromium Steel, AAX.

steel

The carbon provides a useful comparison for the others.

Rate of cooling has no effect whatever on its specific volume, while while the hardness falls slightly and practically continuously due to extra-tempering.

The fall in specific volume and in hardness in the nickel-chromium steels at intermediate rates of cooling is fully confirmed. The changes in hardness are small, and are somewhat masked by the softening effect of extra-tempering. It is easy to see from these results how the variation in hardness with varying cooling rate has not been hitherto detected, as the standard tempering temperature has almost invariably been  $650^{\circ}\text{C}$ . or lower. When the tempering temperature is raised to  $670^{\circ}\text{C}$ . the change in hardness is considerably accentuated, due, as previously indicated from the impact tests, (Figs 7, 8, and 9) to an increase in the condition of toughness above  $650^{\circ}\text{C}$ . and a consequent increase in the resulting physical change on cooling.

Probably the most interesting and significant result of this series of experiments is the decided indication in the nickel steels and in the chromium steel of similar changes to those found in the nickel-chromium steels. The high-phosphorus nickel steel NP5 has been shown<sup>(4)</sup> to have a high susceptibility to temper-brittleness, and it shows (Fig. 15) changes both in specific volume and in hardness. Steel N3 (Fig. 14) shows a slight change in hardness only. Its susceptibility was not known, but was probably low. The change in specific volume in this steel is probably completely masked by extra-tempering, which is considerable in nickel steels, as previously pointed out.

The chromium steel was known to be susceptible to brittleness, and it shows an appreciable change in hardness, and possibly the indication of a change in specific volume (Fig. 16).

The changes in all the steels are rendered even more significant when it <sup>is</sup> remembered that they oppose the effects of extra-tempering.

That physical changes of the same nature are involved in all these steels of widely varying composition is an inevitable conclusion from these results, and that these are the changes involved in temper-brittleness is scarcely open to doubt. It is now clear that a substantial transformation takes place in steels susceptible to brittleness when they are slowly cooled from the tempering temperature.

It may also be said here that the condition of high hardness and high specific volume in water-quenched steels, as compared with the condition of low hardness and low specific volume in steels cooled at a moderate rate, is not evidently essential to reasonable toughness in the steels.

The moderate rates of cooling which produce a considerable contraction and softening in the steels may produce only a slight fall in the impact value. It is probable then that the toughness of a steel is dependent not nearly so much on any special condition which in itself gives toughness, as on the absence of the brittle condition which is induced by very slow cooling rates.

TEMPERING CURVES OF NICKEL-CHROMIUM STEELS.

The five nickel-chromium steels already experimented with were used in a series of experiments to find the effect of progressively increasing temperature. Long soaking times were used in order to bring about complete equilibrium at each temperature.

Specimens of steels AH, NC, NR3, AW23 and AW22 were first oil-quenched from 850°C. and then tempered for six hours at 300°C. The specific volume and hardness were determined and the tempering repeated (without intervening oil-quenching) at 400°C. The experiments were continued at various temperatures up to 670°C., six hours soaking being given at each temperature, except at 670°C., where three hours soaking was given in each of two successive treatments.

The results are plotted in Figs. 17 and 18.

With the exception of steel AH no outstanding change is shown by any of the steels. It had been thought that a slight rise in specific volume might have been observed as the temperature was raised through the brittleness range. (Later it will be seen that had the carbon content been lower this would probably have been obtained). No rise has taken place, but it is evident from some of the curves (notably steel AH) that, whereas the hardness falls continuously, there are halts in the specific volume curves. The hardness falls continuously and evenly in all the steels, but the specific volume does not. From 450°C. to 650°C. in steel AH the specific volume is almost unaltered in spite of a softening of 100 Brinell. A similar halt is seen in the other steels at about 600°C to 650°C. The specific volume while it does not rise opposes

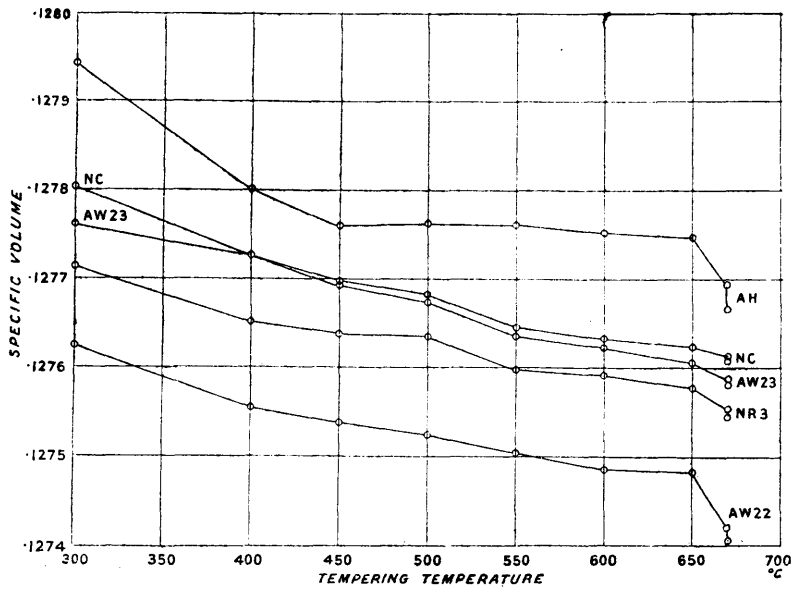


FIG. 17.—Five Nickel-Chromium Steels.

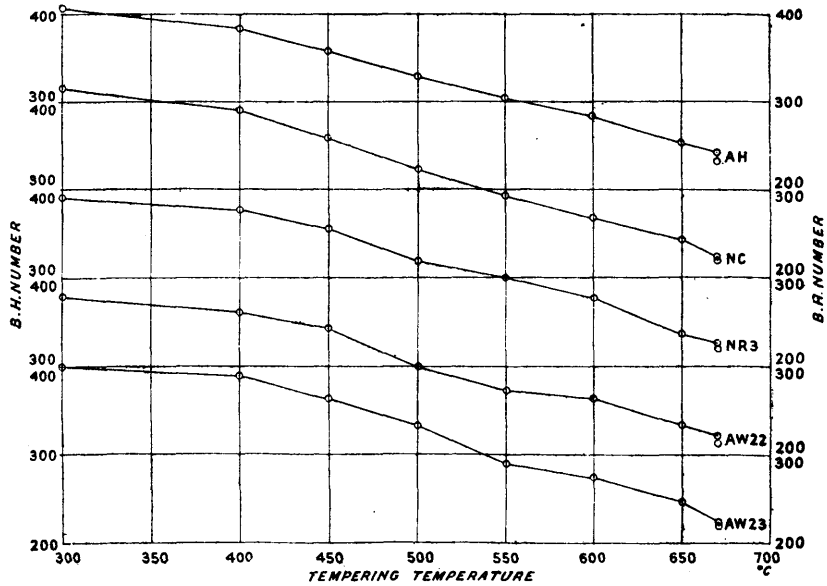


FIG. 18.—Five Nickel-Chromium Steels.



the contraction one would expect from the extra-tempering received by the steels. It is likely that this is due to increasing solubility of carbon in ferrite as the temperature is raised. This is fully considered at a later stage in the research.

The curves give further proof of the small effects on these properties of extra-tempering in nickel-chromium steels at high tempering temperatures. It will be noted that three hours extra-tempering at 670°C. gave a very small fall in all the steels.

Steels AH, NR3, and AW22 show a much larger fall in specific volume between 650°C. and 670°C. than between any of the preceding temperature intervals. This effect must be due to globularisation at high temperatures, and is further proof that the state of division exerts a decided effect on the specific volume of a steel.

#### AN ANALOGY TO THE OBSERVED PHYSICAL CHANGES.

In connection with some experiments which had been carried out by the author in an investigation into the behaviour of special steels in the  $Ac_1$  critical range, a result had been observed in a nickel steel which, it was thought, might throw light on the physical changes which had been found to take place in special steels in the "brittleness range".

The nickel steel concerned was steel N3, which has been used in earlier experiments (for analysis see Table 6). Bars of this steel had been heated at 695°C. until complete solution of carbide in  $\gamma$ -iron had taken place. Some of the bars were slowly cooled after this treatment at a very slow rate (0.3°C./min.). Tensile and Izod test-pieces were machined from the bars and mech-

anical tests carried out.

Examination of a micro-specimen which had been placed in the furnace along with the bars in order to follow the heat-treatment showed that the carbide of the slowly cooled steel had separated out in a remarkably complete film round the grain boundaries. A micrograph of this is shown in Fig. 20. (It will be seen later, in connection with work on the  $Ac_1$  range, that this structure was produced by a film of  $\gamma$ -solid solution formed at the soaking temperature breaking down to carbide and  $\delta$ -iron on cooling.) It was noticed also that the hardness of the micro-specimen was unusually high - considerably higher than is obtained in an annealed steel of this composition.

When the Izod Impact test-piece, which had been subjected to the same treatment as the micro-specimen, was broken, it was found that the impact value varied in a manner not obtained in any of the many other bars subjected to other treatments. When the hardness at the fracture faces was taken it was found to vary also from one end of the bar to the other, and to be higher than what was expected in the annealed state.

It was thought that the variation in physical properties of this steel containing grain-boundary carbide might provide an analogy to the behaviour of the special steels in the brittleness range. The test-bar and the micro-specimen were consequently subjected to a number of experiments.

A diagrammatic sketch of the Izod impact test-piece referred to is shown in Fig. 19. The manner in which the impact value and the hardness varied from one end of the bar to the other (and

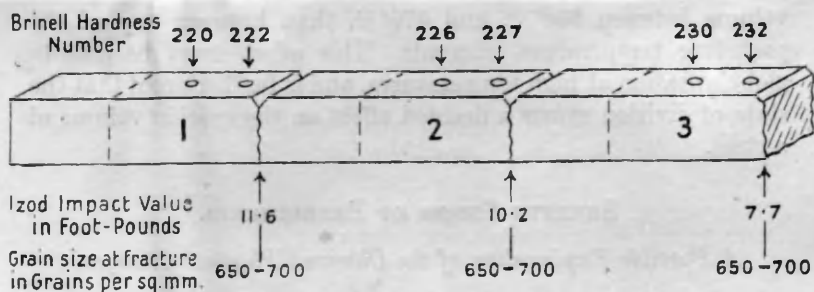


FIG. 19.—Diagrammatic Sketch of IZOD Impact Test-Piece of Nickel Steel containing Grain-Boundary Carbide. For specific volume of specimens, see Table 7

(The notches are drawn all on one face to avoid confusion. In the actual test-piece they were cut on three different faces.)

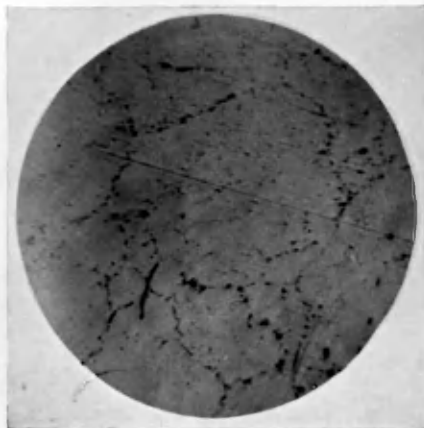


FIG. 20.—Nickel steel, N3. Etched in boiling sodium picrate.  $\times 370$ .

Specimen.	Experiment (b). Grain Boundary Condition.		Experiment (c). Tempered Fifteen Minutes at 650° C.		Experiment (d). Retempered One Hour at 650° C.		Experiment (e). Annealed at 760° C.	
	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.	Specific Volume.	Brinell Hardness.
1	0.127427	220	0.127372	177	0.127265	166	0.127375	198
2	0.127479	226	0.127389	191	0.127279	164	0.127356	201
3	0.127456	230	0.127395	194	0.127284	168	0.127395	203
4	0.127458	243	0.127363	183	0.127270	176	(not treated)	...

TABLE 7.

inversely to each other) is clearly indicated.

The following experiments were carried out:

(a) Microsections were prepared at each of the fracture faces, and the polished faces were boiled in sodium picrate to etch up the carbide only. It was found that the amount of carbide round the grains varied along the length of the bar in a similar manner to the impact figure and the hardness. As the impact value decreased and the hardness increased, the boundary became more apparent. The original micro-specimen, which had a higher hardness than any part of the test-piece, had a more complete boundary film than any part of the latter. The variation of the amount and completeness of the boundary in the different specimens was clearly beyond doubt. This observation was confirmed by an independent observer.

The grain-size of each specimen was estimated and found not to vary. The possible influence of variation in grain-size was thus eliminated.

(b) Specific volume test-pieces were then taken from each fracture end of the test-bar and from the original micro-specimen, and the specific volume determined. It was found that the specific volume was also much higher than the annealed value. See Table 7.

(c) The four specimens were then tempered at  $650^{\circ}\text{C}$ . for fifteen minutes and cooled quickly in the furnace. The specific volume and the hardness after this treatment were both much lower (Table 7), and micro-examination showed that the grain boundary was largely broken up into small globules. This was the only apparent change in structure, and the difference in properties seemed to be attributable only to the difference in state of distribution of the

carbide.

(d) The specimens were retempered at  $650^{\circ}\text{C}$ . for one hour, and this treatment resulted in a further decrease in specific volume and in hardness, and the grain boundary was completely destroyed. The arrangement of the larger globules which had been formed by globularisation from the carbide of the boundary indicated faintly in parts the original granular structure.

(e) Three of the specimens were then quickly annealed by heating to  $760^{\circ}\text{C}$ . for a few minutes and cooling quickly in the furnace. The results (Table 7) show that the specific volume and the hardness are much lower than when the carbide was present at the boundaries in the same specimens.- experiment (b). It would be expected that the steel cooled more quickly from above the  $A_{r1}$  point and from a higher temperature would show a higher hardness and possibly a higher specific volume. The opposite, however, is obtained. The steel cooled extremely slowly has much the higher specific volume and hardness, and the only apparent physical difference between the two structures is in the distribution of the carbide round the boundaries in the slowly cooled steel and the production of the usual mixture of ferrite and pearlite in the other.

It will be seen later that there was no possibility of the retention of some martensite explaining the high values in the "grain-boundary" bar.

It is easy to see why a steel with a network of hard carbide completely surrounding the grains should give a higher hardness than the same steel with the carbide distributed in a fine state of division throughout the mass. In the first case the hard net-

work (which is really the matrix of the steel) surrounding the grains will interfere with the flow of the iron of the grains in a decisive manner, whereas, with a homogeneous mixture of carbide and iron, the flow is not restricted by any such interference.

A tensile test-bar having the carbide distributed as a network round the grains (produced in exactly the same treatment as the Izod test-piece above) gave a tensile strength of 56.4 tons per square inch and an elongation of 9.0 per cent. The figures supplied by the makers of this steel were 55 tons per square inch tensile strength and 20 to 25 per cent elongation (oil-hardened 820°C. and water-tempered 620°C.) These figures may not be strictly comparative, but it is evident that the grain boundary has not produced any great difference in the tensile strength. The elongation is lowered by about half, but the difference in Izod values is much greater. The average Izod value for the grain-boundary bar was 9.8 foot-pounds, whereas in the oil-hardened and water-tempered state it was given as 60 foot-pounds. There is thus the strong indication that the distribution of the carbide at the grain-boundaries has a much greater effect on the impact than on the other mechanical properties.

#### Further Consideration of the Foregoing Results.

It has been clearly proved that in steels susceptible to temper-brittleness a moderate rate of cooling (2°C. or 3°C. per minute) produces a considerable fall in specific volume and in hardness. The moderate rates of cooling which produce this physical change are known to produce comparatively small changes in impact value.

It would appear that there is a connection between the magnitude of this physical change and the degree of brittleness which may be produced by very slow cooling. Thus in nickel-chromium steels, which have a high susceptibility to brittleness, the change in specific volume and in hardness is very marked, whereas in nickel and in chromium steels which have a low susceptibility the change is small. As the phosphorus content of a nickel steel is raised the change is accentuated.

This physical change, as has been previously pointed out, may be explained by the deposition, on moderately slow cooling, of a solute which is in solid solution in the steel at the tempering temperature and which is retained in solid solution by quick cooling. Honda and Yamada<sup>(6)</sup> have found that a susceptible nickel-chromium steel became non-susceptible in the absence of carbon. This points to this element being the one concerned in temper-brittleness and also in the changes accompanying it. This conclusion is supported in many ways. Thus carbide (either simple carbide of iron or double carbide of iron and chromium) is the only constituent common to all the steels, with the exception of impurities which are of such small amount that they could not be made to explain the substantial changes in nickel-chromium steels at any rate. Oberhoffer, Hochstein, and Hossenbruch<sup>(7)</sup> found that although oxide specially introduced into solid solution in steels might produce brittleness no matter how the steels were treated yet there was no definite effect in the production of temper-brittleness. Andrew and Green<sup>(4)</sup> found that phosphorus added to nickel steels produced temper-brittleness in them, but unless abnormally high all previous experimenters agree

that phosphorus has no effect. Thus Greaves and Jones<sup>(3)</sup> find no indication in their work that phosphorus up to .04 per cent has any effect. Monypenny in the discussion to Rogers' paper<sup>(9)</sup> found phosphorus up to .039 had no effect. Brearley in the same place states that there is as much brittleness with low phosphorus as with high. Observations by the present author point to the fact that the influence of abnormally high phosphorus depends on its influence on the behaviour of the carbide. Griffiths<sup>(5)</sup> found that nitrogen specially introduced into nickel steels produces temper-brittleness in them, but there is no indication that nitrogen has any effect except when specially added in this way in relatively large amount. Possibly the effect of high nitrogen affects the behaviour of the carbide in the same way as phosphorus does. On the other hand it is quite possible that nitrides may behave in the same manner of solution and deposition as carbide. That, however, would be a special case of temper-brittleness and can be disregarded in the consideration of commercial steels.

It is thus suggested that a certain amount of carbide is present in solid solution in  $\alpha$ -iron (which may be nickel or chromium ferrite) at high tempering temperatures, and that this carbide is deposited throughout the mass on moderately slow cooling.

The deposition of carbide from solid solution will not, however, in itself produce brittleness in a steel, and it is evident from the present work that another physical change produced during very slow cooling is responsible for the brittleness. It has been clearly proved that very slow rates of cooling give a considerable increase in the specific volume and hardness when compared



with the values obtained by moderate cooling rates. It appears that the state of distribution of the carbide must be the predominating influence in this increase and also in the production of the high degree of brittleness which usually accompanies it.

The evidence provided by the experiments on a nickel steel containing grain boundary carbide points strongly to the fact that, when the carbide is distributed round the grain boundaries, the specific volume and the hardness are considerably raised over the values obtained in the same steel with the same amount of carbide present but distributed more or less homogeneously throughout the mass. The grain-boundary condition results also in the production of brittleness in the steel, whereas the steel in its normal quenched and water-tempered condition is tough.

These experiments give, therefore, a complete analogy to the physical changes observed in steels susceptible to temper-brittleness and provide a reasonable explanation of the variations in impact value.

The rise in specific volume and hardness on cooling very slowly is believed to be due to the expulsion of the carbide, which is deposited out of solution, to the grain boundaries. The amount of brittleness developed will depend on the amount of carbide involved in this separation and also probably on the physical nature of this constituent. If a complete network of carbide is formed during cooling it is not difficult to see how it will affect the physical properties. The actual grains of the steel will become virtually separated from each other by the network, and the coefficient of contraction of the latter will exercise a determining

influence on the final volume of the mass. From work by Honda<sup>(19)</sup> on the coefficient of expansion of steels it is clear that the coefficient of expansion of carbide is lower than that of iron. This no doubt applies to all the common carbides in steels. Consequently when a network is present in the steels the slowly cooled mass will have a larger volume. The effect on the hardness is clearly explicable by the interference of the network with slip or flow of the mass of the steel. No such interference takes place when the carbide is distributed throughout the mass.

Microscopical examination of the steels used in the present work did not produce complete confirmation of the above theory, but partial success in this respect has been attained. It is certain that any grain boundary which is produced is extremely small in magnitude and therefore difficult of detection. The grain boundary which was found in the nickel steel (Fig. 20) was easily detected by etching in sodium picrate, but was extremely difficult to pick out by ordinary etching - in fact, its existence could not have been established at all had it not been possible to etch up the carbide in the polished specimen. The grain boundary in this case must be much larger than any that is produced in the tempering zone in steels susceptible to temper-brittleness. In the nickel-chromium steels, which have high susceptibilities, it has not been found possible to etch up the carbide in the polished specimens. This has made the detection of a boundary apparently impossible until some new method of etching the polished specimens is discovered.

In the high phosphorus nickel steel, however, the slow

cooled specimens etched by sodium picrate revealed an unmistakable grain-boundary network of carbide. This was exactly similar in structure, but not so clearly marked, as the grain-boundary shown in Fig. 20. There was also the faint indication of a boundary in the low phosphorus nickel steel which is only slightly susceptible to brittleness. No boundary was present in these steels in the water-tempered state or in the moderately slowly cooled state.

It was found impossible to produce satisfactory photographs of the boundary in these steels with the apparatus available owing to the indistinct nature of the structure and the glare from the polished specimen. That a carbide boundary was present in the steels mentioned was, however, fully admitted by independent observers.

The effect of the state of aggregation of the carbide, apart altogether from the effect of its distribution round the grain boundaries, may be commented on. The results have shown that the fall in specific volume with rise in tempering temperature is comparatively small, <sup>in carbon steels</sup> but that it is very pronounced in nickel steels and appreciable in nickel-chromium steels. This effect must be due to globularisation of the carbide, which microexamination has shown to be slow in carbon steels but which becomes rapid in nickel steels when the temperature is raised to near the critical range.

The contraction in the nickel steels as the tempering temperature is raised (Figs. 2 and 3) is surprisingly large, but it seems certain that globularisation must account for it entirely. The results in Table 7 provide further confirmation of the remarkable changes in specific volume (and also in hardness) which can be brought about by tempering nickel steels at high temperatures.

CHANGES IN MAGNETIC PROPERTIES AND RESISTIVITY.

The variations in specific volume and hardness being now well understood it became desirable to find how other properties, such as magnetic properties and specific electrical resistance, varied in the different conditions of highly susceptible nickel-chromium steels. Steels AH, NC, and MR3, being now available in quantity, were used for this work. Their analyses are shown in Table 8.

EXPERIMENTAL METHODS.

Magnetic Tests. - These were taken by the bar-and-yoke ballistic method, using the usual standard circuit, full details of which are to be found in Ewing's "Magnetic Induction in Iron and Other Metals". Current was supplied by twelve Edison cells, and it was measured by standard shunts on a Cambridge and Paul Testing Set. Various resistances were made to desired values for insertion in the circuit so as to set the field strength at any desired value. When the apparatus was properly set up the galvanometer and scale were permanently fixed so that no variation in their position could affect the results. The accuracy of the apparatus was checked by the use of two of the author's specimens specially standardised by the National Physical Laboratory. The author's figures for these specimens were found to agree very closely with the standard figures supplied. The specimens used for the magnetic determinations were bars 1 cm. in diameter and 28 cm. in length, the clear length within the yoke being 25 cm. The test-bars were machined from 5/8ths. inch square bars after heat-treatment. Hysteresis loops for a max-

imum magnetising force of 150 c.g.s. units were determined, and also the variation of magnetic induction (B) and remanent induction ( $B_{rem.}$ ) from  $H = 0$  to  $H = 250$ . The remaining magnetic properties were calculated from the readings obtained.

Specific Electrical Resistance. - The specimens for the determination of resistivity were about 9 cm. in length, and were machined down to 3 mm. in diameter after heat-treatment. Specimens obtained from Izod impact test-pieces, being shorter than the above, were machined down to  $2\frac{1}{2}$  mm. to give an actual resistance of about the same value. One of the specimens was taken as a standard and its resistance between permanently fixed knife-edges of nickel-chromium steel was determined at various room temperatures, a steady current of 1.5 amp. being passed through the specimen and the voltage drop between the knife-edges read on a Tinsley vernier potentiometer. The current was accurately determined by reading on the potentiometer the voltage drop across a standard resistance in the circuit. The various results, after calculation to resistivity, were plotted on a temperature-resistivity graph, and the specific resistance at  $20^{\circ}\text{C}$ . read off. This was taken as the absolute specific resistance of the standard specimen at that temperature. The resistance of the other specimens was determined by comparison with the standard, the "unknown" being placed in the circuit across another set of knife-edges. Readings were taken on the standard before and after each reading on the unknown, and this was repeated a number of times after moving the unknown along the knife-edges between each set of readings. For the calculation of the specific resistance the diameter of each specimen was measured at cross-diameters each

3 mm. along its length and the mean diameter taken. The distance between the knife edges was also accurately determined. The knife-edges were screwed on a wooden block so that they were exactly parallel to one another, and the specimens were firmly held on them by means of powerful elastic bands.

By this method the effects of variations in the current and in the temperature are eliminated, and the results are strictly accurate relative to the standard, assuming that the temperature-coefficient is the same for all the specimens used. A number of tests showed that the temperature-coefficient did not vary appreciably in different specimens and, as the lowest temperature of any test was 19°C. and the highest 21.5°C., it may be taken that the results are of a high degree of accuracy. Numerous complete re-determinations were carried out at various times, and of these 90 per cent. were within 0.06 microhms per cu. cm. or less of the original determination, and 10 per cent. differed by from 0.07 to 0.10 microhms per cu. cm. One or two particular specimens which varied in diameter along their length more than the others were found to be liable to give the larger variation indicated. In these cases a greater number of readings along the length were, as a rule, taken.

Specific Volume and Brinell Hardness. - These properties were determined by the methods previously described.

#### HEAT TREATMENT.

It was desired to obtain specimens of the steels AH, NC, and NR3 suitable for magnetic, resistivity, and other tests in the tough, intermediate, and fully brittle conditions, with tempering

effects equalised as far as possible in all the specimens, so as to eliminate largely this factor from the results. Suitable lengths of 5/8ths. inch square bar of each steel were subjected to the following heat treatments, use being made of the well known phenomenon of impact reversibility. (2)

All the bars were first oil-hardened after being maintained for half-an-hour at 850°C.

First Treatment. - AH<sub>2</sub>, NC<sub>2</sub>, NR3<sub>2</sub> and AH<sub>3</sub>, NC<sub>3</sub>, NR3<sub>3</sub>, were tempered for two hours at 660°C. and quenched in water.

Second Treatment. - AH<sub>3</sub>, NC<sub>3</sub>, NR3<sub>3</sub>, from first treatment, and AH<sub>1</sub>, NC<sub>1</sub>, NR3<sub>1</sub>, were tempered for two hours at 660°C., and slowly cooled at the rate of 0.3°C. per minute.

Third Treatment. - AH<sub>1</sub>, NC<sub>1</sub>, NR3<sub>1</sub>, from second treatment, were tempered for two hours at 660°C. and quenched in water.

Fourth Treatment. - AH<sub>2</sub>, NC<sub>2</sub>, NR3<sub>2</sub>, from first treatment, were tempered for two hours at 660°C. and slowly cooled at the rate of 2°C. per minute.

Each bar was thus tempered for a total of 4 hours at 660°C and was subjected to a slow cooling and to a quenching treatment from that temperature. As a result of these treatments it may be said that tempering effects were as nearly as possible equalised in the tough condition (AH<sub>1</sub>, NC<sub>1</sub>, NR3<sub>1</sub>) and the fully brittle condition (AH<sub>3</sub>, NC<sub>3</sub>, NR3<sub>3</sub>), but that in the intermediate condition (AH<sub>2</sub>, NC<sub>2</sub>, NR3<sub>2</sub>) the bars received slightly less tempering, due to the quicker rate of final cooling.

Heat treatment was carried out in an electric tube furnace wound over a length of two feet. The variation of temperature from

end to end of the specimens was small. This is commented on at a later stage. The temperature at the centre was kept at exactly  $660^{\circ}\text{C}$ . (measured on Tinsley) in the tempering treatments. This temperature was chosen to give as large changes as possible on slow cooling. It has been found, however, that slight solution at the commencement of the  $\text{Ac}_1$  range takes place at this temperature in steel AH. For the other steels this temperature is well below the start of the  $\text{Ac}_1$  range.

After the treatments suitable specimens of the dimensions previously noted were machined for the various tests.

#### EXPERIMENTAL RESULTS.

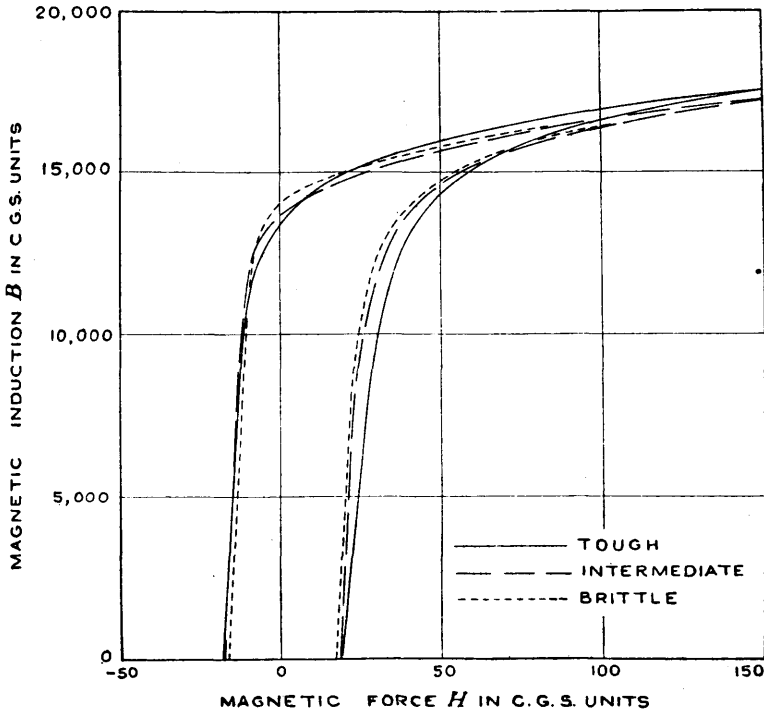
Hysteresis half-loops for a maximum magnetising force of 150 c.g.s. units are shown in Figs. 21, 22, and 23. The curves for the tough, intermediate, and brittle states of each steel have been superimposed for easy comparison. It will be seen that after the slow cooling treatments the shape of the curves is modified in a characteristic manner, due to a rise in retentiveness and an increase in permeability at the lower values of the magnetising force. In steel AH (Fig. 21) a small amount of carbide had been dissolved in  $\gamma$ -iron at the tempering temperature, and the effect of this is apparent when the magnetic properties of this steel are compared with those of the others. In steels NC and NR3 (Figs. 22 and 23), in which changes in the ferrite are alone concerned, the tempering temperature having been clearly below the start of  $\text{Ac}_1$ , the properties of the intermediate and the fully brittle specimens are very similar, and are distinctly different from those of the tough specimens.



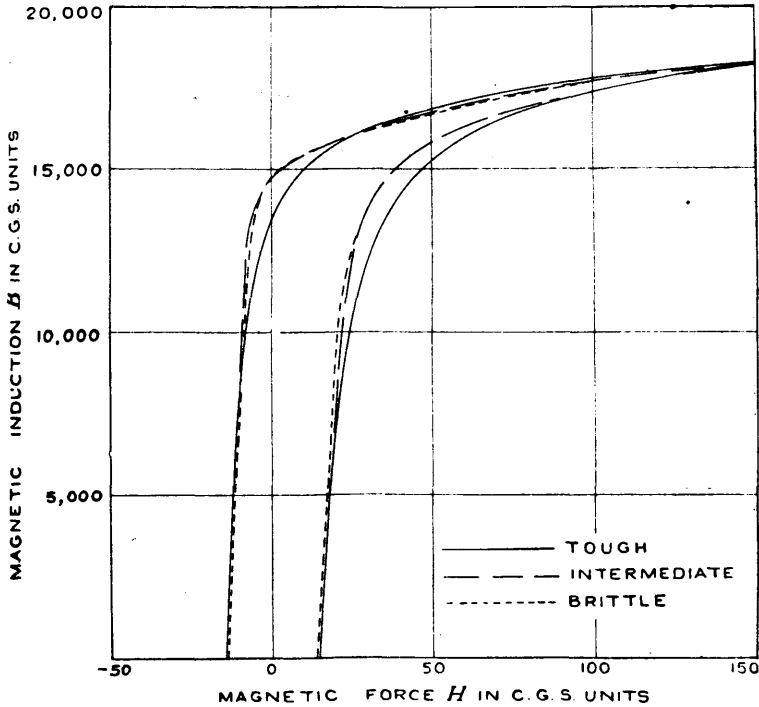
*Analysis of Steels.*

Steel.	Carbon. %	Silicon. %	Sulphur. %	Phosphorus. %	Manganese. %	Nickel. %	Chromium. %
AH	0.31	0.310	0.021	0.015	0.47	4.46	1.41
NC	0.31	0.145	0.029	0.026	0.57	3.20	0.83
NR3	0.36	0.275	0.021	0.016	0.34	1.90	1.15

**TABLE 8.**



**Fig. 21.—Cyclic Curves of Steel AH.**



**Fig. 22.—Cyclic Curves of Steel NC.**

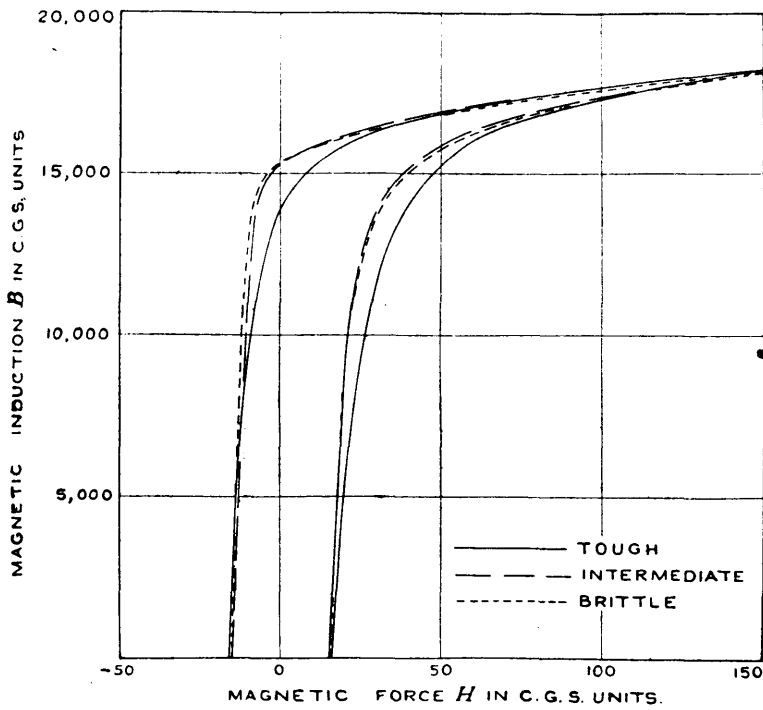


FIG. 23.—Cyclic Curves of Steel NR3.

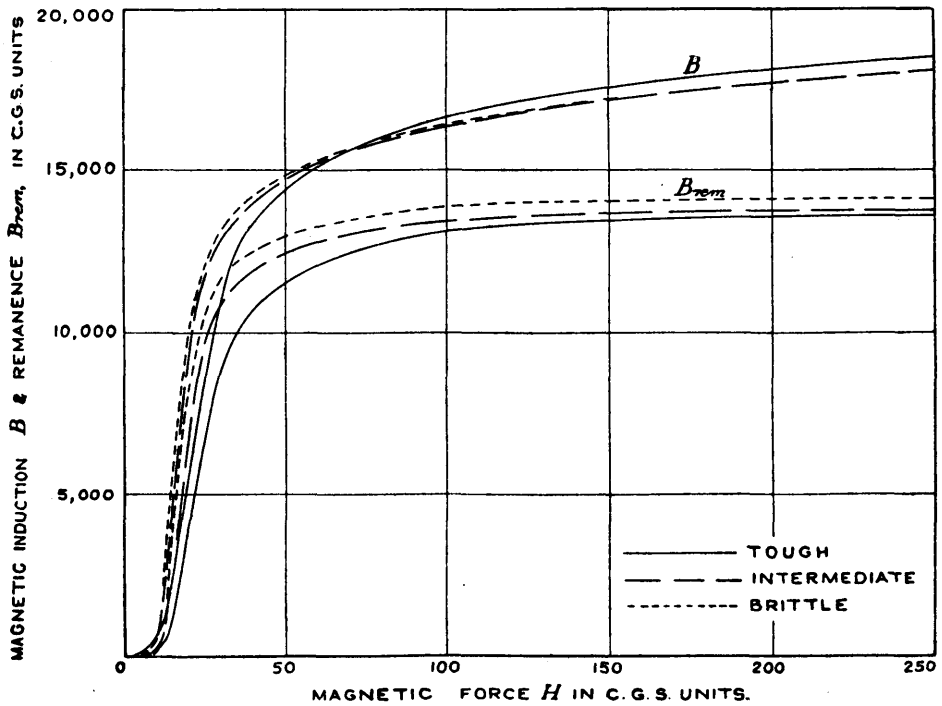


FIG. 24.—Steel AH. Variation of  $B$  and  $B_{rem}$  with  $H$ .

In Figs. 24, 25, and 26 are shown curves for the variation of magnetic induction and remanent induction from  $H = 0$  to  $H = 250$  for the various states of each steel. Here again the similarity of the intermediate and brittle states in steels NC and NR3 is very apparent. The difference between the remanence of the various states is shown more distinctly in Fig. 27., where the percentages of the maximum induction remaining as remanent induction are plotted against the corresponding values of the magnetising force. It is seen that after the lower values of  $H$  have been exceeded the percentage of induction remaining as remanent magnetism increases about 7 or 8 per cent on slow cooling in steels NC and NR3, the total increase being somewhat less in steel AH. The variation of the permeability for the various states of each steel is plotted in Figs. 28, 29, and 30. The maximum permeability in each case rises on slow cooling, and the maximum values of the intermediate and brittle states for the respective states are very similar. Small differences in the maximum permeability of these two states correspond inversely to small differences in the coercive force. (Figs. 21, 22, and 23, and Table 9)

Table 9 shows a summary of the chief magnetic properties, including the hysteresis loss, calculated from the area of the hysteresis loops. It will be seen that the latter property decreases in each steel after the slow cooling treatments.

Table 10 shows the results of determinations of resistivity, specific volume and Brinell hardness.

The specific volume and Brinell hardness show in each case the double effect discovered in previous work.

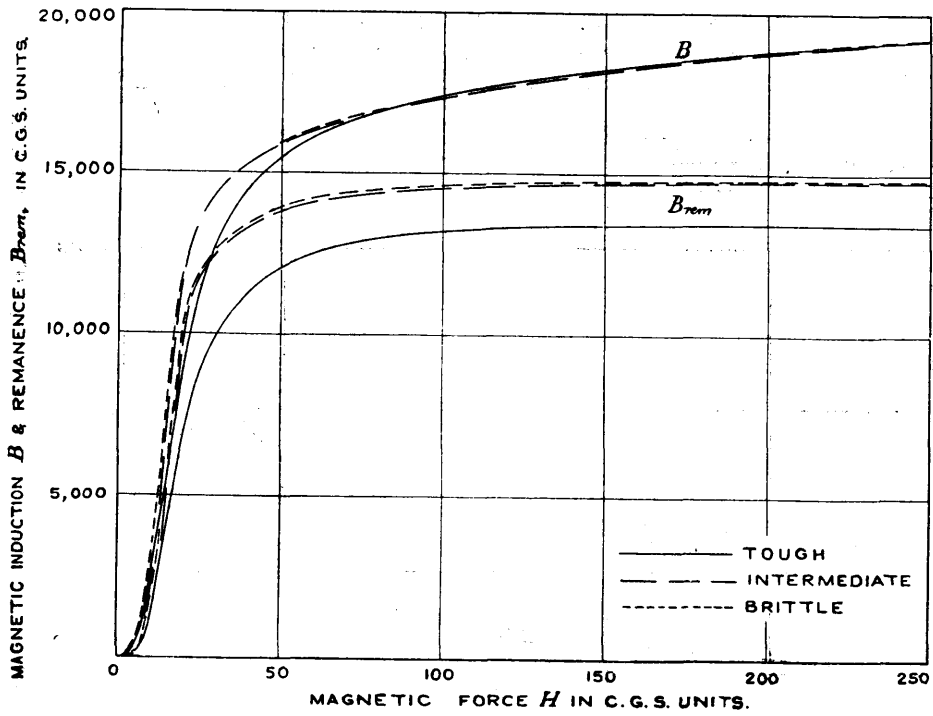


FIG. 25.—Steel NC. Variation of  $B$  and  $B_{rem}$ . with  $H$ .

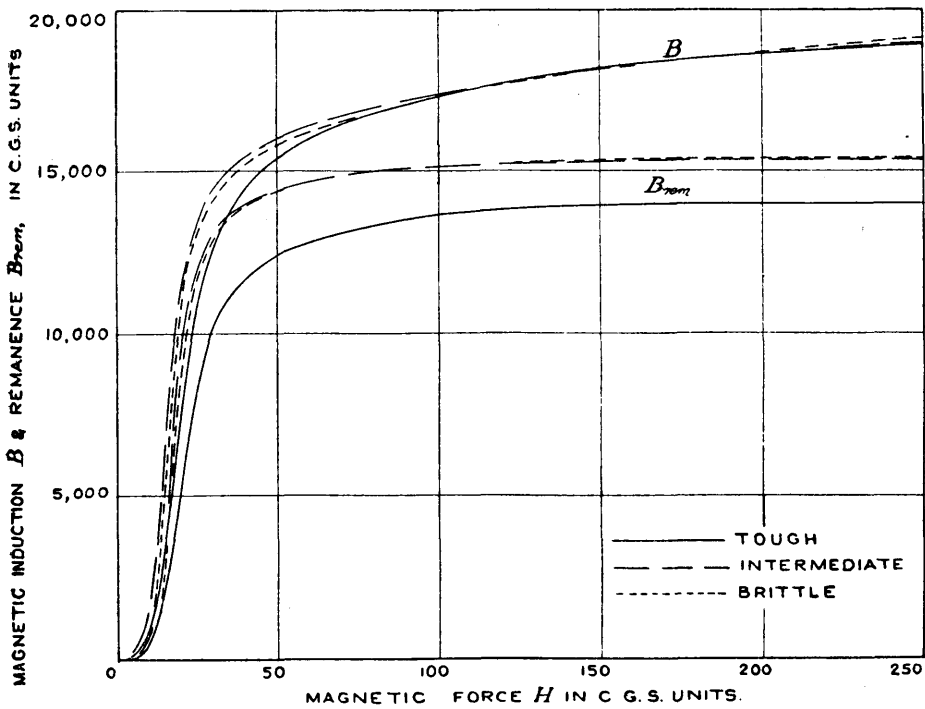


FIG. 26.—Steel NR3. Variation of  $B$  and  $B_{rem}$ . with  $H$ .

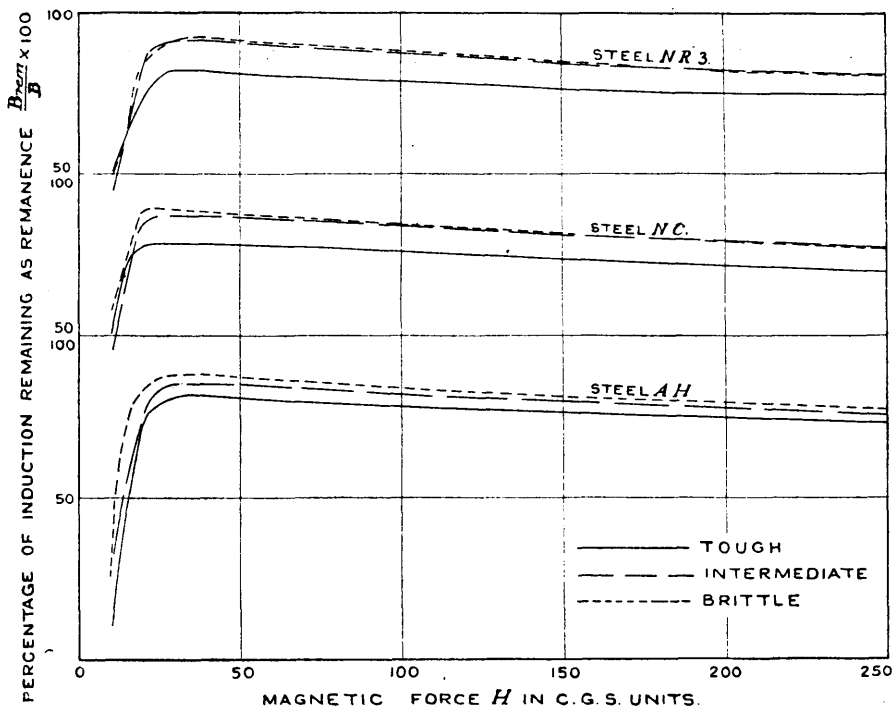


Fig. 27.—Steels AH, NC, and NR3. Variation of  $B_{rem}$ . per cent. with  $H$ .

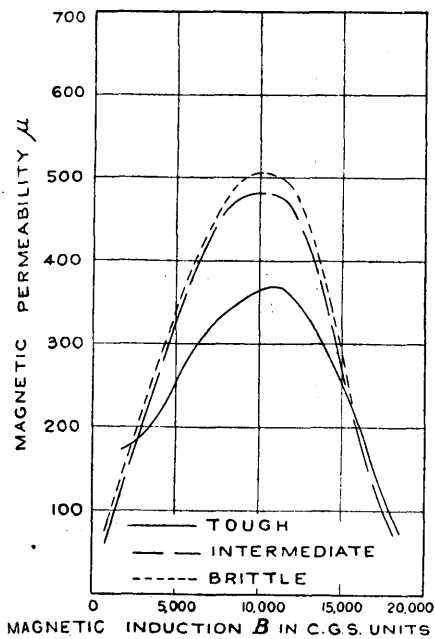


Fig. 28.—Permeability of Steel AH.

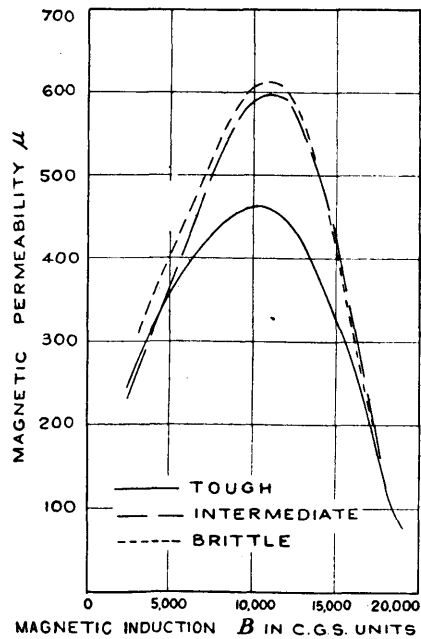


Fig. 29.—Permeability of Steel NC.

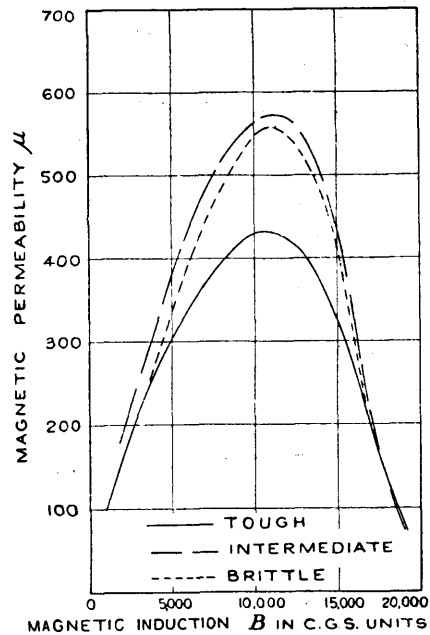


Fig. 30.—Permeability of Steel NR3.

**TABLE 9**—*Summary of Magnetic Properties from Hysteresis Loops for*  
 $H_{max.} = 150 \text{ c.g.s. Units.}$

Steel.	Condition.	Coercive Force. $H_c.$	Maximum Induction. $B_{max.}$	Remanent Induction. $B_{rem.}$	$\frac{B_{rem.}}{B_{max.}} \times 100.$	Percentage Increase in $B_{rem.}$	Hysteresis Loss. Ergs per c.c.	Maximum Permeability. $\mu_{max.}$
AH	Tough . . .	18.5	17,540	13,400	76.4	} 3.1 } 5.2	102,000	368
	Intermediate . . .	18.0	17,180	13,660	79.5			
	Brittle . . .	16.5	17,210	14,040	81.6			
NC	Tough . . .	14.7	18,270	13,400	73.4	} 7.4 } 7.6	87,400	465
	Intermediate . . .	14.7	18,200	14,720	80.8			
	Brittle . . .	14.0	18,220	14,760	81.0			
NR3	Tough . . .	16.0	18,220	13,930	76.5	} 7.8 } 8.3	96,000	432
	Intermediate . . .	14.8	18,160	15,300	84.3			
	Brittle . . .	15.1	18,120	15,360	84.8			

**TABLE 10**—*Resistivity, Specific Volume, and Brinell Hardness Values.*

Steel.	Condition.	Specific Resistance at 20° C. Microhms.	Decrease in Specific Resistance.	Specific Volume.	Brinell Hardness.
AH	Tough . . .	32.20	} 0.58 } 0.99	0.127735	258
	Intermediate . . .	31.62			
	Brittle . . .	31.21			
NC	Tough . . .	30.47	} 0.37 } 0.55	0.127736	252
	Intermediate . . .	30.10			
	Brittle . . .	29.92			
NR3	Tough . . .	24.23	} 0.29 } 0.54	0.127613	246
	Intermediate . . .	23.94			
	Brittle . . .	23.69			

In this connection it should be noted that the specimens in the intermediate condition received less tempering than the others, and consequently the difference in values, being in opposition to the contracting and softening effect of extra-tempering, is all the more significant. Also, it is probable that there is a definite rate of cooling (probably varying in different steels) which would give a larger contraction and softening than that obtained in these experiments. In some cases larger changes had been obtained in these properties in the same steels treated without equalisation of tempering effects. (Table 5).

The resistivity (Table 10) varies directly with the rate of cooling, but it is likely that the difference in tempering effect between the 2°C. per minute and the 0.3°C. per minute rates of cooling accounts entirely for the difference in values between the intermediate and the brittle specimens, and that, if the tempering effects had been exactly equalised in these two states, their resistivity would be practically equal. It has been found by Campbell and Mohr<sup>(20)</sup> that even in carbon steels spheroidisation of carbides below  $A_{r1}$  on annealing at a slow rate, may produce a decrease of 0.1 to 0.2 microhm in the resistivity when compared with the values obtained on annealing at a moderate rate. This property would appear to be more sensitive than others to such variation. This effect may be expected to be apparent in the resistivity determinations of the present paper. Spheroidisation of the carbide would not be expected to have an appreciable effect on the magnetic properties.

The effect of extra-tempering on the resistivity is shown

more fully in connection with the results of further experiments below.

The present experimental results confirm the observation of Kayser<sup>(11)</sup> who noted that in a steel susceptible to brittleness the remanence increased considerably on slow cooling.

It has been shown in the present work that changes in specific volume and in hardness are accentuated when the tempering temperature is raised, especially near to the  $A_{c1}$  range. This, no doubt, applies to the other physical properties, and may account for the absence of detectable changes in resistivity up to  $600^{\circ}\text{C}$ . in the steels examined by Greaves and Jones<sup>(3)</sup>.

#### CORRELATION OF PHYSICAL PROPERTIES AND IZOD IMPACT VALUES.

It was thought advisable to determine the physical properties of actual test-pieces, the impact values of which were known. From previous experiments on steels AH, NG, and NR3 there were available heat-treated Izod specimens which could be used to show the effect of tempering treatments at rising temperatures near to and in the  $A_{c1}$  range on the resistivity and specific volume, and also to give a direct correlation of these properties with the Izod values. The long broken ends (about 5 cm. in length) were machined down to  $2\frac{1}{2}$  mm. diameter and their resistivities determined. Other parts of the Izod bars were used for specific volume determinations. The bars had been treated by first oil-quenching from  $850^{\circ}\text{C}$ . and then tempering for two hours at  $650^{\circ}\text{C}$ .,  $670^{\circ}\text{C}$ .,  $680^{\circ}\text{C}$ ., and  $690^{\circ}\text{C}$ .. Bars of each steel were obtained in the quenched and the slowly cooled conditions ( $0^{\circ}3^{\circ}\text{C}$ . per minute) from each of these temperatures.



The results are shown in Table 11. The average Izod and Brinell hardness figures are given for comparison with the resistivity and specific volume values.

It will be seen that the difference in resistivity between the tough and brittle specimens is greater at the lower temperatures than was the case in the earlier experiments. This is due to the fact that the tempering effects were not equalised, the brittle specimens receiving a greater amount of tempering during the slow cooling treatment. The difference between the resistivity of the tough and brittle specimens is in each case similar until solution in  $\gamma$ -iron at the commencement of the  $Ac_1$  range takes place, when the difference increases sharply, due to the marked effect of the quenched  $\gamma$  areas in raising the resistivity.

The specific volume of the quenched and the slow-cooled specimens are very similar after treatment at the lower temperatures, the specific volume of the slow cooled specimens being in general slightly lower than that of the quenched, due to extra-tempering. Similar remarks apply to the Brinell hardness results.

#### Further Consideration of Results.

It has been shown that no double effect similar to that obtained in specific volume and in hardness is apparent in the magnetic properties or in the resistivity. The results show that the magnetic properties are modified by cooling the steels slowly from the tempering temperature, and that the magnetic state of the intermediate condition is similar to that of the brittle condition. These facts, together with a consideration of the manner in which the magnetic properties change on slow cooling, give strong support

TABLE 11—Resistivity, Specific Volume, Brinell Hardness, and Izod Values.

Steel.	Tempering Temperature, ° C.	Final Treatment.	Mean Izod Value. Ft.-lb.	Mean Brinell Hardness.	Specific Resistance at 20° C. Microhms.	Decrease in Specific Resistance.	Specific Volume.
AH	650	{ W.-Q.	58.7	254	32.61	1.12	0.127759
		{ S.C.	5.5	274	31.49		0.127600
	670	{ W.-Q.	34.4	297	33.64	1.72	0.127740
		{ S.C.	7.7	268	31.92		0.127728
	680	{ W.-Q.	27.2	308	33.82	3.10	0.127768
		{ S.C.	5.2	260	30.72		0.127750
690	{ W.-Q.	8.6	346	38.83	6.24	0.127823	
	{ S.C.	5.2	272	32.59		0.127715	
NC	650	{ W.-Q.	58.8	260	26.51	0.81	0.127571
		{ S.C.	5.2	250	25.70		0.127543
	670	{ W.-Q.	70.5	253	26.53	0.64	0.127538
		{ S.C.	5.0	223	25.89		0.127515
	680	{ W.-Q.	71.4	237	26.29	0.62	0.127537
		{ S.C.	5.1	228	25.67		0.127558
690	{ W.-Q.	20.0	297	29.19	3.55	0.127612	
	{ S.C.	7.2	228	25.64		0.127536	
NR3	650	{ W.-Q.	69.5	253	24.78	0.72	0.127624
		{ S.C.	8.3	256	24.06		0.127623
	670	{ W.-Q.	79.5	238	24.54	0.60	0.127609
		{ S.C.	15.0	234	23.94		0.127607
	680	{ W.-Q.	78.7	236	24.70	0.72	0.127605
		{ S.C.	10.9	237	23.98		0.127592
690	{ W.-Q.	68.4	220	25.27	0.97	0.127585	
	{ S.C.	10.2	231	24.30		0.127582	

W.-Q. = water-quenched.

S.C. = slowly cooled at the rate of 0.3° C. per minute.

to the view that temper-brittleness is connected with solution and redeposition of carbide.

The rise in remanence accompanied by a rise in maximum permeability and a small decrease in coercive force and in hysteresis loss are features which would be expected to characterise deposition from solid solution on slow cooling. These are, for example, the changes which take place when martensite in quenched steels is tempered. The fall in resistivity would similarly be expected.

Thus at the tempering temperature some carbide is held in solid solution in ferrite, and is retained in that form on quenching from that temperature but separates out on slow cooling. The double effect in specific volume and in hardness has already been discussed fully and need not be enlarged upon.

As the result of the foregoing work it is clear that, far from there being no changes accompanying the transition from tough to brittle steel, all the important physical properties examined show marked changes.

Only the specific volume and the hardness, however, show the true changes involved in temper-brittleness.

The magnetic properties and the resistivity show solution and deposition of carbide but not the state of distribution of the carbide.

#### EXPLANATION OF TEMPER-BRITTLENESS.

The explanation of temper-brittleness appears to be, briefly, as follows:

When a steel susceptible to temper-brittleness is cooled

slowly from a high tempering temperature, a portion of the carbide, which exists at that temperature in solid solution in the ferrite of the steel, separates out, giving definite modifications of magnetic properties and specific resistance. This also results, at moderate cooling rates, in a contraction and softening, as shown by specific volume and hardness tests. When, however, the rate of cooling is extremely slow, the steel expands and hardens again - relative to the moderately cooled state - and this is evidently due to the formation of a network of carbide round the grains, producing, by its predominant effect on the coefficient of contraction and its influence in increasing the resistance to penetration, an increase in specific volume and in hardness respectively.

Deposition of carbide will not in itself induce brittleness in the steel. It is only when the rate of cooling is sufficiently slow to allow of expulsion of the carbide to the grain boundaries - or if the steel is treated in other ways such as reheating to about 520°C. - that brittleness develops. Variation in the amount of deposition, the state of completeness or consistency of the boundary, and the physical nature of the particular carbide concerned will give rise to various degrees of brittleness, according to the composition and treatment.

Possibility of a Test for Brittleness without Destruction.

A consideration of the physical changes which have been shown to accompany temper-brittleness led to the conclusion that, although the hardness of the quenched tough condition and the brittle condition are in most cases nearly the same, yet the hardness of the two conditions must be of a different nature. If it were possible to measure the hardness of the grains in the brittle state then the hardness of them would differ from the hardness of the mass. In order to see whether any of the known hardness tests would show a different behaviour from the Brinell method some experiments were carried out as follows. Three 5/8ths. inch square bars of each of the three steels AH, NC, NR3 were treated to give the three conditions found to be physically different by the foregoing work, namely the quenched tough condition, the moderately slowly cooled condition and the fully brittle condition. The bars were ground on all surfaces to give ample area for numerous determinations on the same specimens. Hardness tests by the Brinell method, the Herbert Pendulum, and the Shore Schleroscope were carried out. The mean results are shown in Table 12. In the various tests using the Herbert Pendulum there was a good deal of inconsistency in the results. By some of the tests it is difficult to tell which of two specimens is the harder when a distinct difference in hardness, as shown by the Brinell method, exists. It was found that considerable differences in the values of the time test were obtained due to slight variations in the standard swing on glass. It was found possible, however, by the exercise of great care to obtain fairly consistende results with the time test. The results from these

TABLE 12.

<u>Steel.</u>	<u>Condition.</u>	<u>B.H.</u>	<u>Herbert Pendulum.</u> Time Test after 2,4,6,8 swings.	<u>Herbert Pendulum.</u> Scale W-H. Time tests. Test. Cap. 6,10swings.	<u>Shore</u>	<u>Schler</u>
AH	Tough	258	36,37,37,36	25.5 43.9	27	27.5 34.7
	Intermed.	250	34,31,33,36	20.5 47.8	29	28.5 32
	Brittle	255	37,37,37,37	19 48	28.2 28.2	31.4
NC	Tough	252	33,43,43,39	24 39	28.5 28.2	33.7
	Intermed.	243	47,40,35,34	21.5 37	28.2 27.6	31
	Brittle	252	44,39,42,40	21 44	28.5 28.2	33.2
NR3	Tough	246	37,37,39,37	19 48.2	27.2 28.3	34.2
	Intermed.	238	35,35,35,35	22.5 51.5	25 26.3	30.9
	Brittle	248	39,40,37,35	20 40.5	27.7 27	32

showed that in steels NC and NR3 the order of hardness was the same as with the Brinell method. In steel AH this was not so and it is possible that this shows a difference in the kind of hardness measured, AH having had slight solution at the start of the  $A_{c1}$  range by the treatment given. None of the other tests with the pendulum were considered good. The schleroscope gave the same order of hardness as the time tests on the pendulum. With hardnesses of this order the schleroscope is unreliable and it is difficult to be sure of small variations in hardness.

The results of these experiments were thus negative, and it would evidently be necessary to devise a microscopical method of measuring the hardness of individual grains in order to reveal a difference between them and the hardness of the mass in brittle specimens. With such a method it would seem quite possible to tell whether a specimen was brittle or not without breaking it in a testing machine. The condition of an engineering casting or forging could thus be determined without resort to a separate test-piece which might or might not have the same condition as the main piece.

Similarly, if the remanence or the permeability and the Brinell hardness could be measured with accuracy the same end would be attained.

It is by no means unlikely that such methods may be evolved by future work.

THE SOLUBILITY OF CARBIDE IN FERRITE.

The successful detection of the physical changes involved in temper-brittleness pointed to the possibility of determining the effects of carbide solubility in any steel, whether susceptible to brittleness or not, and as this subject has for long been an outstanding one in the physical metallurgy of steel, it was decided to make use of the discoveries already made in order to attempt to place the whole matter on a more comprehensive and fundamental basis.

The investigation was thus extended with a view to determining the effect of various elements on the solubility of carbide in ferrite and to the determination of the form of the solubility curves in a wide range of steels.

A number of new steels were obtained and these were arranged in series so that the nickel, manganese, and chromium contents varied, the carbon content being kept approximately constant in each series. The analyses are shown in Table 13.

The steels marked with an asterisk were crucible steels. They were specially made for this research by Messrs. Kayser, Ellison and Co., Ltd., Sheffield, with the aid of a Grant from the Carnegie Trust for the Universities of Scotland. These steels were made as low as possible in undesired elements. The crucible steels in the nickel and the chromium series, therefore, were notably lower in manganese than the remainder, which were commercial steels. The latter were gifted to the author by Dr. M'Cance, Managing Director of the Clyde Alloy Steel Co., Ltd., Motherwell. Steels CN3 and CN5, although classed as nickel steels, contained small



quantities of chromium. The other nickel steels were entirely free from this element.

#### EXPERIMENTAL METHODS.

The experimental methods employed were substantially the same as previously described. A few details of the magnetic apparatus were modified to give greater accuracy of readings, particularly in low fields. The magnetic test-pieces were machined to a few thousandths of a centimetre more than formerly so as to give a very tight fit in the yoke. One or two of the earlier test-pieces were a little slack in the yoke and it was found difficult to get over the effects of this. If even a very slight air-gap exists the curve for  $B_{\max}$  is apt to be erroneous, but relative properties such as per cent. remanence and permeability are not affected.

#### ELIMINATION OF THE EFFECTS OF UNEQUAL SPHEROIDISATION.

It is very well <sup>known</sup> that large alterations in all the physical properties of quenched steels take place when these steels are tempered. At low temperatures these changes are due, in the main, to the breakdown of martensite and austenite, and at high temperatures to spheroidisation or coalescence of the finely divided carbide particles of the steel. These changes are so large that they completely obscure the minute but fundamentally important changes concerned in the solubility or deposition of carbide in the ferrite matrix of the steels.

In order to show up these small changes it is essential that changes due to other factors, chief of which in the ranges of temperature concerned in the present work is spheroidisation, should be entirely eliminated. Spheroidisation gives rise, as has

been shown , to a decrease in the specific volume, hardness and resistivity, which are the same effects as are produced by the deposition of carbide out of solid solution in ferrite.

In previously recorded work on the physical changes concerned in temper-brittleness a method of double heat-treatment was used in order to equalise tempering effects in the various specimens. As a result of this method of treatment the steels were obtained in the tough and brittle conditions after a total tempering time of the same, or nearly the same, duration for each specimen. In order to compare the properties of tough and brittle specimens this type of treatment was necessary, but for the purpose of the present part of the research the mechanical condition of the steels was not directly concerned, and the question arose whether a better method of eliminating the effects of unequal spheroidisation could not be evolved. The old method had been successful in showing the nature of the changes concerned in the temper-brittleness of nickel-chromium steels in which the solubility changes were relatively large, but there was a doubt as to whether these changes could be accepted as an accurate measure of solubility only. Also, as it was desired to determine solubility changes in steels in which they would be relatively much smaller, it was essential that complete elimination of changes due to spheroidisation should be achieved, if possible.

It has been shown that the effects of spheroidisation are increased as the temperature is raised, and that they are particularly noticeable in nickel and nickel-chromium steels above about 600°C. Any slight inequality in the treatment at high temperatures

might result in a small difference in the amount of spheroidisation in two specimens to which the same treatment had apparently been applied. It was thought that any such difference might be eliminated and the effects due to solubility only determined by first quenching the specimen from the temperature at which it was desired to measure the solubility and then retempering at a lower temperature sufficiently high to redeposit the carbide out of solid solution without bringing about any further spheroidisation.

To test this view a number of specimens which had been subjected to the old method of heat-treatment were treated at progressively rising temperatures. The steels used and the original treatments to which they had been subjected are shown in Table 14.

Specific volume specimens treated as shown were taken of steels AH, NC, and NR3 - that is, three steels in the final water-quenched tough condition - and also resistivity specimens of steel NR3, one each in the quenched tough condition, the intermediate slow-cooled condition, and the slow-cooled brittle condition. As shown in previous work, the water-quenched state contains carbon in solid solution in the ferrite, and both the slowly cooled states have the carbide deposited out of solution.

These six specimens were treated by tempering for one hour in vacuo at various temperatures from 400°C. up to 575°C., followed by slow cooling at the rate of 2°C. per minute after each treatment. The first part of the treatment would precipitate out any dissolved carbide if the temperature were high enough, but might also cause some re-solution. It was essential, therefore, to complete the treatment by slow-cooling, in order to allow any such

TABLE 13 Analyses of Steels.

Mark.	Carbon. %	Silicon. %	Sulphur. %	Phosphorus. %	Manganese. %	Nickel. %	Chromium. %
<i>Nickel Steels, 1st Series.</i>							
CN2	0.15	0.10	0.024	0.018	0.46	1.95	...
CN3	0.12	0.168	0.032	0.016	0.63	2.80	0.38
CN5	0.10	0.070	0.017	0.007	0.40	4.86	0.23
<i>Nickel Steels, 2nd Series.</i>							
3N	0.33	0.104	0.030	0.028	0.51	3.28	...
E92*	0.24	0.095	0.032	0.027	0.22	5.13	...
E331*	0.22	0.05	0.024	0.020	0.16	6.96	...
<i>Manganese Steels.</i>							
E	0.26	0.10	0.028	0.009	0.60	...	...
1M	0.32	0.205	0.034	0.048	1.01	...	...
E161*	0.27	0.18	0.016	0.018	1.96	...	...
<i>Chromium Steels.</i>							
2AX	0.31	0.13	0.032	0.031	0.74	...	1.00
E247*	0.20	0.05	0.022	0.024	0.14	...	1.85
E248*	0.22	0.08	0.014	0.023	0.10	...	2.80
E22*	0.21	0.10	0.032	0.024	0.185	...	3.88
E271*	0.295	0.12	0.016	0.021	0.08	...	5.54
<i>Nickel-Chromium Steels.</i>							
AH	0.31	0.310	0.021	0.015	0.47	4.46	1.41
NC	0.31	0.145	0.029	0.026	0.57	3.20	0.83
NR3	0.36	0.275	0.021	0.016	0.34	1.90	1.15
Armco iron	0.024	Nil	0.028	0.004	0.021	...	...

Steel.	Original Treatment.	First Tempering Treatment.	Second Tempering Treatment.
AH	O.-H. from 850° C.	T. 2 hr. at 660° C., slowly cooled at 0.3° C. per min.	W.T. 2 hr. at 660° C.
NC	O.-H. from 850° C.	T. 2 hr. at 660° C., slowly cooled at 0.3° C. per min.	W.T. 2 hr. at 660° C.
NR3	O.-H. from 850° C.	(1) T. 2 hr. at 660° C., slowly cooled at 0.3° C. per min. (2) W.T. 2 hr. at 660° C. (3) W.T. 2 hr. at 660° C.	W.T. 2 hr. at 660° C. T. 2 hr. at 660° C., S.C. at 2° C. per min. T. 2 hr. at 660° C., S.C. at 0.3° C. per min.

TABLE 14.

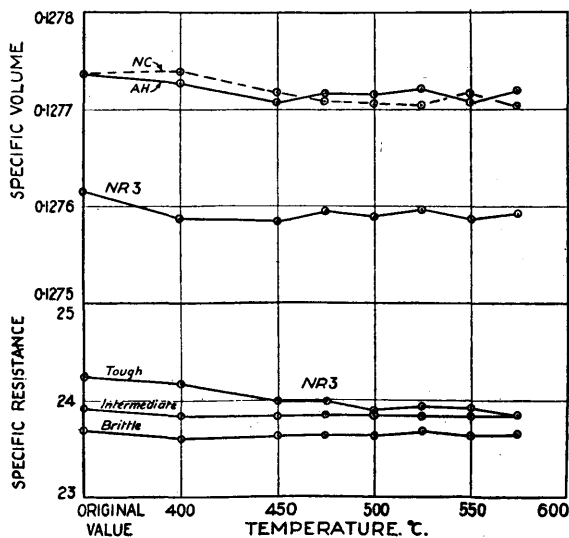


FIG. 21.—Re-tempering Curves of Nickel-Chromium Steels.

redissolved carbide to separate. The specific volume and the resistivity were determined after each treatment, and the results are plotted in Fig. 31.

The resistivity results of the three different conditions of steel NR3 show clearly that in the quenched tough condition the carbide is deposited out of solution gradually until at about 500°C. deposition is complete, whereas in the two slowly cooled conditions no change takes place, no carbide having been left in solid solution after the original treatments. It is clear, from the entire absence of any change in these latter specimens, that no extra-spheroidisation had taken place at any temperature up to 575°C. This is what one might expect, spheroidisation having been promoted to a large extent by the original high temperature treatments. The specific volume curves of the three steels in the quenched tough condition confirm the resistivity determinations, but it is evident that in the case of this property the inception of the brittle condition with rise in temperature prevents the full effect of deposition from being revealed. Thus specific volume and hardness results would give entirely erroneous results if used for the present object of estimating the changes due to solubility only.

As a result of the above experiments the following standard treatment was adopted for the treatment of the fourteen nickel, manganese, and chromium steels to determine the changes brought about by carbide solubility: Specimens of each steel were heated for one hour at the temperature at which it was desired to measure the solubility, and quenched in water; a second specimen of each steel, which had been treated along with the other, was retempered

at 500°C. for one hour and cooled in the furnace at a rate of 2°C. per minute. In later work to determine the solubility curves one specimen only was used for these two treatments in order to eliminate any possible variation in composition or soundness in different specimens, but the results throughout the research show that any such variation was negligible as far as its effect on the magnetic properties or resistivity was concerned, except, as will be seen later, in the case of two specimens of Armco iron.

### DETERMINATION OF THE COMMENCEMENT OF $Ac_1$ .

#### Thermal Analysis.

It was important, in the first instance, to determine for each steel the upper limit of the tempering zone, so that determinations after treatment in that zone could be accepted as referring only to carbide solubility in ferrite. To determine the start of  $Ac_1$ , thermal specimens of each steel were treated in vacuo as described later in this thesis at progressively rising temperature intervals of 5°C. followed, after each treatment, by inverse-rate cooling curves. In one or two cases it was found difficult to determine within 5°C. the exact commencement of  $Ac_1$ , owing to the small carbon contents of the steels. The temperatures recorded in Table 15 are those at which the first sign of a cooling point or range was noticed on the cooling curves, and in the few cases where any doubt existed the temperatures given are on the safe (low) side.

#### IZOD IMPACT EXPERIMENTS.

The seven new crucible steels were treated to obtain their Izod values in different conditions. The other steels were not

TABLE 15 - Thermal Determinations of the Commencement of  $A_{c1}$ .

Steel.	Commencement of $A_{c1}$ , °C.	Steel.	Commencement of $A_{c1}$ , °C.	Steel.	Commencement of $A_{c1}$ , °C.	Steel.	Commencement of $A_{c1}$ , °C.
CN2	700	3N	680	E	720	2AX	745
CN3	690 (or higher)	E92	660	1M	720	E247	770
CN5	675 (,, ,, )	E331	650	E161	710	E248	765
						E22	765
						E271	770

TABLE 16 - IZOD Impact Values and Brinell Hardness Numbers.

Steel.	Treatment.	Average IZOD Value. Ft.-lb.	Average Brinell Hardness Number.
E92	O.-H. 830° C., W.T. 660° C.	74.3	173
	,, ,, W.T. 660° C., re-T. 500° C.	92.9	178
	,, ,, T. 660° C., and S.C.	85.2	160
	O.-H. 850° C., W.T. 650° C.	79.1	167
	,, ,, W.T. 650° C., re-T. 500° C.	86.6	178
	,, ,, T. 650° C., and S.C.	82.3	178
	,, ,, W.T. 640° C.	85.7	181
	O.-H. 830° C., W.T. 610° C.	83.7	192
	,, ,, T. 610° C., and S.C.	83.8	187
	E331	O.-H. 830° C., W.T. 650° C.	53.4
,, ,, W.T. 650° C., re-T. 500° C.		88.4	191
,, ,, T. 650° C., and S.C.		78.4	197
O.-H. 850° C., W.T. 640° C.		67.8	203
,, ,, W.T. 640° C., re-T. 500° C.		77.3	195
,, ,, T. 640° C., and S.C.		58.4	211
,, ,, W.T. 630° C.		70.6	197
O.-H. 830° C., W.T. 600° C.		79.6	208
,, ,, T. 600° C., and S.C.		76.3	208
E161		O.-H. 900° C., W.T. 700° C.	64.7
	,, ,, W.T. 700° C., re-T. 500° C.	98.6	179
	,, ,, T. 700° C., and S.C.	61.3	174
	,, ,, W.T. 690° C.	97.0	184
	,, ,, W.T. 690° C., re-T. 500° C.	97.0	186
	,, ,, T. 690° C., and S.C.	85.7	180
	,, ,, W.T. 680° C.	97.0	194
	,, ,, W.T. 650° C.	91.3	207
	,, ,, T. 650° C., and S.C.	25.4	200
	E247	O.-H. 900° C., W.T. 750° C.	113.2
,, ,, W.T. 750° C., re-T. 500° C.		113.6	140
,, ,, T. 750° C., and S.C.		111.0	130
,, ,, W.T. 650° C.		105.2	178
,, ,, T. 650° C., and S.C.		105.7	153
E248	O.-H. 900° C., W.T. 750° C.	111.7	162
	,, ,, W.T. 750° C., re-T. 500° C.	108.3	163
	,, ,, T. 750° C., and S.C.	108.6	153
	,, ,, W.T. 650° C.	99.7	191
	,, ,, T. 650° C., and S.C.	98.7	188
E22	O.-H. 900° C., W.T. 750° C.	111.9	169
	,, ,, W.T. 750° C., re-T. 500° C.	106.0	171
	,, ,, T. 750° C., and S.C.	108.4	164
	,, ,, W.T. 650° C.	97.4	205
	,, ,, T. 650° C., and S.C.	50.0	206
E271	O.-H. 900° C., W.T. 750° C.	108.8	170
	,, ,, W.T. 750° C., re-T. 500° C.	93.2	205
	,, ,, T. 750° C., and S.C.	107.8	170
	,, ,, W.T. 650° C.	88.7	219
	,, ,, T. 650° C., and S.C.	22.3	240

S.C. = slowly cooled at a rate of 1° C. per 3 min. below 600° C. After the treatments at 500° C. the steels were also cooled slowly in the furnace.

available in a form suitable for Izod impact test-pieces, and, in any case, being of usual commercial composition, were not of the same interest in this connection, since many researches have included impact tests of such steels.

Bars of each steel were heat-treated in various ways and then machined to standard 1 cm. square, 3 V-notch Izod impact test-pieces. The Izod values and the hardness near to each fracture were determined. Details of the treatments and results are shown in Table 16. Treatments corresponding to those used for the physical tests were included and also treatments from two or more temperatures to show the tough Izod values and the susceptibility, if any, to brittleness.

It will be seen from the results that in the manganese and nickel steels the start of  $Ac_1$  might be judged as slightly lower than the temperatures determined by the thermal method, Table 15, if a small drop in Izod value be accepted as showing the formation of some  $\gamma$ -iron solid solution. The 2 per cent. manganese steel (E161) and the 4 and 5.5 per cent. chromium steels (E22 and E271) show a decided development of impact-brittleness when slowly cooled from 650°C., but not when cooled from higher temperatures.

#### DETERMINATION OF THE EFFECTS OF MAXIMUM CARBIDE SOLUBILITY IN FERRITE.

Bars of suitable length of each steel were treated by the standard method described above at temperatures near to the start of  $Ac_1$  in order to find the maximum solubility of carbide in ferrite. It was thought advisable, to start with, to magnify the vary small changes as much as possible in case they were so small as to be



difficult to detect in some of the steels. Later, as will be shown, it was found quite possible to determine such changes in all the steels at much lower temperatures.

The heat treatments were carried out in a large electric tube-furnace wound over a length of 2 feet to give as even a temperature as possible over the middle 27 cm. in which the bars were treated. Tests of the variation of temperature along the length of the magnetic bars (27 cm.) showed that the temperature dropped 7°C. from the centre to the extreme end. Most of this drop was in the last 5 cm. or so of the ends, and the resistivity bars (9 cm.) at the middle were within a few degrees of the maximum soaking temperature at all points. The thermocouple junction was embedded in a small specimen of Armco iron in the middle of the tube, and the bars were placed over and around this specimen. Several dummy bars were added to the charge, as it was found that they helped in the even distribution of heat from end to end. The variation of temperature from centre to end was thus probably reduced to at least half that recorded above. The furnace temperature was raised extremely slowly in order to avoid overstepping the desired temperature in the treatments near to  $A_{c_1}$ .

After treatment the bars were machined to the necessary size, 1 cm. diam. by 27 cm. length for the magnetic tests, and 3 mm. diam. by 9 cm. length for the resistivity. Subsequent treatments were carried out in vacuo in a porcelain tube placed through the large tube of the same furnace. A small fused-silica tube-furnace was used for the later work on the resistivity specimens for the solubility curves.

Magnetic cyclic curves for a maximum field strength of  $H = 150$  c.g.s. units and also the variation of induction and remanence from  $H = 0$  to  $H = 250$  were determined. From the readings observed all the magnetic characteristics were obtained by calculation and graphical work.

Table 17 shows details of the heat treatments, a summary of the magnetic properties taken from the drawn curves, and values for other physical properties.

The nature of the changes is in all cases the same as had been found previously in nickel-chromium steels. Solution of carbide in ferrite is shown up particularly by pronounced decreases in remanence and in permeability. The maximum induction is also lowered and the coercive force raised slightly on solution, as a general rule. It will be seen that in some cases the magnetic changes are as large as, or even larger than, those found earlier in nickel-chromium steels. Many of the steels used in this portion of the work are not susceptible to temper-brittleness, and yet show as large changes as highly susceptible steels do. The magnetic changes are therefore not an indication of temper-brittleness. As has been previously noted, this was suspected from a perusal of magnetic work on steels by other investigators. It is also certain that, when comparing widely different classes of steels, variations of magnetic properties are not proportional to the amount of carbon concerned in the physical changes. It is likely, however, that in steels of the same class, that is, where small variations of composition only are concerned, the changes are practically proportional to the amount of carbon concerned.

TABLE 17 -Magnetic Properties, Specific Resistance, Specific Volume, and Brinell Hardness.

Steel.	Specimen.	Treatment. °C.	Magnetic Properties.					Specific Resistance at 20° C. Microhms per cu. cm.	Specific Volume.	Brinell Hardness No.
			From Cyclic Curves for $H = 150$ .			Between $H = 0$ and $H = 250$ .				
			$B$ .	$B_{rem}$ .	$H_c$ .	$B_{rem}$ . % Max.	$\mu_{max}$ .			
CN2	a	O.-H. 850 W.T. 690	18,560	10,950	9.0	77.5	675	21.19	0.127399	163.0
	b	O.-H. 850 W.T. 690 re-T. 500	18,700	14,120	8.3	86.2	942	20.93	0.127412	159.0
	b	re-W.T. 685	18,400	8,900	6.0	70.2	843	...	...	...
CN3	a	O.-H. 850 W.T. 680	18,500	11,800	9.4	76.2	675	24.09	0.127413	182.0
	b	O.-H. 850 W.T. 680 re-T. 500	18,600	15,000	8.6	89.7	955	23.58	0.127441	176.0
	b	re-W.T. 670	18,430	12,080	8.8	84.3	760	...	...	...
CN5	a	O.-H. 850 W.T. 670	17,420	11,600	12.0	74.0	505	25.87	0.127262	194.0
	b	O.-H. 850 W.T. 670 re-T. 500	19,200	15,100	9.0	87.3	920	24.78	0.127280	169.0
	b	re-W.T. 660	17,330	10,400	9.4	74.8	585	...	...	...
3N	a	O.-H. 830 W.T. 670	17,800	13,210	13.8	80.5	509	24.17	0.127394	222.0
	b	O.-H. 830 W.T. 670 re-T. 500	18,700	15,650	12.0	92.0	770	23.50	0.127360	215.0
	b	re-W.T. 660	18,430	14,300	12.0	85.5	650	...	...	...
E92	a	O.-H. 830 W.T. 660	16,880	11,300	12.2	72.6	470	24.88	0.127491	180.0
	b	O.-H. 830 W.T. 660 re-T. 500	18,980	15,500	10.2	91.0	945	23.91	0.127319	175.0
	b	re-W.T. 650	17,980	11,850	10.3	78.0	630	...	...	...
E331	a	O.-H. 830 W.T. 650	14,640	9,350	14.0	67.0	320	26.56	0.126837	197.5
	b	O.-H. 830 W.T. 650 re-T. 500	18,350	14,570	11.8	87.0	760	25.54	0.127102	193.0
	b	re-W.T. 640	14,250	8,300	13.0	63.5	325	...	...	...
E	a	O.-H. 900 W.T. 710	17,920	9,840	9.4	76.1	530	16.18	0.127372	158.0
	b	O.-H. 900 W.T. 710 re-T. 500	18,100	12,920	9.2	83.0	745	16.10	0.127364	141.0
	b	re-W.T. 700 S.C. from 575	17,780 17,800	9,950 13,800	9.7 10.0	78.6 83.0	585 770	... ...	... ...	... ...
1M	a	O.-H. 900 W.T. 710	17,850	11,710	11.3	80.0	545	19.80	0.127586	182.0
	b	O.-H. 900 W.T. 710 re-T. 500	17,920	14,920	10.7	90.0	735	19.81	0.127586	177.0
	b	re-W.T. 700 S.C. from 575	17,600 17,635	12,400 14,870	10.8 11.0	85.6 91.0	560 735	... ...	... ...	... ...

TABLE 17 (continued).

Steel.	Specimen.	Treatment. ° C.	Magnetic Properties.					Specific Resistance at 20° C. Microhms per cu. cm.	Specific Volume.	Brinell Hardness No.
			From Cyclic Curves for $H = 150$ .			Between $H = 0$ and $H = 250$ .				
			$B$ .	$B_{rem}$ .	$H_c$ .	$B_{rem}$ . % Max.	$\mu_{max}$ .			
E161	a	O.-H. 900 W.T. 700	17,050	11,400	13.0	77.5	435	23.14	0.127563	181.5
			b	O.-H. 900 W.T. 700 re-T. 500	17,625	14,730	12.0	90.2	664	22.82
	re-W.T. 690 S.C. from 575	17,400			12,000	11.5	82.6	545	...	...
		W.T. 500 W.T. 575		17,680	14,800	11.0	90.0	690	...	...
				17,680	12,830	11.3	88.0	628	...	...
		17,600	12,100	11.3	86.0	580	...	...	...	
24X	a	O.-H. 900 W.T. 735	17,040	12,400	17.0	78.6	365	20.52	0.127627	198.0
			b	O.-H. 900 W.T. 735 re-T. 500	17,800	14,900	14.8	88.6	560	20.18
	re-W.T. 725	17,400			12,500	14.9	84.8	450	...	...
E247	a	O.-H. 900 W.T. 750	17,880	10,450	10.0	77.2	535	18.65	0.127568	142.5
			b	O.-H. 900 W.T. 750 re-T. 500	18,000	12,870	9.8	84.6	698	19.09
	re-W.T. 650	17,800			10,400	9.8	82.2	576	...	...
E248	a	O.-H. 900 W.T. 750	17,810	10,975	12.1	79.0	465	22.15	0.127822	163.0
			b	O.-H. 900 W.T. 750 re-T. 500	17,810	13,430	11.6	86.9	615	22.09
	re-W.T. 650	17,730			11,400	11.2	85.3	540	...	...
E22	a	O.-H. 900 W.T. 750	17,780	10,920	12.5	81.0	455	26.23	0.128033	157.5
			b	O.-H. 900 W.T. 750 re-T. 500	17,780	12,850	11.3	86.0	585	26.46
	re-W.T. 650	17,660			10,750	11.3	83.0	520	...	...
E271	a	O.-H. 900 W.T. 750	17,300	11,330	13.0	81.4	435	31.18	0.128401	168.5
			b	O.-H. 900 W.T. 750 re-T. 500	17,320	12,780	12.4	86.5	535	31.47
	S.C. 575	16,970			10,450	12.3	83.1	473	...	...
		17,400	12,700	12.0	87.0	535	...	...	...	
Armco iron	a	O.-H. 950 W.T. 710	...	...	...	...	...	11.50	0.127298	173.0
			b	O.-H. 950 W.T. 710 re-T. 500	...	...	...	...	...	11.29

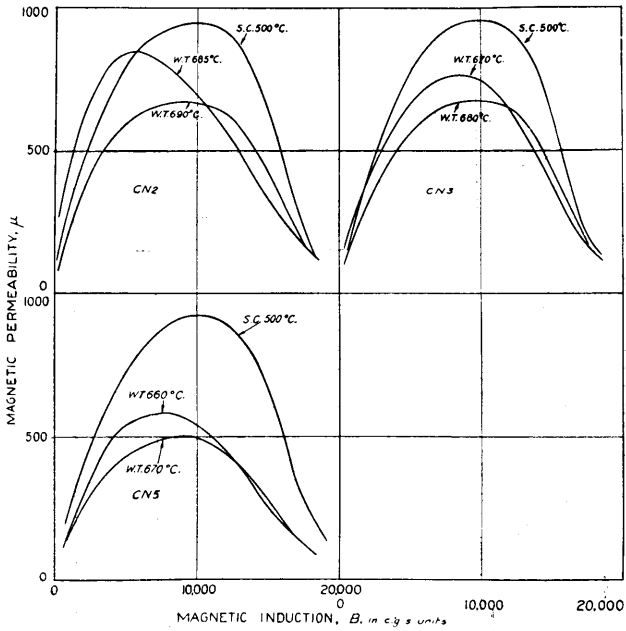


Fig. 32.—First Nickel Series.

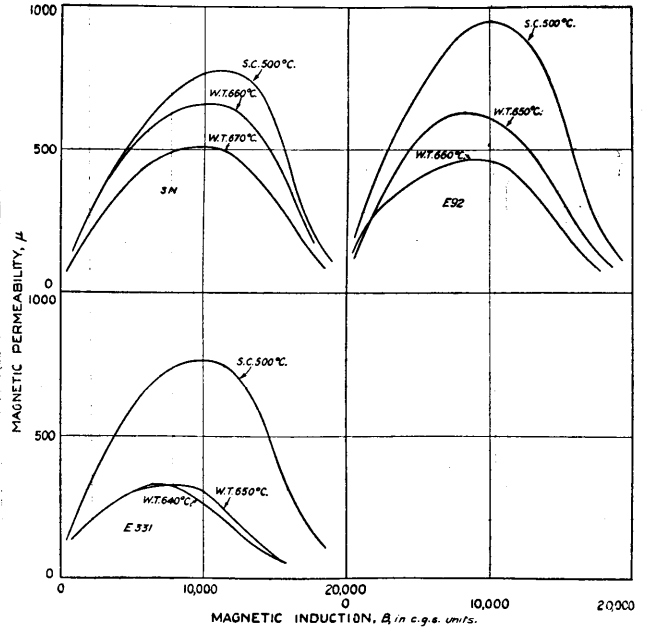


Fig. 33.—Second Nickel Series.

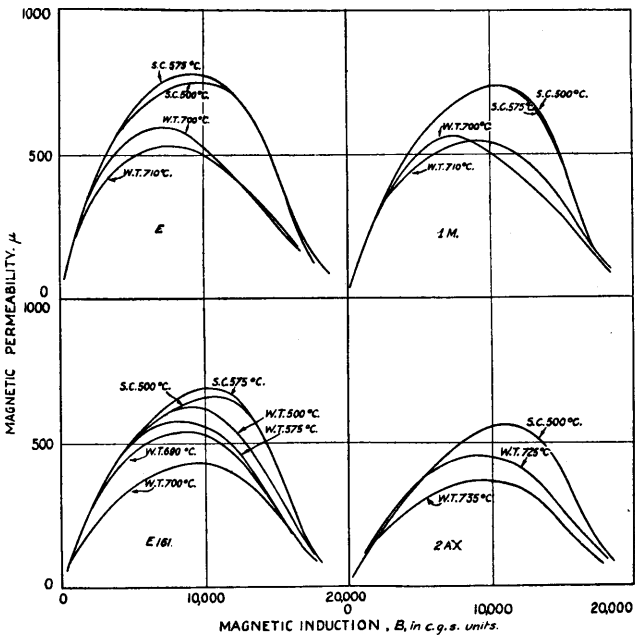


Fig. 34.—Manganese Series, and one Chromium Steel.

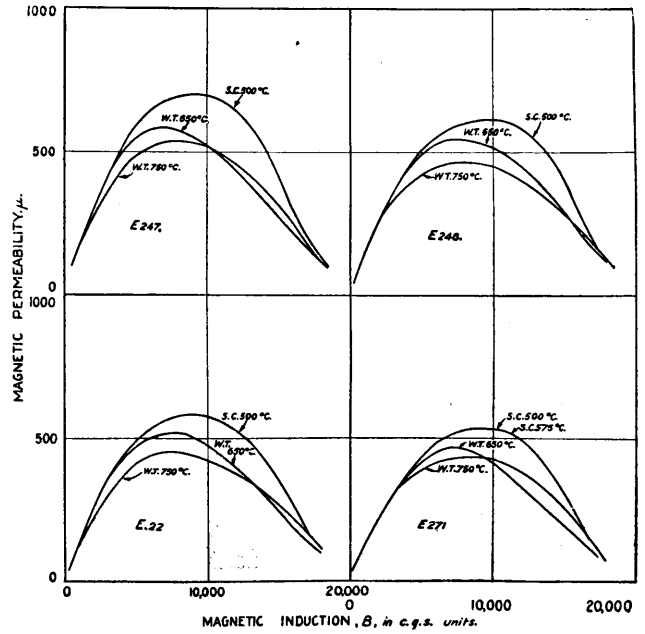


Fig. 35.—Chromium Series.

The properties which might be expected to give the best indication of the purity of the ferrite are the permeability and the remanence. The latter property should be taken, not at its actual value, but as a percentage of the induction remaining on the withdrawal of the magnetising force.

The variation in permeability is fully illustrated in Figs. 32, 33, 34, and 35. The percentage remanence varies in a somewhat similar way, and the graphs are not reproduced. The maximum values of the latter property are shown in Table 17.

The difference produced in the purity of the ferrite is indicated by the difference between the values for these properties. The difference between the maximum values of the permeability and the percentage remanence in the conditions representing maximum and minimum carbide solubility are plotted against percentage of the special element in each series in Figs. 36, 37, and 38. The smallest difference between the properties after quenching from a high temperature and after tempering at  $500^{\circ}\text{C}$ . is plotted for each steel. The smallest difference was taken, as some of the higher temperature treatments may have touched the  $\text{Ac}_1$  range. In the chromium series, however, which was treated at  $650^{\circ}\text{C}$ . as well as at  $750^{\circ}\text{C}$ ., curves for both these temperatures are shown.

In the case of the nickel steels (Fig. 36), an increase in nickel increases the difference in both properties, thus indicating a rise in solubility at high temperatures with increase in nickel. When chromium is present in the nickel steels the permeability changes are slightly increased. With manganese (Fig. 37), the change is indefinite, and may be taken as indicating a constant

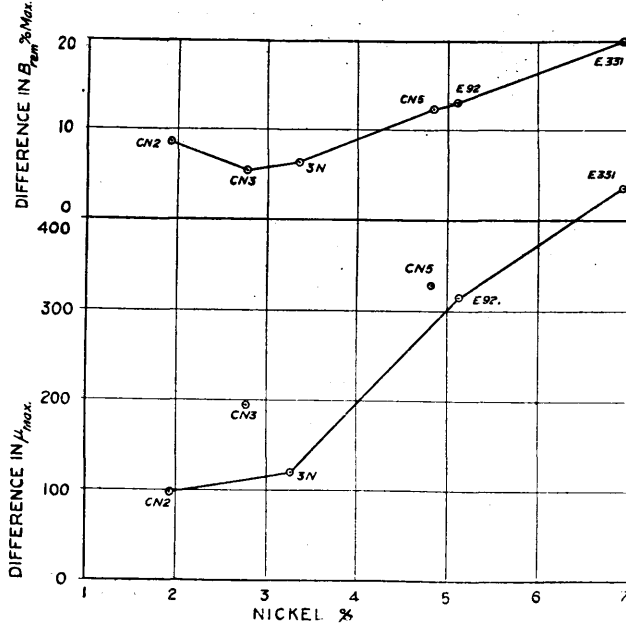


FIG. 36.

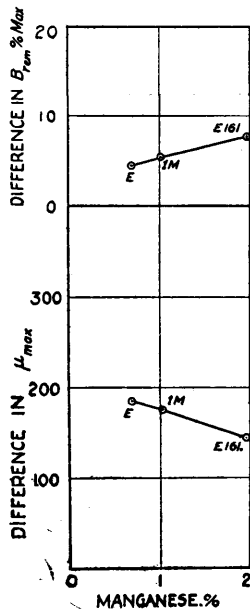


FIG. 37.

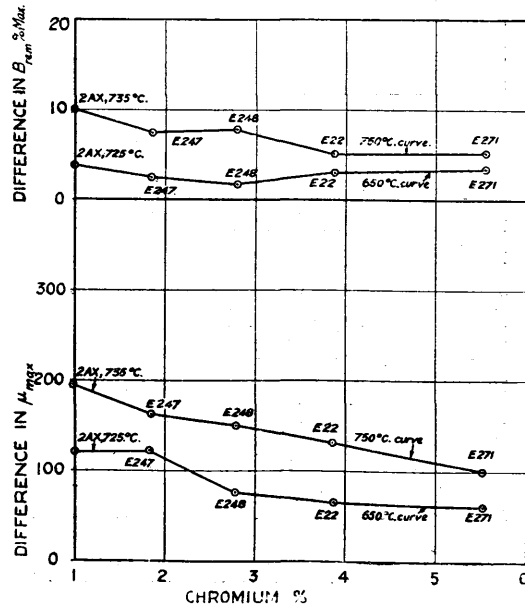


FIG. 38.

TABLE 18 - Specific Resistances at 20° C.

Steel.	Specimen a. O.-H. 900° C., W.T. 750° C. Specific Resistance. Microhms per cu. cm.	Specimen b. O.-H. 900° C., W.T. 750° C.; re-T. 500° C. Specific Resistance. Microhms per cu. cm.	Difference. Microhms per cu. cm.	Specimen a, re-T. 500° C. Specific Resistance. Microhms per cu. cm.	Difference. Microhms per cu. cm.
E247	18.65	19.09	+ 0.44	18.70	+ 0.05
E248	22.15	22.09	- 0.06	22.10	- 0.05
E22	26.23	26.46	+ 0.23	26.26	+ 0.03
E271	31.18	31.47	+ 0.29	31.12	- 0.06

value. The chromium series (Fig. 38) gives a definite decrease with rise in chromium, the solubility falling by half from 1 per cent. to 5.5 per cent. chromium. At 650°C., the solubility in chromium steels varies in the same way, and is evidently about half what it is at 750°C. Evidently the carbon which is in combination with chromium in the (21) the mixed carbide of chromium steels is less soluble than the carbon of iron carbide in pure  $\alpha$ -ferrite.

The changes in resistivity in Table 17 will be found to be nearly proportional to the magnetic properties plotted in Figs. 36, 37, and 38. In the four chromium steels there appeared discrepancies in the resistivities. That this was due to some difference between the two specimens of each steel was proved by re-treating the quenched specimens at 500°C., with the results shown in Table 18. Any difference in resistivity due to solubility falls within the experimental error, as one would expect from a comparison of the magnetic changes with those of the other steels.

#### DETERMINATION OF THE SOLUBILITY CURVES.

Having found that the purity of the ferrite in the condition of maximum and minimum solubility was easily detectable by the methods used, it next became desirable to determine the solubility at all temperatures and so draw the solubility curves. Magnetic tests have been shown to be more sensitive to small changes than is the resistivity, but it is evident that there is not a proportionality between the amount of dissolved carbon and the magnetic changes produced. The resistivity did not seem to have this defect and although less sensitive to small changes it was clear from the results already referred to that, except in the chromium series,



TABLE 19.

SPECIFIC RESISTANCES at 20°C. in Microhms per cu. cm.

<u>Steel.</u>	<u>Treatment, °C.</u>	<u>Sp. Resist.</u>	<u>re-T. 500°C.S.C.</u> <u>Sp. Resist.</u>	<u>re-T. 550°C.S.C.</u> <u>Sp. Resist.</u>
CN2	W.T. 685	21.24	21.11	21.16
CN3	W.T. 670	23.70	23.50	23.44
CN5	W.T. 660	25.17	24.88	24.83
3N	W.T. 660	23.68	23.52	23.39
E92	W.T. 650	24.37	23.67	23.67
E331	W.T. 640	27.07	25.62	25.60
E	W.T. 700	15.99	16.00	15.91
1M	W.T. 700	19.63	19.63	19.51
E161	W.T. 690	22.75	22.48	22.43
2Ax	W.T. 725	20.17	20.15	19.99
E247	W.T. 650	18.88	18.92	18.76
E248	W.T. 650	22.13	22.03	21.95
E22	W.T. 650	26.41	26.40	26.50
E271	W.T. 650	31.33	31.39	31.38

W.T. = Water Tempered.

S.C. = Slowly Cooled at 2°C./min.

TABLE. 20.

SPECIFIC RESISTANCES at 20°C. in Microhms per cu. cm.

<u>Steel.</u>	<u>Treatment, °C.</u>	<u>Original</u> <u>Sp. Resist.</u>	<u>re-T500, SC</u> <u>Sp. Resist.</u>	<u>re-T525, SC</u> <u>Sp. Resist.</u>	<u>re-T550, SC</u> <u>Sp. Resist.</u>
CN2	OH850 WT640	20.79	20.71	20.72	20.70
CN3	OH850 WT640	23.57	23.53	23.40	23.41
CN5	OH850 WT640	25.12	25.03	25.06	24.97
3N	OH850 WT640	23.81	23.62	23.68	23.64
E92	OH850 WT640	24.24	23.93	23.92	23.94
E331	OH830 WT640	26.63	25.74	25.71	25.80
E	OH900 WT640	15.83	15.80	15.85	15.82
1M	OH900 WT640	19.45	19.36	19.36	19.41
E161	OH900 WT640	22.28	22.21	22.06	21.99
2AX	OH900 WT640	20.55	20.59	20.54	20.43
E247	OH900 WT640	19.38	19.37	19.49	19.47
E248	OH900 WT640	22.76	22.66	22.72	22.68
E22	OH900 WT640	26.42	26.47	26.43	26.36
E271	OH900 WT640	31.23	31.36	31.24	31.32
AH	OH850 WT640	32.63	32.16	31.98	32.06
NC	OH850 WT640	31.39	30.97	30.78	30.72
NR3	OH850 WT640	25.10	24.79	24.79	24.63
Armco Iron	OH950 WT640	11.43	11.22	11.17	11.18

OH = Oil-Hardened, WT = Water Tempered, SC = Slowly Cooled at 2°C/m.

the changes were sufficiently large to be revealed by this method. Magnetic tests could be used to clear up any doubtful points.

First of all, similar treatments to those recorded for nickel-chromium steels in Fig. 31 were applied to all the other steels after quenching from various temperatures. It was found from the results (Tables 19 and 20) that the resistance decreased slightly between the 500°C. and the 525°C. treatments in a few cases thereafter remaining constant. This was probably due to the quicker heating-up of the small furnace used for this work, giving a smaller actual period of heating than in the large furnace used in earlier experiments. In subsequent work a re-treatment temperature of 525°C. was used in order to be sure that complete separation had taken place in all cases.

To determine the solubility curves the steels were treated at temperatures rising from 500°C., where the solubility was found to be small, up to near the  $A_{c1}$  range by steps of 25°C. or 20°C., by the same method of treatment and re-treatment as had been adopted in earlier experiments. At temperatures below 600°C. no re-tempering treatments were carried out in the majority of cases as it had been found that no extra-spheroidisation takes place at these temperatures, but above 600°C., in all cases, re-tempering and re-determination were carried out. One specimen only of each steel was used throughout. The difference between the quenched value at any temperature and the retreatment value gives a measure of solubility effect entirely free from any other tempering effects, and in Figs. 39, 40, 41, 43, and 44, where the form of the solubility curves for each steel is shown, a correction has been made, in cases in



which it was necessary, for extra-tempering effects as found by the experimental values in Tables 17, 19, 20, and 21. The full line curves in Figs. 39, 40, 41, 43, and 44 thus show the effects of solubility only, entirely free from other tempering effects or variation in homogeneity or composition.

Figs. 39 to 44 also show ordinary tempering curves for each steel obtained by oil-quenching the specimens and tempering at progressively rising temperatures, followed by quenching from each temperature and determination of the resistivity. A different specimen to that used for the solubility curves was used for each steel in this series of experiments.

The solubility curves for the chromium series were not determined by the resistivity method, as it had been found (Tables 17 and 18) that the maximum changes produced in the resistivity were so small as to be within the experimental error. The magnetic data for these steels show clearly the magnitude of the changes in them in relation to the changes in the other steels.

The values at high tempering temperatures for the increase in resistivity on the solubility curves give a general confirmation of the earlier magnetic determinations for these temperatures.

The curve for Armco iron (Fig. 44) shows that the resistivity differences are greater in it than in the manganese steels (Fig. 41) indicating a greater solubility of carbide in Armco iron. This is in accordance with microscopical observations by Whiteley<sup>(18)</sup>. The changes in the other steels are also, at the lower tempering temperatures, in general, smaller than those of Armco iron, except in the nickel-chromium steels (Fig. 43). The presence of 3 to 5.5

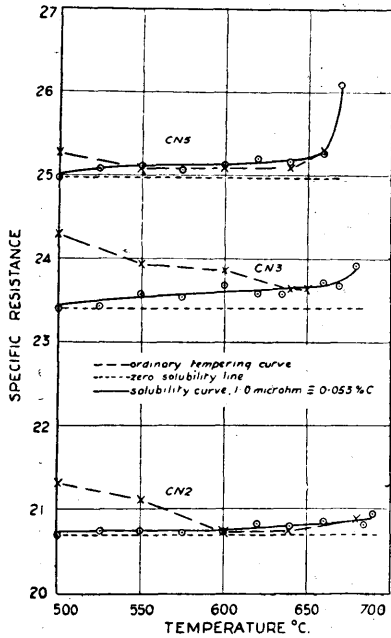


FIG. 39.—First Nickel Series.

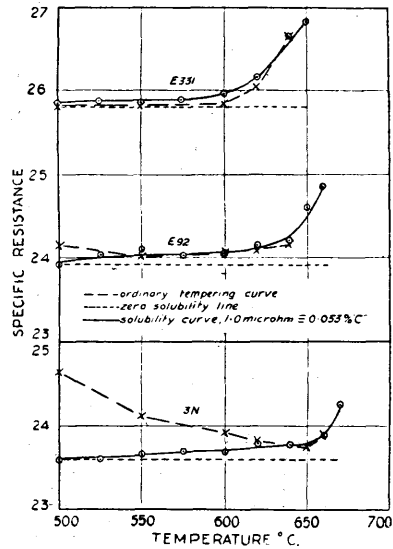


FIG. 40.—Second Nickel Series.

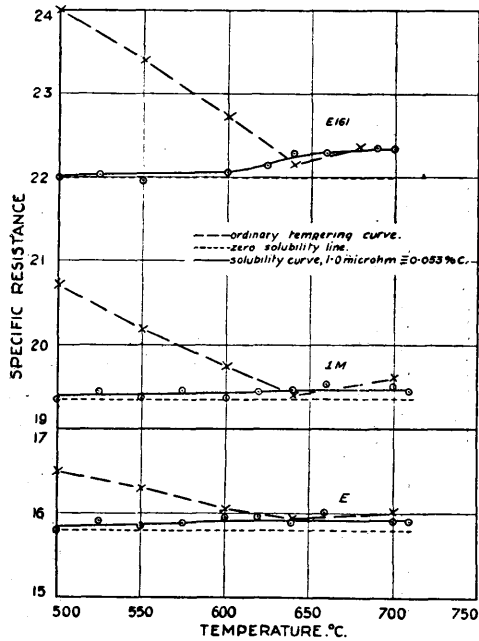


FIG. 41.—Manganese Series.

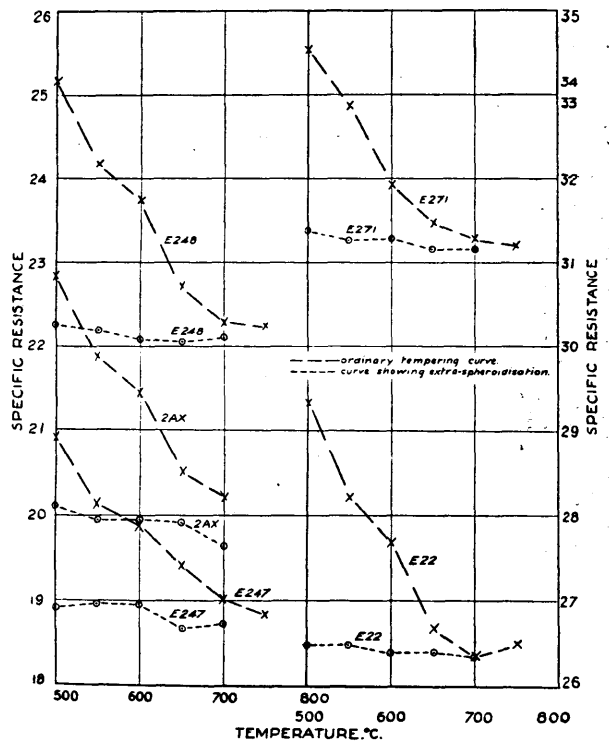


FIG. 42.—Chromium Series.

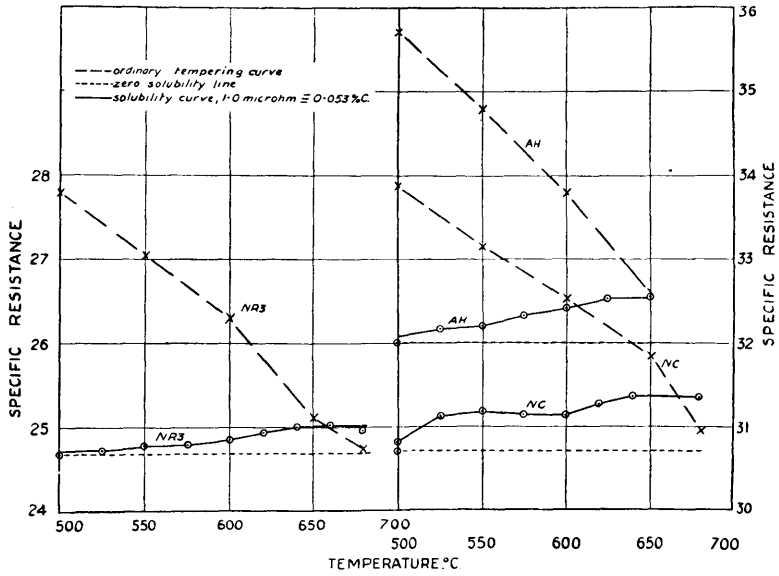


Fig. 43.—Nickel-Chromium Series.

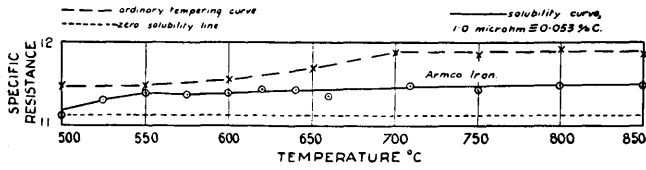


Fig. 44.

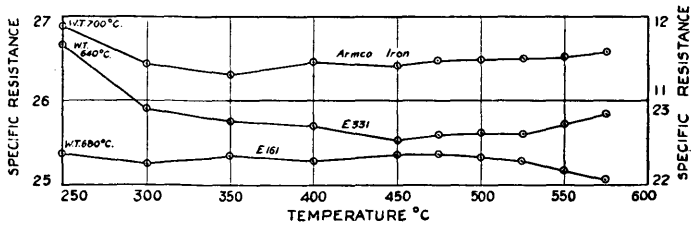


Fig. 45.

per cent. of nickel to the ferrite considerably increases the solubility of the mixed carbide of chromium and iron at normal temperatures.

The fall in solubility with decreasing temperature in the normal tempering range is much greater in the nickel-chromium steels than in the others. These steels develop impact-brittleness, as has been seen, to a very marked degree. The sharp fall in solubility on cooling from the usual temperatures of 600°C. to 650°C. down to 500°C. will allow of readier separation at the grain boundaries than in the case of the other steels. The physical nature of the carbide also appears to be an important factor in the production of brittleness. In the chromium series it has been found (Table 16) that brittleness is developed as the chromium content is raised, although the solubility changes are relatively smaller than in the others. However, when the solubility of carbide containing chromium is greater, as in the nickel-chromium steels, a much greater degree of brittleness is produced.

#### STABILITY OF THE FERRITE SOLID SOLUTIONS.

A series of experiments was carried out to determine more fully the stabilities of ferrite solid solutions other than nickel-chromium, which had already been investigated (Fig. 31). Specimens of 2 per cent. manganese steel, 7 per cent. nickel steel, and Armco iron were, after quenching from a high tempering temperature, re-tempered at progressively rising temperatures, with the results shown in Fig. 45. The specimens were heated for 1 hour at each temperature and quenched in water.



The Armco iron solid solution is seen to be the least stable having completely broken down at 350°C. At higher temperatures progressive re-solution takes place. The nickel solution does not reach its lowest value until 450°C., which is, however, lower than the temperature for the nickel-chromium steels, (Fig 31). Deposition in the manganese steel apparently still continued up to 575°C. This cast doubt on the extent of the changes already determined in these steels when using re-treatment temperatures of 500°C. or 525°C., and a number of extra experiments were carried out to find the full effect of carbide deposition in the three steels containing manganese. It will be seen from results in Table 17 and in Fig. 34 that deposition in these steels had, in fact, been almost complete at 500°C., after treatment in the large furnace. The resistivity results in the other experiments with the 2 per cent. manganese steel showed in some cases values not apparently in strict accordance with the magnetic values, and indicated a greater solubility by the resistance method than by the magnetic. This apparent anomaly is probably due to a modification in the nature of the carbide by addition of manganese.

The results of these latter experiments suggested that the chromium series might not have been re-heated to a sufficiently high temperature for complete deposition in the original experiments. The curves shown with small dots in Fig. 42 were obtained as a result of continuing the re-treatment of these steels to higher temperatures, the specimens being water-quenched from each temperature except 700°C. from which they were slowly cooled. The resistivity was found to fall almost continuously as the temperature was

raised. That this was due to extra-spheroidisation only was proved by re-treating steel E271 at 575°C. and cooling slowly in the furnace. The results of magnetic tests (Table 17 and Fig. 35) show that the magnetic properties were practically identical in every respect with those obtained after the original 500°C. treatment. The treatments for this series at 500°C. are therefore taken to represent the greatest possible deposition of carbide in the chromium steels. These results also show that although extra-spheroidisation is revealed by resistivity determinations and is particularly marked in chromium steels, it is not, as a rule, apparent in the magnetic properties, a fact which is supported by many other results.

In regard to the ordinary tempering curves (the dotted curves in Figs. 39 to 44) the resistivity is seen to decrease in each series approximately in proportion to the carbon content of the steels. The total decrease is much greater in the chromium and nickel-chromium steels, and this is probably due to a modification by chromium of the physical nature of the carbides in these steels. The evidence of these experiments might suggest that the amount of solubility had no connection with spheroidisation, yet when past specific volume results (Figs. 2, 3, 4, and 5) <sup>are compared</sup> with the solubility determinations above it is seen that a rapid decrease in specific volume is associated with a more or less rapid increase in solubility at high tempering temperatures in nickel and nickel-chromium steels.

ESTIMATION OF THE AMOUNT OF CARBON INVOLVED IN THE PHYSICAL CHANGES.

A review of the variations in all the physical properties shows that in the fundamental properties of resistivity and specific volume the relative variations are proportional, even when widely different classes of material are compared. Thus, in specific volume the change in Armco iron (Table 17) is in the same proportion to the changes in the nickel-chromium steels (Table 10) as is the change in resistivity of the former (Fig. 44) to the changes in the latter (Fig. 43). A similar proportionality is apparent throughout the other steels in almost all cases. For example, the changes in specific volume are greater for Armco iron and the nickel-chromium steels than for the other steels, the same being true for the resistivity changes. Also the changes in specific volume, resistivity, and magnetic properties are all smaller in the chromium series than in any of the others.

It appears certain that the carbon atoms in solid solution will be in the same form in every case, whatever may be their position in the space-lattice. The fundamental properties would therefore be influenced in proportion to the amount of carbon in solid solution. Consequently, to estimate the percentage of carbon corresponding to the physical changes, it is only necessary to know the percentage of carbon giving rise to the physical changes in one case; if this be known, then the carbon percentage in all the other steels can be calculated.

The experiments with Armco iron were continued up to 850°C. as shown in Fig. 44, and it was found that the resistivity of

quenched specimens reached a constant maximum value above 700°C. This is taken to mean that all the carbon remains dissolved in the ferrite after quenching from a high temperature. The carbon contents of the actual resistivity test-pieces of Armco iron were determined and found to be 0.023 and 0.025 per cent., the larger value being that of the specimen showing a slightly larger change in resistivity. The average carbon content, 0.024 per cent., corresponds to an average change in resistivity of 0.45 microhm per cu. cm.

The percentage solubility of carbon can thus be measured on the resistivity graphs at any temperature in any of the steels, a change of 1.0 microhm being equal to a solubility of 0.053 per cent of carbon. The percentages of the chromium series can be estimated by a comparison of their magnetic changes with those of the other steels. The magnetic effects were determined at 650°C. and 750°C. in the chromium series, and the solubility being known to be very small at 500°C. the course of the solubility curves in each steel can be calculated from the data.

The maximum solubility in the nickel steels is uncertain owing to the difficulty of being sure of the temperature at which the first trace of eutectoid solution is formed.

The high value to which the percentage remanence rises after slow-cooling shows that almost the whole of the carbide has separated out of solid solution, and certainly if any is left in solution it is only a small proportion of that which gives rise to the physical changes at high tempering temperatures. Observations

by Whiteley,<sup>(18)</sup> Yensen,<sup>(22)</sup> and Yamada<sup>(23)</sup> point towards zero solubility in slow cooled ferrite.

The possibility that all the carbon which is in solution at a high tempering temperature is not retained by quenching seems to be discountenanced by the consistency of the results for quenched specimens throughout the investigation, the results being notably different in this respect from those obtained by quenching steels from the  $\gamma$ -region.

Although pearlite has been found to be absent in annealed steels containing 0.06 per cent. of carbon (Sauveur and Krivobok<sup>(24)</sup> 0.05 per cent. (Hatfield and others<sup>(25)</sup>), 0.04 per cent. (Bramley and Haywood<sup>(26)</sup>), 0.03 per cent. (Scott<sup>(27)</sup>), it appears that the carbon in these steels cannot be in solid solution in the ferrite.

The estimations of Whiteley (0.03 per cent.<sup>(18)</sup>), and of Tamura (0.034 per cent.<sup>(28)</sup>) may well be correct for the solubility of carbon in pure  $\alpha$ -iron at about 700°C. The value for pure iron could be exactly determined on a series of pure alloys by the methods used in the present research.

The impurities in steels no doubt account for the smaller carbide solubility at most temperatures when compared with pure iron. Metallic special elements added to steels have, however, undoubtedly a pronounced effect.

Summarising the above work on the solubility of carbide in ferrite the following points may be emphasised:

(1) The impurities present in steels reduce the solubility when compared with pure iron.

(2) Small percentages of nickel in the ferrite increase slightly the solubility of iron carbide.

(3) Manganese has probably a slightly increasing effect on the solubility.

(4) Chromium, which replaces iron in the carbide, definitely decreases the solubility when no other special elements are present.

(5) The presence of nickel and chromium together increases considerably the solubility when compared with ordinary steels.

(6) The stability of the various solid solutions varies considerably, pure iron being the least stable, nickel increasing the stability, chromium giving an even greater stabilising effect than nickel, and the exact position of manganese being a little doubtful, but certainly raising the stability greatly when compared with pure iron.

### The $A_{c1}$ Range.

It has been noted by Brayshaw,<sup>(29)</sup> Brearley,<sup>(30)</sup> Jones,<sup>(31)</sup> and Greaves<sup>(32)</sup> that partial hardening of certain special steels is brought about by tempering at temperatures considerably below the normal  $A_{c1}$  maximum (as obtained on a thermal curve), followed by quenching in water. Carpenter, Hadfield, and Longmuir<sup>(33)</sup> drew attention to the fact that in thermal heating curves of nickel steels the  $A_{c1}$  change was revealed by an absorption of heat over a range of temperature commencing well below the  $A_{c1}$  maximum. Jones,<sup>(34)</sup> from thermal and microscopical work on this subject, showed clearly that in many alloy steels  $A_{c1}$  takes place over a considerable range of temperature. He explained this as being due to selective solution of isomorphous carbides present in alloy steels.

The present investigation was extended to throw some light on the extent of, and the reactions involved in, the  $A_{c1}$  range.

### SPECIFIC VOLUME DETERMINATIONS.

Experimental method. Suitable specimens of the steels, of about 25 gm. weight, were heat-treated in vacuo in a wire-wound electric furnace. In the earlier experiments a thick vitreous silica tube was used; selected tubes of this material kept a high vacuum excellently below about 700°C., but above that temperature their efficiency in this respect was found to fall away with rising temperature. Later experiments were carried out in tubes of transparent fused silica, and these were found perfect at all the temperatures used. Polished specimens could be soaked at high temperatures in these tubes for long periods with only a slight tinting

of the surfaces by oxidation. That complete immunity from oxidation and variation in composition can be obtained by this method has already been shown experimentally.

A platinum, platinum-iridium thermocouple was used, and this was frequently checked throughout the work. The e.m.f.'s recorded by the couple did not alter in the slightest degree in spite of many hundreds of hours of heating in vacuo.

The temperatures were read on a Cambridge and Paul Universal Test Set in the earlier experiments, and on a Siemens temperature indicator in the later ones. In the soaking experiments within the critical range the retention of the temperature within a variation of a few degrees over six consecutive hours was found difficult but the difficulties were overcome. The temperature was controlled by means of a sliding resistance to within  $\pm 2^\circ$  or  $3^\circ\text{C}$ . The mean soaking temperature was taken as  $2^\circ$  to  $3^\circ\text{C}$ . below that desired, so that the temperatures shown on the graphs are the maxima reached in each case.

The specimens were prepared and the specific volume determined by the method previously described.

#### EXPERIMENTS ON STEELS WITH CONSTANT NICKEL AND VARYING CARBON.

Three nickel steels with constant nickel and varying carbon were chosen for this work, together with a plain carbon steel for comparison. The analyses are shown in Table 22.

Specimens of each of these steels, of about 25 gm. weight, were first quenched in oil after half-an-hour at  $850^\circ\text{C}$ . They were then tempered as shown in Table 23.

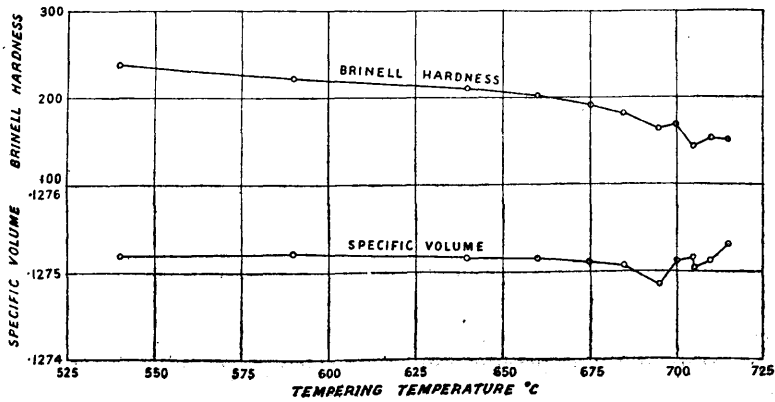


Steel.	C %.	Mn %.	P %.	S %.	Si %.	Ni %.
A4	0.71	0.16	Low	Low	0.10	Nil
2	0.26	0.27	0.014	0.025	0.103	3.64
4	0.44	0.33	0.015	0.038	0.125	3.65
6	0.87	0.41	0.013	0.025	0.149	3.64

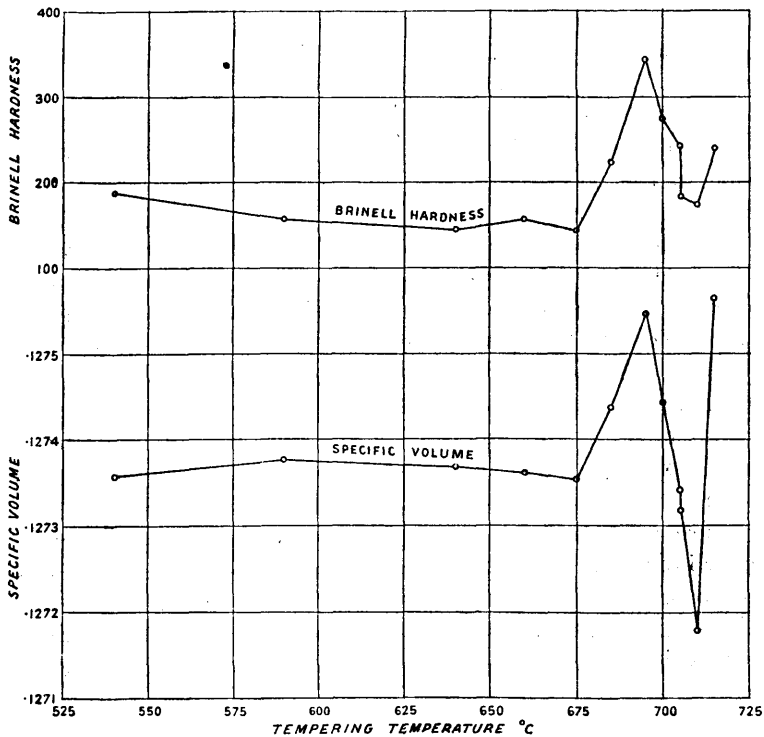
**TABLE 22.**

Treatment.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Temperature, °C.	540	590	640	660	675	685	695	700	705	705	710	715
Period of heating, hours	24	12	12	12	12	12	12	12	12	12 an extra	12	12

**TABLE 23.**



**Fig. 46 Carbon Steel A4.**



**Fig. 47 Nickel Steel 2.**

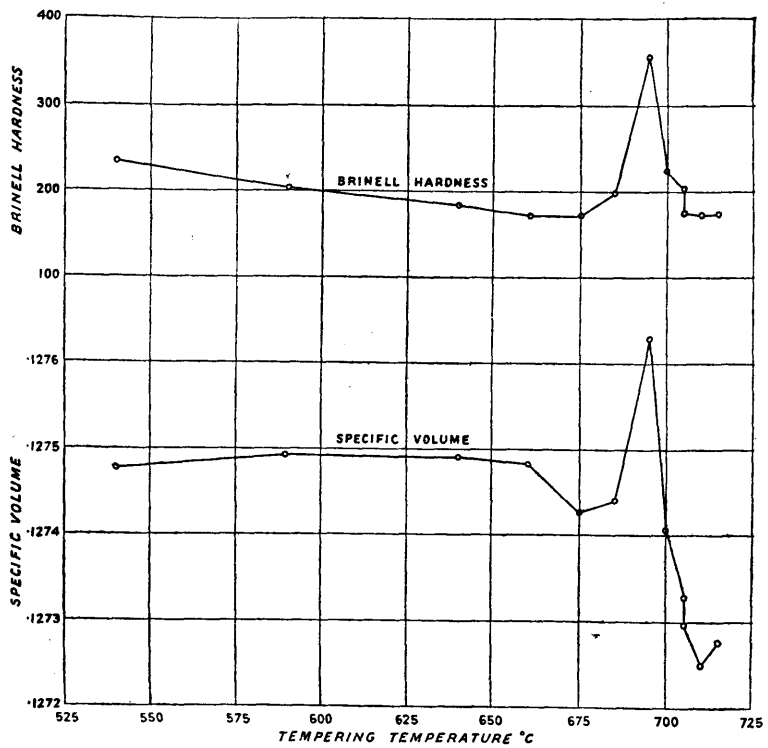


FIG. 48-Nickel Steel 4.

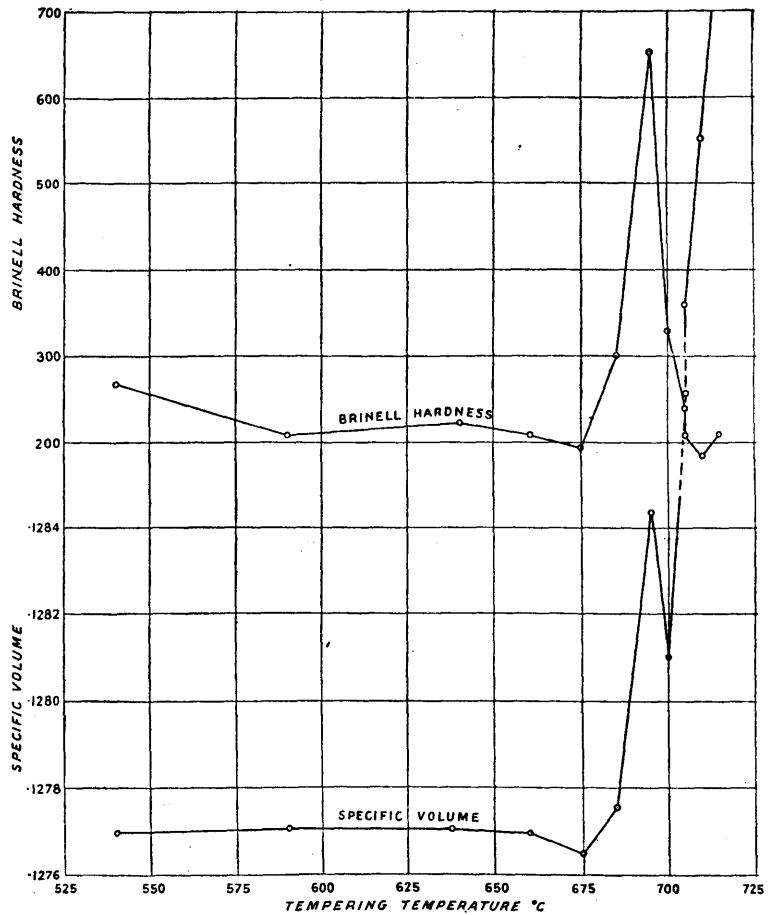


FIG. 49-Nickel Steel 6.

Each twelve-hour period was made up of two periods of six hours each, and rapid quenching in cold water followed each treatment. There was no intervening treatment between the various tempering treatments, and on heating up for each treatment the temperature was raised as quickly as possible without overstepping the desired soaking temperature, thus preventing as far as possible any redistribution of constituents during the heating up.

The specific volume and Brinell hardness after each treatment are plotted in Figs. 46, 47, 48, and 49. The microstructure was examined in all the specimens after each treatment and micrographs taken where it was thought advisable. Some of the latter are shown in Figs. 68 to 79.

The experiments were discontinued after treatment No. 12, as the specimens had become rather small for accurate work, owing to the necessity for grinding off the Brinell marks after each experiment.

The carbon steel (Fig. 46) showed a softening as the temperature was raised, but little or no change in the specific volume. In the nickel steels the fall in specific volume noted in earlier experiments as the temperature is raised (Figs. 2, 3, and 4) is not nearly so marked. This must be due to the lengthy treatments having promoted spheroidisation to a considerable extent at the lower temperatures so that raising the temperature has not the same effect as in shorter and separate treatments (with intervening oil quenching). Figs. 47, 48, and 49 show that when solution in  $\gamma$ -iron had first taken place in the nickel steels at 685°C. the quenched specimens showed an expansion and a hardening, and these increased with



FIG. 68—Nickel steel 6. Heated for 12 hours at 685° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid and boiling alkaline sodium picrate.  $\times 600$ .



FIG. 69—Nickel steel 2. Heated for 12 hours at 700° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

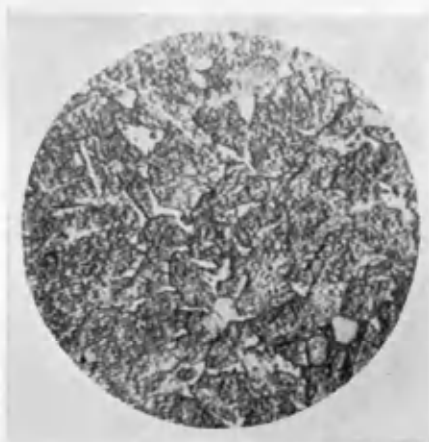


FIG. 70—Nickel steel 2. Heated for 12 hours at 705° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

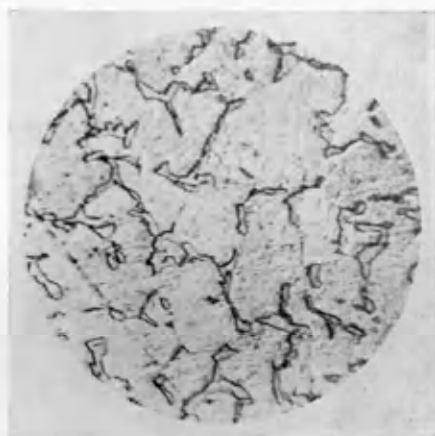


FIG. 71—Nickel steel 2. Heated for 24 hours at 705° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

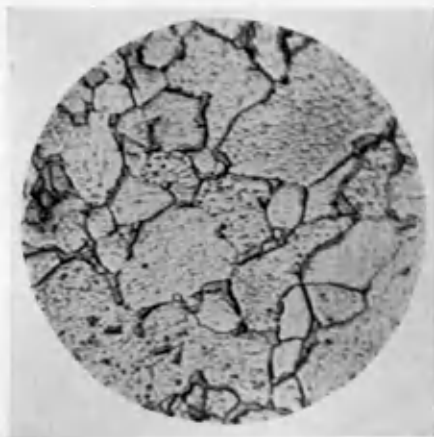


FIG. 72—Nickel steel 2. Heated for 12 hours at 710° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

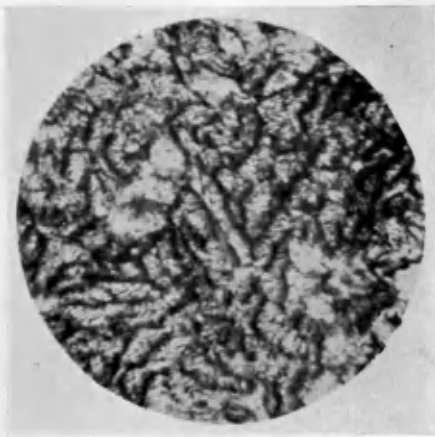


FIG. 73—Nickel steel 4. Heated for 12 hours at 700° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

(The above micrographs have been reduced to four-fifths linear in reproduction.)

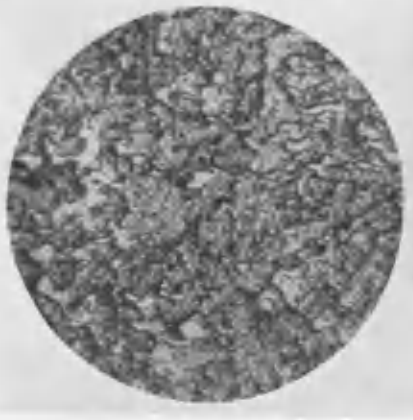


FIG. 74—Nickel steel 4. Heated for 12 hours at 705° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

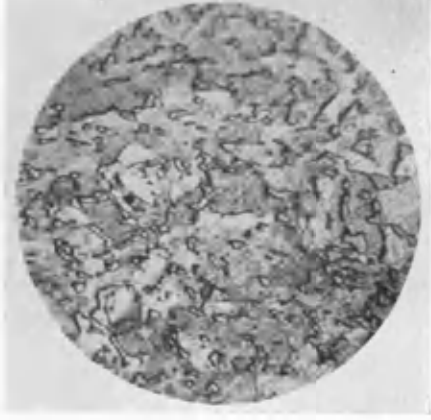


FIG. 75—Nickel steel 4. Heated for 24 hours at 705° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

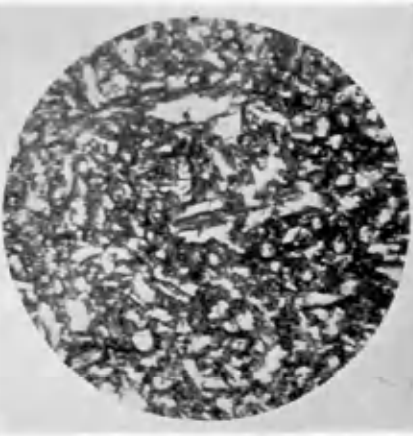


FIG. 76—Nickel steel 6. Heated for 12 hours at 700° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

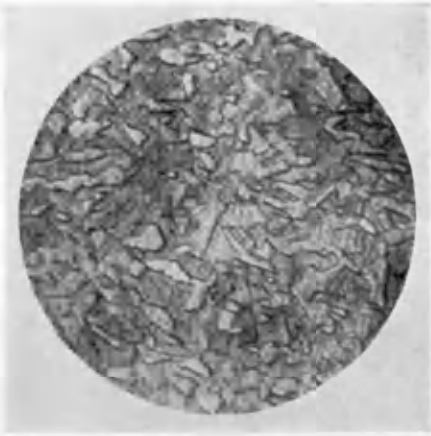


FIG. 77—Nickel steel 6. Heated for 12 hours at 705° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .



FIG. 78—Nickel steel 6. Heated for 24 hours at 705° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

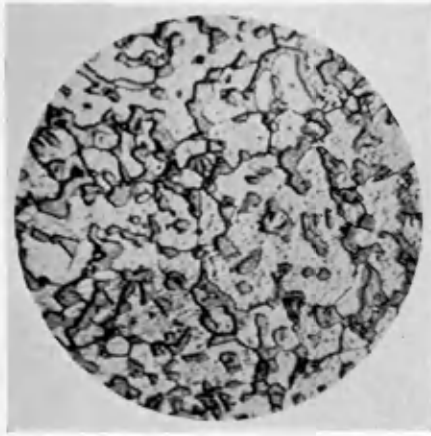


FIG. 79—Nickel steel 6. Heated for 12 hours at 710° C. and water-quenched. Etched with alcoholic 1 per cent. nitric acid.  $\times 600$ .

(The above micrographs have been reduced to four-fifths linear in reproduction.)

time and temperature. When the temperature was still further raised a contraction and softening set in, and this was followed by a second expansion and hardening at still higher temperatures. The first expansion and hardening was associated with a marked duplex structure (Fig. 68). The white constituent in the microsections was seen to increase with an increase of carbon content and also of soaking temperature. It was thus evident that it was this constituent which caused the expansion and hardening. The white areas, it is suggested, existed at the soaking temperatures as  $\gamma$ -iron solid solutions, but quenching had failed to retain them as austenite, and it is concluded that they consist of an unstable solid solution of carbon in  $\alpha$ -iron containing nickel. It will be shown later that the concentrations of these areas vary with a number of factors, but that they are, in general, relatively high in nickel and low in carbon when only a part of the carbide has dissolved. It was clearly seen in all the specimens that the carbide dissolved progressively as the temperature was raised. Fig. 68 shows the white areas formed at the soaking temperature (685°C.) together with undissolved carbide, the specimen having been etched in alcoholic nitric acid and also in a boiling alkaline solution of sodium picrate. The undissolved carbide globules are etched black.

As the temperature of soaking was raised the well defined duplex structure was broken down, and Figs. 69, 70, 73, 74, 76, 77, and 78 show indefinite broken-up structures which are the result of a rearrangement of equilibrium. The drop in specific volume and in hardness which follows the first rise in the curves is associated with the formation of another well-defined duplex structure

which gradually separates out from the broken up conglomerate obtained at intermediate temperatures. This structure is shown in Figs. 71, 75, and 79. It is evident from the curves, Figs. 47, 48, and 49, that austenite is being retained on quenching, and, as the amount of globularised constituent in Figs. 71, 75, and 79 clearly varies with the carbon content, it is concluded that this constituent consists of austenite and the ground mass of ferrite. As the temperature is further raised this constituent disappears into the ground-mass and less austenite and more martensite is formed, due to the gradual dilution of the  $\gamma$ -iron areas.

The unusual nature of the results obtained in this series rendered it advisable that they should be confirmed by other experiments, and a further series of similar treatments was carried out on fresh specimens of the same steels. It was thought that better quantitative results would be obtained by shorter and unbroken treatments at regular temperature intervals, and this was found to be the case.

#### ADDITIONAL SPECIFIC VOLUME EXPERIMENTS.

Fresh specimens of the steels used in the foregoing series were oil-quenched from 850°C. They were then tempered at 670°C. for six hours and quenched in water. This tempering was repeated at intervals of 5°C. for periods of six hours each up to 705°C. Above 705°C. the temperature intervals were the same, but the time of soaking was reduced to three hours. The steels were quenched in water after each treatment. Hardness determinations were not made, as it was clear from the first series of experiments and from many

other results that the hardness always followed the specific volume after treatment in the  $Ac_1$  range except when graphitisation occurred, as in one case, namely, steel No. 6. The microstructures were examined after each treatment, and the previous observations were fully confirmed.

The results are shown in Fig 50. The specific volume undergoes changes similar to those in the first series, but the regular temperature intervals of the successive treatments has led to better quantitative results. There is little alteration in the carbon steel throughout the whole range of treatment. This serves as an excellent contrast to the nickel steels, in which the expansion beginning at  $685^{\circ}C.$  and continuing up to  $695^{\circ}C.$  or  $700^{\circ}C.$  is directly proportional to the carbon content, as is shown in Fig. 51, where the increases up to the peak values in Fig 50 are plotted against the percentage of carbon. Above  $695^{\circ}C.$  or  $700^{\circ}C.$  the specific volume falls, and this fall is again proportional to the carbon content in steels Nos. 2 and 4, but is largely obscured by graphitisation in steel No. 6. In both series of experiments a small amount of graphitisation took place in steel No. 6 after all the carbide had gone into solution, that is at the dip in the specific volume curve. The formation of even a small amount of graphite has a pronounced effect on the specific volume. The graphitisation was plainly seen in the polished specimens as lines of small dots, which seemed to be situated along the boundaries of the original dendrites in the steel.

A further series of three nickel steels with increasing phosphorus content, and two nickel-chromium steels, were subjected to a series of treatments similar to that used in the second series



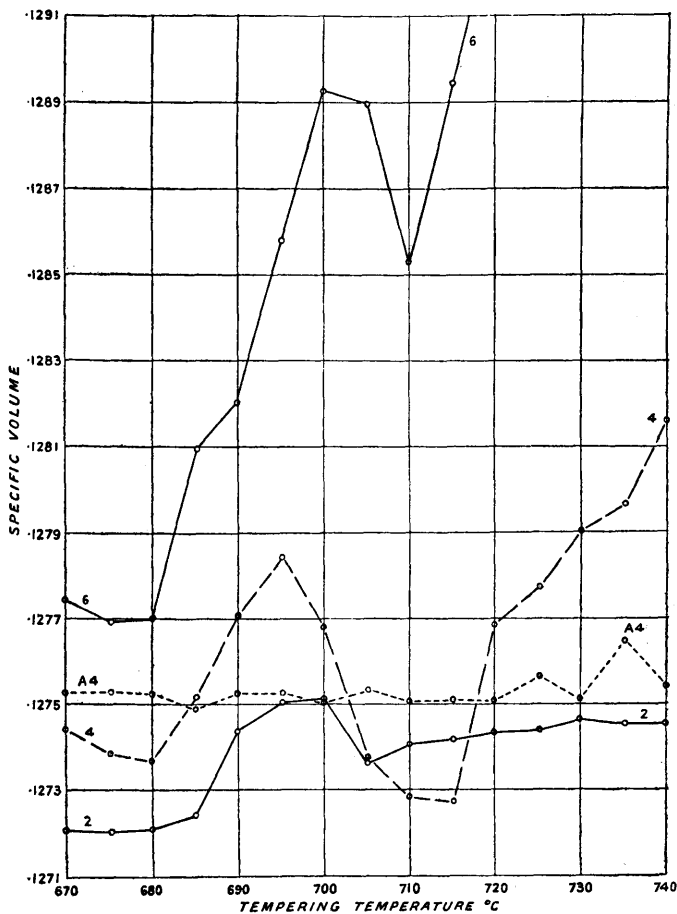


Fig. 50-Steels A4, 2, 4, and 6.

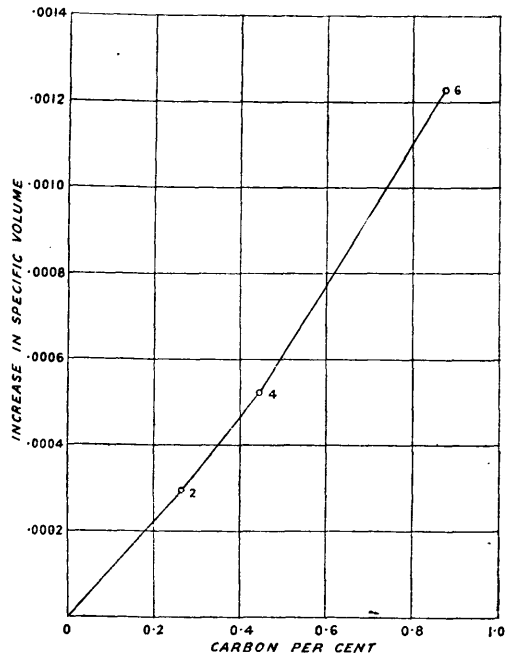


Fig. 51-Increase in Specific Volume with Carbon Content up to "Peak" Values in Fig. 50. Steels 2, 4, and 6.

*Analysis.*

Steel.	C %.	Mn %.	Si %.	P %.	S %.	Ni %.
N3	0.29	0.65	0.113	0.036	0.032	3.22

**TABLE 24.**

**TABLE 25-Nickel Steel, N3. Mechanical Test Results after Various Heat-Treatments.**

Specimen.	Treatment.	Reduction of Area. %.	Elongation on 2 in. %.	Maximum Stress. Tons per sq. in.	Isod Value. Ft.-lb.	Brinell Hardness.
1	Oil-hardened at 850° C., then tempered for one week at 680° C. to 690° C., and water-quenched	18.5	17.5	51.2	22.7	214
2	Same as 1, but slowly cooled at 0.3° C. per minute	17.9	23.4	46.4	18.3	193
3	Oil-hardened at 850° C., then tempered for 4 days at 695° C. to 700° C., and water-quenched	6.45	8.8	78.4	8.3	297
4	Same as 3, but slowly cooled at 0.3° C. per minute	9.0	11.0	56.4	9.8	227
5	Oil-hardened at 820° C., water-tempered 620° C.	...	20-25	55.0	60	245

of experiments. Hardness determinations were made, and they confirmed the previous observation that the hardness increases or decrease along with the specific volume. The variation of phosphorus content did not give any marked alteration in the cycle of changes. The nickel-chromium steels gave a less pronounced increment and a smaller dip at slightly higher temperatures. As nothing substantially new was revealed by this series of experiments details are omitted.

Experiments within the  $Ac_1$  range of a slightly different nature have already been recorded. In Figs. 2 and 3 of this thesis it will be seen that the nickel steels pass through changes similar to those already described. The difference between these experiments and those just described is that the specimens were quenched in oil from  $850^{\circ}C.$  between each tempering treatment. It is clear that the cycle of changes is similar in both types of treatment.

#### MECHANICAL TESTS.

It was thought that it would be of interest to determine the effect of heat-treatment within the  $Ac_1$  range on the mechanical properties of a nickel steel.

The analysis of the steel used is shown in Table 24.

Treatment in each case was carried out on the bars before machining. Four bars of the steel, 6 in. long and 1 in. in diameter, were first oil-quenched from  $850^{\circ}C.$  and were then subjected to a very drastic treatment at  $680^{\circ}C.$  to  $690^{\circ}C.$  for one week. The treatment was carried out in an electric tube furnace wound differentially over a length of 2 feet, so that the 6 in. bars in the centre were uniformly treated throughout their length. The course of the

treatment was followed by quenching-out from time to time a number of small microspecimens which were placed in the furnace along with the bars.

Treatment for a week at the temperature indicated brought about only a partial solution of the carbide, the microstructure showing the usual duplex structure obtained in this region along with a fair amount of undissolved carbide, well globularised.

At the end of the treatment two of the bars were quenched in iced brine, and the other two were very slowly cooled at a rate of  $0.3^{\circ}\text{C.}$  per minute to  $400^{\circ}\text{C.}$  Tensile and Izod test pieces were machined from the treated bars. The results of the mechanical tests are shown in Table 25.

Four other bars of the same steel were subjected to a similar treatment at  $695^{\circ}\text{C.}$  to  $700^{\circ}\text{C.}$  for four days. Two bars were quenched from the soaking temperature, and two were slowly cooled at a rate of  $0.3^{\circ}\text{C.}$  as before. All the carbide appeared to have been in solution at this higher soaking temperature, a prolonged boiling of the quenched microspecimen in sodium picrate failing to show up any carbide. The slowly cooled specimen showed a very interesting structure, in which a large part of the carbide had separated out round the grain boundaries. The effect of this structure on the physical properties of this steel has been used to provide an analogy to the behaviour of special steels in the "brittleness range". The mechanical test results are also shown in Table 25.

The mechanical properties have not been greatly impaired by either treatment No.1 or No.2 when the very drastic nature of the treatments is considered. In the case of treatments Nos. 3 and 4,

in which all, or nearly all, of the carbide had been brought into solution in  $\gamma$ -iron at the soaking temperature, the mechanical properties are greatly affected. A large amount of martensite was produced in specimen No. 3, and, as would be expected, this gave a large increase in the tensile strength, and poor figures for the elongation, the reduction of area and the Izod impact test.

In the bars from treatment No. 4 the carbide was found to have separated largely at the grain boundaries. It was clear from subsequent work that this was not due to segregation to the boundaries during slow cooling, but to the fact that the  $\gamma$ -iron solid solution had segregated to the grain boundaries at the soaking temperature, and in breaking down to pearlite at the  $A_{r1}$  point a fairly uniform layer of carbide had become deposited at the boundaries. There is no doubt that all the carbide which had been in solid solution was completely deposited by the slow-cooling treatment (the specimen was held at  $430^{\circ}\text{C}$ . for seventeen hours after extremely slow cooling to that temperature), and it is interesting to note how little effect the distribution of the carbide has on the tensile strength.

It would have been expected that the complete separation of the carbide in specimen No. 4 would have raised the Izod value considerably when compared with specimen No. 3, but, in this case, the production of brittle carbide around the grain boundaries has kept it low.

#### THERMAL ANALYSIS.

It was evident from the specific volume and hardness experiments that the changes within the  $A_{c1}$  range must be due to a redistribution of the constituents. Consequently the effect of similar

heat-treatments followed by thermal cooling curves might be expected to give indications of the distributions involved.

Work of this kind had been carried out previously in only one case, by Jones<sup>(31)</sup>; in his work he found in some steels a slight lowering of the  $Ar_1$  point after tempering in the lower part of the  $Ac_1$  range.

It has been established<sup>(33, 35, 36, 37, 38)</sup> that in nickel steels an increase of carbon content has no effect on the temperature of the  $Ar_1$  change, but that an increase of nickel progressively lowers that change. Thus if nickel is redistributed in a pure nickel steel at the commencement of the  $Ac_1$  range it would be revealed on a cooling curve by a lowering of the normal  $Ar_1$  change, whereas if the carbide alone were concerned, no alteration of the temperature of the  $Ar_1$  change would be observable.

The steels in Table 26 were used in the thermal work to be described.

The thermal specimens were treated in a high vacuum so that oxidation would be avoided. It was discovered by experience that this was absolutely essential if the changes were to be revealed. The specimens, in the form of cylinders, about  $1\frac{1}{2}$  in. long by  $\frac{3}{4}$  in. in diameter, with a hole drilled to the centre, were contained in a thick wrapping of asbestos paper, and the platinum, platinum-iridium thermocouple junction was rammed into the drilled hole with asbestos wool. The temperature was measured by means of a Tinsley vernier potentiometer. The curves were taken by the inverse-rate method, time readings being taken at every 0.1 millivolt increment or decrement of the thermal e.m.f.

The nickel steel, N3, after oil-quenching from  $850^\circ\text{C}.$ , was tempered at  $690^\circ\text{C}.$  ( $24^\circ\text{C}.$  below the normal  $Ac_1$  maximum, Fig 52) for

one hour, and a cooling curve, shown in Fig. 53, was taken. It is seen that an evolution of heat occurred over a range of temperature from 479°C. to 412°C., whereas the normal  $Ar_1$  maximum is 577°C. (Fig. 52). The specimen was then reheated to 700°C. for one hour, and a cooling curve again taken. The evolution of heat obtained in the previous treatment still persisted, and, in addition, a new evolution appeared at from 595°C. to 534°C., this being very nearly coincident with the  $Ar_1$  evolution obtained on a normal cooling curve taken from high temperatures. The soakings, followed by cooling curves, were repeated at 5°C. intervals up to 715°C., and then at 725°C., 750°C., and 800°C., with the results shown in Fig. 53. The lower heat evolution persisted until the temperature was raised to 715°C., but became progressively smaller. At 715°C. the lower transformation was practically identical with respect to temperature to that obtained in the original treatment at 690°C. The upper transformation increased in magnitude as the soaking temperature was raised, until at 725°C. the lower range was eliminated. It is clearly seen from the curves (Fig. 53) that, after the two ranges are produced at 700°C., treatment at 705°C. and 710°C. tends progressively to bring them together, but when the lower point is almost eliminated at 715°C. the lower limit of the upper range rises.

Other experiments were carried out on this steel, and the curves are shown in Figs. 54 and 55. After soaking at 675°C. no evolution of heat was revealed. In order to be certain that this was so a curve was taken down to 40°C., and this showed no discontinuity. At 685°C. an evolution was obtained (Fig. 54, b) extending from 450°C. to 358°C., which is decidedly lower than that after

Steel.	C %.	Mn %.	Si %.	P %.	S %.	Ni %.	Cr %.
N3	0.29	0.65	0.113	0.036	0.032	3.22	Nil
AH	0.31	0.47	0.310	0.015	0.021	4.46	1.41
NC	0.31	0.57	0.145	0.026	0.029	3.20	0.83
NR3	0.36	0.34	0.275	0.016	0.021	1.90	1.15
AAx	0.32	0.91	0.145	0.026	0.027	Nil	0.97

TABLE 26.

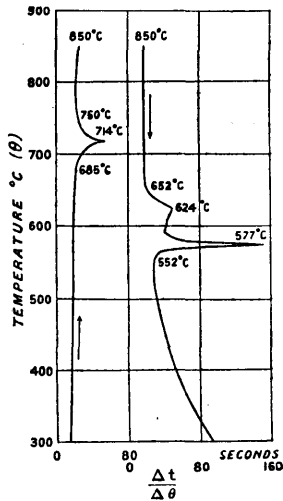
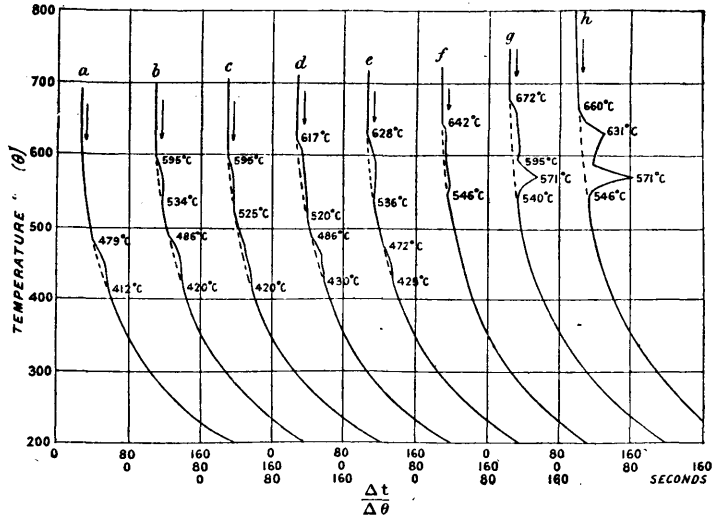
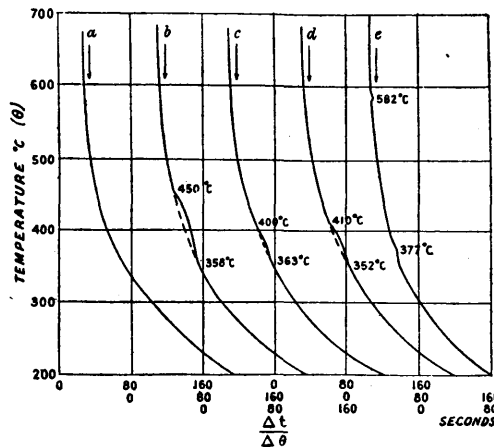


FIG. 52—Heating and Cooling Curves of Nickel Steel N3.



- a. Oil-hardened at 850° C., tempered at 690° C. for 1 hour, and cooled.
- b. Retempered at 700° C. for 1 hour, and cooled.
- c. " " 705° C. " "
- d. " " 710° C. " "
- e. " " 715° C. " "
- f. " " 725° C. " "
- g. " " 750° C. " "
- h. " " 800° C. " "

FIG. 53—Nickel Steel N3.



- a. Oil-hardened at 850° C., tempered at 675° C. for 1 hour, and cooled.
- b. " " " " 685° C. " "
- c. " " " " 680° C. " "
- d. Specimen c retempered at 685° C. for 4 hours, and cooled.
- e. Oil-hardened at 850° C., heated to 700° C., and immediately cooled.

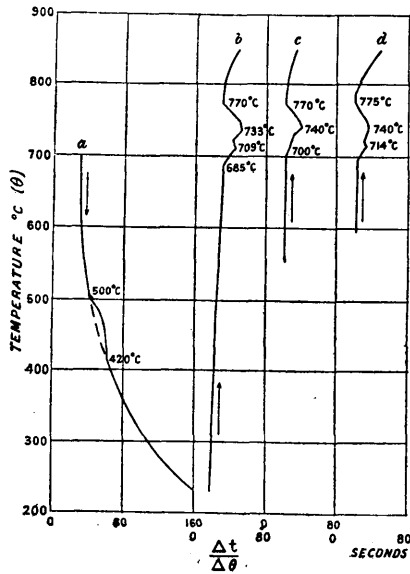
FIG. 54—Nickel Steel N3.

treatment at  $690^{\circ}\text{C}$ . (Fig. 53, a). On soaking the oil-quenched specimen at  $680^{\circ}\text{C}$ ., a very low point was produced at from  $400^{\circ}\text{C}$ . to  $363^{\circ}\text{C}$ . This specimen was reheated (without intervening oil-quenching) at  $685^{\circ}\text{C}$ . for four hours, and it is seen that the point produced by the previous treatment at  $680^{\circ}\text{C}$ . was slightly increased. Four hours at  $685^{\circ}\text{C}$ . did not produce nearly such a large evolution as was previously observed after one hour at the same temperature (Fig. 54, b). This is due, of course, to the difference in the previous treatment, the higher range of heat evolution having been produced when the steel was heated to the soaking temperature  $685^{\circ}\text{C}$ . immediately after oil-quenching.

In order to determine how rapid was the redistribution of constituents, a curve was taken after heating the oil-hardened steel quickly to  $700^{\circ}\text{C}$ . and switching off the current just before that temperature was reached. The steel by this treatment was in the lower part of the  $A_{c1}$  range for as short a period as could reasonably be arranged, certainly under half a minute. Fig. 54, e, shows that two very small points were produced on the curve, one at  $582^{\circ}\text{C}$ ., that is, slightly above the normal  $A_{r1}$  point, and a low point at  $377^{\circ}\text{C}$ .

In the specimen previously heated to  $700^{\circ}\text{C}$ . (Fig. 53, b) two points were produced on the cooling curve. That this was due to its previous treatment was shown by another curve (Fig. 55, a) taken after heating the oil-hardened steel at  $700^{\circ}\text{C}$ . without previous treatment at lower temperatures. Only one point was obtained, the heat evolution extending over a range of  $80^{\circ}\text{C}$ . from  $500^{\circ}\text{C}$ . to  $420^{\circ}\text{C}$ . The lower limit ( $420^{\circ}\text{C}$ .) is the same as that in the previous





- a. Oil-hardened at 850° C., tempered at 700° C. for 1 hour, and cooled.
- b. Heating curve after treatment a.
- c. Oil-hardened at 850° C., tempered at 700° C. for 1 hour, cooled to 550° C., and heating curve taken.
- d. Oil-hardened at 850° C., heated to  $A_{c1}$  max. (714° C.), cooled to 595° C., and heating curve taken.

Fig. 55—Nickel Steel N3.

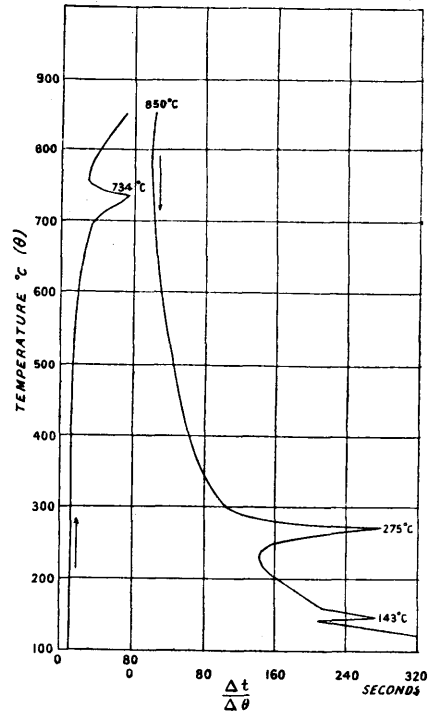
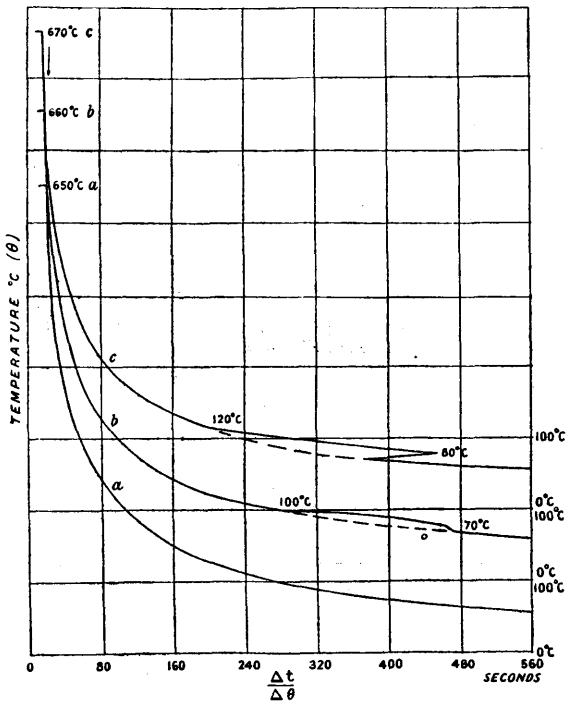


Fig. 56—Heating and Cooling Curves of Nickel-Chromium Steel AH.



- a. Oil-hardened at 850° C., tempered at 650° C. for 1 hour, and cooled.
- b. " " " " 660° C. " "
- c. " " " " 670° C. " "

Fig. 57—Nickel-Chromium Steel AH.

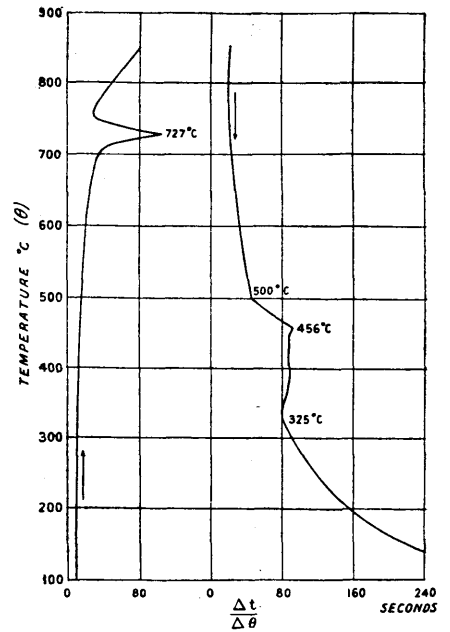


Fig. 58—Heating and Cooling Curves of Nickel-Chromium Steel NC.

treatment at 700°C. (Fig. 53, b), but it commences 14°C. higher and no upper point is revealed.

After this treatment at 700°C. a heating curve was taken, and is shown in Fig. 55, b. This curve shows two points, one with a maximum at 709°C., that is, 5°C. below the normal  $Ac_1$  maximum, due to re-resolution of the carbide which had separated at the previous low point on cooling, and an upper point which is due partly to the remainder of the carbide going into solution and partly to the  $Ac_3$  change.

The oil-hardened steel was subjected to another one hour treatment at 700°C., but this time it was cooled only to 550°C. (which is above the start of the  $Ar_1$  heat evolution previously obtained), and a heating curve taken. This is reproduced in Fig. 55, c. It shows that the upper point is due to changes not brought about in the previous treatment. Absorption of heat commences at a higher temperature, and the normal  $Ac_1$  point is very small.

An experiment was carried out to show whether the upper point in these curves was due to carbide not yet dissolved or to the  $Ac_3$  change. The steel was oil-hardened, and a heating curve taken up to  $Ac_1$  maximum. The current was switched off and the steel cooled to 595°C. (above  $Ar_1$ ), and a heating curve taken. This showed a large upper point (Fig. 55, d) due mainly to the  $\alpha$ - $\gamma$  change ( $Ac_3$ ), and a small low point due to a little carbide not dissolved in the first treatment.

It is shown by the work on this nickel steel that the  $Ac_1$  range starts at about 680°C., that is, 34°C. below the normal  $Ac_1$  maximum. The nickel-chromium steels AH, and NR3, containing 4.46

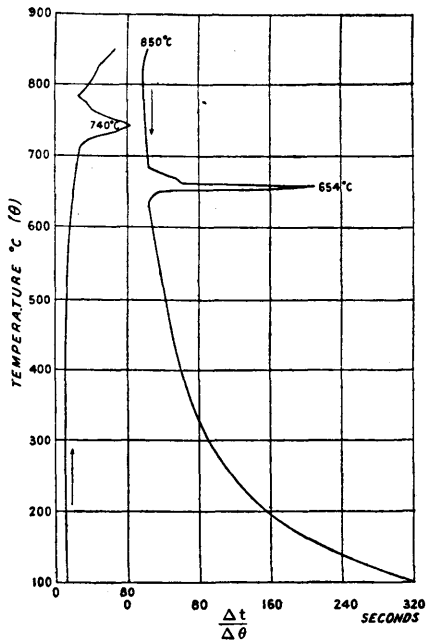
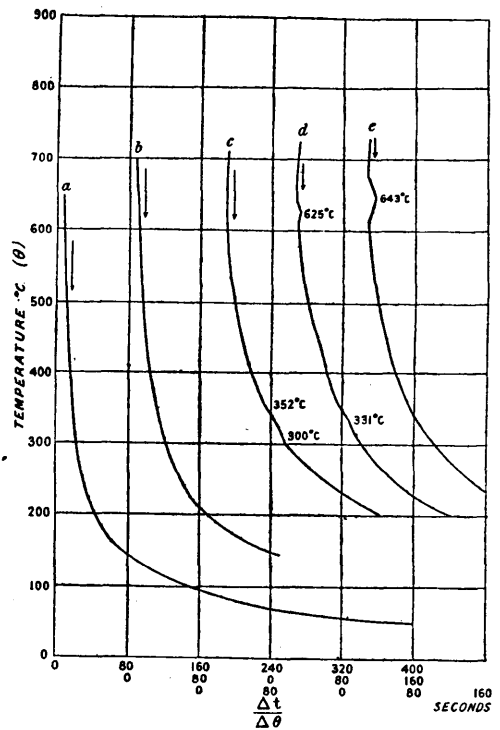


Fig. 59—Heating and Cooling Curves of Nickel-Chromium Steel NR3.



- a. Oil-hardened at 850° C., tempered at 650° C. for 1 hour, and cooled.  
 b. Retempered for 1 hour at every 10° C., up to 700° C., and cooled.  
 c. Oil-hardened at 850° C., tempered at 710° C. for 1 hour, and cooled.  
 d. Retempered at 720° C. for 1 hour, and cooled.  
 e. Oil-hardened at 850° C., tempered at 730° C. for ½ hour, and cooled.

Fig. 60—Nickel-Chromium Steel NR3.

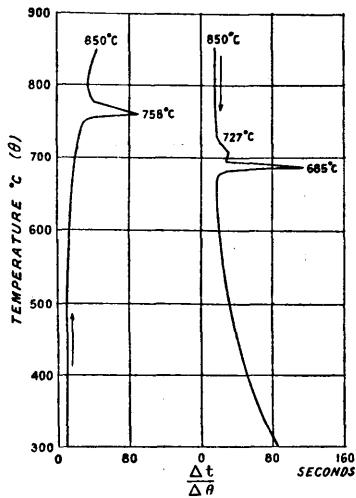
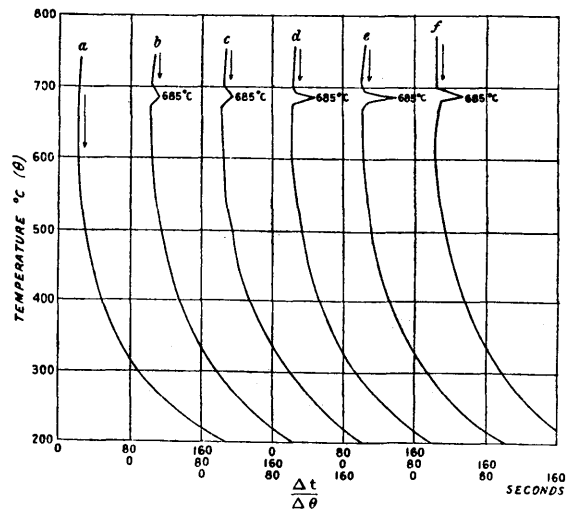


Fig. 61—Heating and Cooling Curves of Chromium Steel AAX.



- a. Oil-hardened at 850° C., tempered at 740° C. for 1 hour, and cooled.  
 b. Retempered at 745° C. for 1 hour, and cooled.  
 c. " 750° C. " "  
 d. " 755° C. " "  
 e. " 760° C. " "  
 f. " 770° C. " "

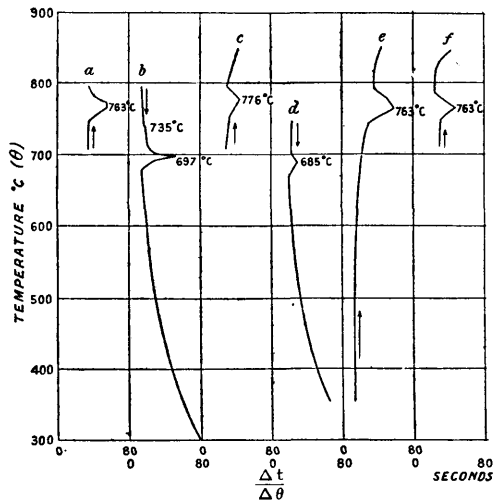
Fig. 62—Chromium Steel AAX.

and 1.90 per cent. nickel respectively, were treated to ascertain the temperature at which the  $Ac_1$  range in them commences. In these steels there is only a small difference in the temperatures of the  $Ac_1$  maxima:  $734^\circ C.$  for steel AH (Fig. 56), and  $740^\circ C.$  for steel NR3 (Fig. 59). As will be seen from Fig. 57, however, the  $Ac_1$  range commences at  $660^\circ C.$  in steel AH, that is,  $74^\circ C.$  below the normal  $Ac_1$  maximum, giving a very low evolution of heat, and in steel NR3 (Fig. 60) no point was evident until after treatment at  $710^\circ C.$  The extent of the  $Ac_1$  range is thus proportional to the nickel content.

Similar experiments to those carried out on the nickel steel were made on a chromium steel. In this steel (AAX) all the chromium (except possibly a minute proportion) is in combination as carbide. The normal  $Ac_1$  maximum is at  $758^\circ C.$  (Fig. 61) and treatment at  $740^\circ C.$  failed to reveal any solution at the soaking temperature (Fig. 62, a) At  $745^\circ C.$  some solution took place, but the point which was observed on cooling (Fig. 62, b) was at the normal  $Ar_1$  temperature, and no redistribution whatever was revealed by subsequent treatments (Fig. 62). It is evident that the  $Ac_1$  range is small in this steel, and indeed the existence of any range whatever may be due to the manganese content which is high. Later experiments on a number of chromium steels free from manganese confirmed this conclusion.

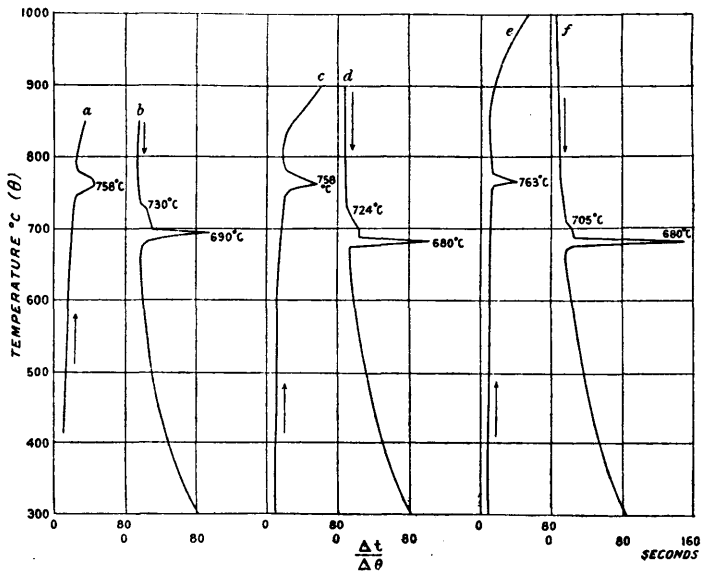
Experiments on a steel free from manganese and high in chromium would be necessary to discover the effect of free chromium in solution. Very faint evolutions of heat are evident at lower temperatures in some of the curves in Fig. 62, and it is thought that these are due to the presence of manganese in this steel.

The results of other experiments on this steel are shown



- a. Oil-hardened at 850° C., tempered at 745° C. for 1 hour, cooled to 710° C., and heating curve taken to 796° C.
- b. Cooling curve immediately following treatment a.
- c. Oil-hardened at 850° C., tempered at 745° C. for 1 hour, cooled to 710° C., and heating curve taken to 850° C.
- d. Oil-hardened at 850° C., tempered at 745° C. for 1 hour, and cooled.
- e. Heating curve after treatment a.
- f. Oil-hardened at 850° C., heated to  $Ac_1$  max. (758° C.), cooled to 705° C., and heating curve taken.

FIG. 63—Chromium Steel AAX.



- a. Heating curve of normalised steel.
- b. Cooling curve, following treatment a.
- c. Oil-hardened at 850° C., and heating curve taken to 900° C.
- d. Cooling curve, following treatment c.
- e. Heating curve to 1000° C., following treatment d.
- f. Cooling curve, following treatment e.

FIG. 64—Chromium Steel AAX.

in Figs. 63 and 64. A specimen was heated just to the  $Ac_1$  maximum in the same way as has already been described in one of the experiments on the nickel steel N3. It was then cooled to  $705^\circ C$ . (above  $Ar_1$ ) and a heating curve taken from there. This curve (Fig. 63, f) shows a very definite point slightly above the normal, which must be due, as in the case of the nickel steel, mainly to the  $\alpha$ - $\gamma$  ( $Ac_3$ ) change. That this is so will be seen from a cooling curve (Fig. 63, b) taken immediately after a similar treatment, in which a distinct  $Ar_3$  point is visible. Other curves (Fig. 64) show that this point is progressively lowered with a rise in the initial temperature.

Cooling curves of the steels AH, NC, and NR3, which have nickel contents of 4.46, 3.20, and 1.90 per cent. respectively, are included to illustrate a matter which will be discussed later (Figs. 56, 58, and 59). Steel AH shows two points on cooling (Fig. 56), and steel NR3 one point (Fig. 59), while steel NC shows an evolution over a wide range of temperature (Fig. 58). This curve of steel NC was repeated and an exact replica obtained.

It may be noted here that in a number of Dejean's curves <sup>(37)</sup> there are indications of redistribution effects similar to those described in connection with the nickel and nickel-chromium steels in the present research. In a high-speed tungsten steel, containing tungsten 18, carbon 0.7, chromium 4 per cent., and a little vanadium, his cooling curves show a small heat evolution at temperatures considerably below the normal  $Ar_1$  point, after the steel had been heated to temperatures within the  $Ac_1$  range. With a steel containing carbon 0.39, nickel 2.44, chromium 1.83, and copper 1.72 per cent. he got similar results. For each steel the lowest heat evolution

obtained on cooling took place after the lowest tempering treatment within the  $Ac_1$  range, and, as the tempering temperature was raised through the  $Ac_1$  range, the low temperature evolution occurred at progressively rising temperatures, finally disappearing. These curves can be seen in Figs. 1 and 2 of Dejean's paper; they give clear evidence of redistribution in the  $Ac_1$  range, but Dejean does not even mention the points referred to above in the text of his paper.

#### THEORETICAL CONSIDERATION OF RESULTS.

It is an inevitable conclusion from the experimental results that redistribution of the special element which is present in solid solution is the salient cause of the  $Ac_1$  change taking place over a range of temperature. It has been shown in the specific volume and hardness experiments that a variation of the carbon content in nickel steels has little or no effect either on the temperature at which the  $Ac_1$  range commences or on the apparent extent of that range. As the carbon content is increased the changes which take place are merely accentuated in proportion to the carbon content, no modification of the temperature range being produced. Thermal determinations on nickel steels containing very low percentages of carbon (Table 15) have shown that the start of  $Ac_1$  is raised somewhat at these low carbon values.

From the thermal curves of nickel and nickel-chromium steels it has been shown that the temperature at which the  $Ac_1$  range commences depends chiefly on the nickel content of the steels. The temperature at which solution in  $\gamma$ -iron commences is rapidly lowered by increase of nickel. Further, it is clear that the amount of redistribution

which takes place in the  $\gamma$ -iron first formed depends upon the amount of nickel originally present in solid solution in the ferrite.

In the chromium steel examined by the thermal method no redistribution due to the chromium (which is combined as carbide) is revealed, but the manganese present in solid solution gives an indication of effects similar to those of nickel. (The amount of lowering of  $Ar_1$  for each 1 per cent. of manganese will be roughly  $2\frac{1}{2}$  times that for the same amount of nickel). The temperature range of  $Ac_1$  in this chromium steel is evidently small, and it may be entirely due to the manganese present. Selective solution of carbides, as suggested by Jones<sup>(31)</sup>, may, however, take place where mixed carbides are present as in this case. In all such cases examined the effect in the production of a temperature range is small.

Where a special element is present in solid solution the  $Ac_1$  change may take place over a range of temperature, provided that there is a difference between the solubilities of the special element in  $\alpha$ - and  $\gamma$ -iron.

The effect of nickel in this connection will be specially dealt with here, since in almost all of the steels used it is the element particularly concerned. Similar considerations must, however, apply to other similar elements.

It is necessary to build a portion of the equilibrium diagram of the system iron-nickel-carbon in order to appreciate what takes place in the  $Ac_1$  range. A general diagram has been drawn by Kase<sup>(39)</sup>, but in the present state of knowledge it is necessarily incomplete, and takes no account of the changes at present under



consideration. The portion of the diagram which is required for this work can, however, be constructed from previously known data, together with data from the present paper. This has been done, and a diagrammatic view is given in Fig. 65. This diagram is given merely as an illustration of the points now at issue, and other points have been purposely omitted from it.

Scott<sup>(38)</sup> found that in steels containing up to 3.5 per cent. nickel, an increase of nickel lowered the  $Ac_1$  point(maximum) by 10.5 °C. for each 1 per cent. of nickel added, and he calculated that the carbon concentration of the eutectoid became smaller by 0.042 per cent. for each 1 per cent. nickel. These figures agree well with those of other workers. Carpenter, Hadfield and Longmuir<sup>(33)</sup> gave figures for the temperature of  $Ac_1$  maximum in steels containing up to 16 per cent. nickel.

From the above figures the mean line AB has been drawn in Fig. 65. This line starts at the eutectoid of the iron-carbon system, and slopes downwards towards an increase of nickel and a decrease of carbon. But this line only represents the maxima of the  $Ac_1$  change at eutectoid compositions, and it is necessary, in order to represent the  $Ac_1$  range, to have two lines diverging from the iron-carbon eutectoid point. The lower line AC represents the start of the  $Ac_1$  change in steels of eutectoid composition, and the top line AE the completion of this change. To include steels of all carbon contents two planes generated horizontally on both sides by these lines make the diagram, in this respect, complete. At low percentages of carbon the two planes will approach each other and meet at a plane representing solubility of carbon in ferrite. The

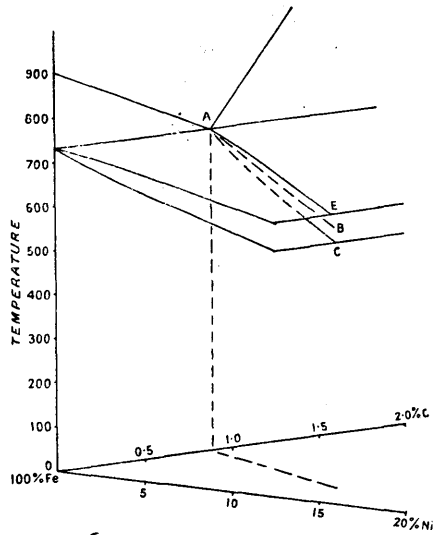
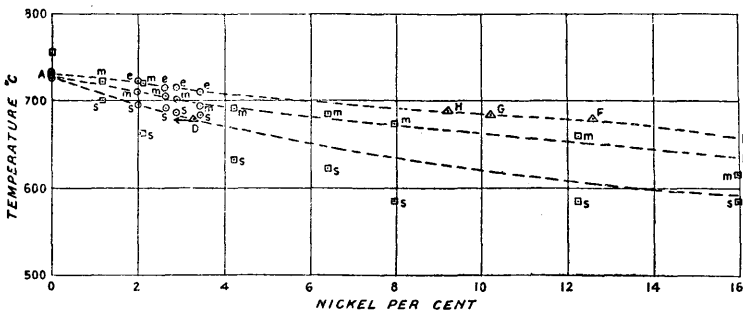


Fig. 65—Portion of Ternary System Iron-Nickel-Carbon for Steels up to 12.5% Nickel.

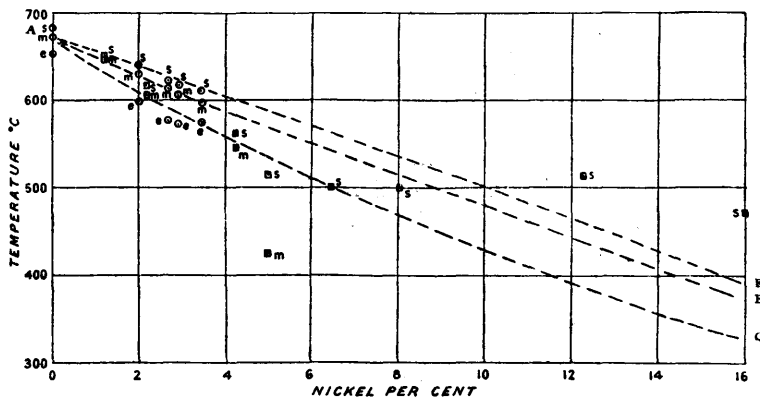


Scott's figures,  $\circ$   
 Carpenter, Hadfield, and Longmuir's figures,  $\square$   
 Authors' figures,  $\triangle$

$s$  = start  
 $m$  = maximum  
 $e$  = end

} of  $Ac_1$  range ( $Ar_1$ , Fig. 67)

Fig. 66—Vertical Section through Eutectoid of Ternary System Iron-Nickel-Carbon (Fig. 65)



Conventions as in Fig. 66 .

Fig. 67—Vertical Section through Eutectoid of Ternary System Iron-Nickel-Carbon for Ordinary Conditions of Cooling.

latter is omitted from the diagram.

A vertical section through the line of eutectoid compositions (AB, Fig. 65) is shown in Fig. 66. Some of the results of Carpenter, Hadfield, and Longmuir, and of Scott, have been plotted as indicated. The mean line AB has been drawn through the maxima of their curves. The first-named investigators used a differential method, and the maxima of their curves agree well with Scott's. The differential method gives, however, the apparent start of the  $Ac_1$  range at temperatures which are undoubtedly much too low. The line AC, representing the start of the  $Ac_1$  range, has been drawn through Scott's figures, taken by the inverse-rate method. This line includes the point D, which has been definitely shown to be the start of  $Ac_1$  in steel N3 of the present research. The position of the line AC at higher nickel contents is doubtful; for lower nickel contents it can be taken as very nearly correct, as shown on the diagram, for commercial nickel steels containing 0.5 to 0.7 per cent. manganese. This line is obviously of considerable practical importance, as it represents the temperature below which all tempering operations must be carried out.

The line AC is analogous to the solidus of a system of continuous solid solutions, and the line AE corresponds to the liquidus. AC represents the start of the  $Ac_1$  range, and AE its completion. At lower nickel contents the line AE has been drawn through Scott's figures, and at higher compositions through points obtained by calculation as described below.

The reactions on heating the steel N3 (3.22 per cent. nickel) may be considered. When the lower plane in Fig. 65 is reached,  $\gamma$ -

solid solution of eutectoid composition commences to form. The point D in Fig. 66 represents the temperature of the start of the formation of  $\gamma$  solution. At this point the composition of the  $\gamma$  solution first separating is given by F, that is, the point on the same horizontal on the line AE. The  $\gamma$  solution first formed thus contains a large proportion of nickel. The carbon content of a eutectoid solution containing this amount of nickel is low, since the higher the nickel content the lower is the carbon content required to form a eutectoid solution. If the temperature is retained at this point D a condition of stability is reached through the impoverishment of the remaining  $\alpha$ -iron in nickel, the composition of the ferrite moving in the direction shown by the arrow. In order to form more eutectoid solution it is thus necessary to raise the temperature further until the line AC is again reached. If, instead of retaining the temperature at 680°C., it is raised at once to 685°C. and retained there, a eutectoid solution of approximately the composition corresponding to the point G is formed. This contains more carbon and less nickel than in the first case when the temperature was retained at 680°C. Similarly, if the temperature is raised at once to 690°C. the composition of the  $\gamma$ -solution extends up to H. The effect of these varying compositions on the  $Ar_1$  change has been shown in Figs. 53 and 54. The lower the soaking temperature the lower is the resulting  $Ar_1$  point. The position of the line AE at higher nickel contents has been calculated on the assumption that an increase of nickel gives a uniform decrease in the temperature of the  $Ar_1$  point. Scott's figures for low nickel steels (which agree closely with those of other workers) have been used, that is,

each 1 per cent. of nickel lowers  $Ar_1$  by  $21.5^\circ C.$ , and the compositions of the eutectoid  $\gamma$  solutions formed at  $680^\circ C.$ ,  $685^\circ C.$ , and  $690^\circ C.$  were calculated from the start of the respective  $Ar_1$  ranges (Figs. 53 and 54). The points F, G, and H (Fig. 66), through which the line AE has been drawn, were thus obtained.

Another factor, however, may have to be taken into consideration. Dejean<sup>(37)</sup>, and Carpenter, Hadfield, and Longmuir<sup>(33)</sup>, showed that above about 8 or 10 per cent. nickel the  $Ar_1$  point is lowered rapidly to a lower range of temperature. These workers used high initial temperatures,  $900^\circ C.$  and higher, whereas the initial temperatures used in the present experiments were below  $700^\circ C.$  It is thus impossible to make a definite deduction from the available data as to the exact position of the line AE at higher temperatures in Fig. 66, or of the corresponding plane in Fig. 65. It would seem, however, that the line as shown cannot be far from its true position.

In the thermal curves in Fig. 53 it is evident that sufficient time has not been given at the soaking temperature in a number of the experiments for stability to be attained. Once a eutectoid solution has been formed by soaking at a lower temperature further raising of the temperature does not readily dilute it. The soaking times used in the specific volume work are likely to have produced reasonable homogeneity of the eutectoid solutions formed.

The first solutions formed on heating in the lower part of the  $Ac_1$  range, being relatively low in carbon, are more readily converted to martensite on quenching. Guillet<sup>(40)</sup> found that in quenched steels with from 7.65 to 25 per cent. nickel the microstructure showed a predominance of martensite. Evidently an increase

of nickel in nickel steels has not the same effect on the retention of austenite as an increase of carbon has. Thus in the eutectoid  $\gamma$  solutions first formed the lower carbon content gives a tendency to the formation of martensite, and it is only when almost all of the carbon is brought into solution that the carbon content of the eutectoid  $\gamma$  solution becomes high enough for the retention of austenite, at least when these low initial temperatures are used. Thus the dip in the specific volume curves is explained.

#### THE $A_{r1}$ RANGE.

Some considerations on the  $A_{r1}$  range may suitably be included in this discussion, since the elucidation of the reactions which take place on heating through the  $A_1$  range inevitably brings out information which can be applied to throw light on the reverse process of cooling through that range.

It has been pointed out by Le Chatelier<sup>(41)</sup>, and commented on by Carpenter, Hadfield and Longmuir<sup>(33)</sup>, that the  $A_{r1}$  change in steels naturally appears on a thermal curve over a wider range of temperature than  $A_{c1}$ . This is due to the fact that the falling temperature opposes the  $A_{r1}$  change, whereas rising temperature assists the  $A_{c1}$  change. To this must, however, be added, in the case of steels containing nickel or other similar elements in solid solution, a factor which a consideration of the ternary diagram makes clear. When nickel steels are cooled, the critical changes take place at lower temperatures than they do on heating. Thus Scott<sup>(38)</sup> calculated that the  $A_{r1}$  point (maximum) is lowered  $21.5^\circ\text{C}$ . for each 1 per cent. nickel, whereas the  $A_{c1}$  point is only lowered by  $10.5^\circ\text{C}$ .

To obtain the position of the  $Ar_1$  range the two planes in Fig. 65 must be altered in position. The iron-carbon eutectoid line will be slightly lowered, and, with this as axis, the planes representing the start and finish of the  $A_1$  change will be turned downwards through an angle of about  $14^\circ C$ .

A vertical section through the line of eutectoid compositions has been drawn in Fig. 67. Some of the results of Scott, and of Carpenter, Hadfield, and Longmuir, have been plotted on the diagram as shown. It is readily seen that on cooling there is a greater temperature interval ~~interval~~ between the two planes for any given composition than is the case on heating. The  $Ar_1$  range in steels which contain nickel or a similar special element in solid solution will for this reason, among others, be greater than the  $Ac_1$  range.

The reactions which take place in the  $Ar_1$  range will be the reverse of those described for the  $Ac_1$  range. The first pearlite separating will have a higher carbide content than that obtained as an average in the pearlite areas after the change is complete. Just as on heating the first  $\gamma$ -iron solid solution which forms tends to absorb nickel in excess, so on cooling, when pearlite starts to separate, the nickel of the steel will tend to remain in the  $\gamma$ -iron solid solution which has yet to change (to pearlite, troostite, or martensite). As the nickel content of the steel rises the  $Ar_1$  range, as shown by the two planes (represented by the two lines AE and AC, Fig. 67) on the ternary diagram, widens. This, combined with the factors just discussed, seems to give the key to the explanation of the doubling of the critical points on cooling certain nickel, nickel-chromium, and other special steels.

Carpenter, Hadfield, and Longmuir<sup>(33)</sup> found in their work on nickel steels that with higher nickel contents the Ar range was revealed by a long evolution of heat, culminating in a critical point near the lower extremity. Dejean<sup>(37)</sup> found in steels of similar composition that two points were revealed in certain steels, and one low point in others. These points he named (along with other workers) Ar' and Ar'', associated with the formation of troostite and martensite respectively. A consideration of the thermal curves published by the above workers, in the light of the new facts brought out by the present research, points strongly to the fact that the doubling of Ar points is often due to reactions which take place in the Ar ranges. When the start of the Ar<sub>1</sub> range is reached on cooling, pearlite (or troostite) starts to separate and, as already pointed out, the remaining  $\gamma$ -iron solid solution becomes progressively richer <sup>in</sup> nickel, thus delaying its change until a lower temperature is reached. Two separate points may be produced in a cooling curve given suitable composition and conditions of cooling. In the present research three cooling curves of nickel-chromium steels have been shown (Figs. 56, 58, and 59). In steel NR3 (nickel, 1.90 per cent.) Ar<sub>1</sub> is shown by a sharp point taking place over a short temperature range. In steel NC (nickel, 3.20 per cent.) the composition and conditions of cooling have led to a continuous evolution of heat throughout the Ar ranges. In steel AH (nickel, 4.46 per cent.) the composition and conditions have caused the production of two definite points, one at or near the start of the Ar<sub>1</sub> range, and the other at or near the end of that range. The Ar<sub>3</sub> point, of course, complicates the thermal evolutions in hypoeutectoid steels.



Other considerations also complicate the reactions on cooling. After heating to higher initial temperatures the critical points of many special steels are lowered. This is due to causes which are not yet understood, but it may be connected with the destruction of nuclei as the temperature is raised. It is sufficient here to recognise the fact, and to point out how the position of the  $A_{r_1}$  range will be altered with it. This, combined with the considerations already discussed, makes clearer the fundamental reasons for the wide ranges of  $A_{r_1}$  found in many special steels.

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#### REFERENCES.

- (1) Greaves: Journal of the Iron and Steel Institute, 1919, No. 2., p. 329.
- (2) Greaves and Jones: Journal of the Iron and Steel Institute, 1920, No. 2, p. 171.
- (3) Greaves and Jones: Journal of the Iron and Steel Institute, 1925, No. 1, 231.

- (4) Andrew and Green: Transactions of the North-East Coast Institution of Engineers and Shipbuilders, 1920, vol. xxxvi, p. 355.
- (5) Griffiths: Journal of the Iron and Steel Institute, 1925, No. 1, p. 257.
- (6) Honda and Yamada: "On the Cause of Temper-Brittleness in Steels," Science Reports of the Tohoku Imperial University, 1927, vol. xvi, April, p. 307.
- (7) Oberhoffer, Hochstein, and Hessenbruch: Stahl und Eisen, May 30th 1929, p. 799.
- (8) Philpot: Proceedings of the Institution of Automobile Engineers, April, 1918, p. 233.
- (9) Rogers: Journal of the Iron and Steel Institute, 1919, No. II, P. 613.
- (10) Guillet: Comptes Rendus, Jan. 25th. 1926, vol. clxxxii, No. 4.
- (11) Kayser: Journal of the Iron and Steel Institute, 1920, No. 1, p. 623.
- (12) Gebert: Proceedings of the American Society for Testing Materials, 1919, vol. xix., Part II, p. 117.
- (13) Dowdell: Transactions of the American Society for Steel Treating, 1924, vol. v., No. 1, p. 27.
- (14) Burrows and Fahy: Proceedings of the American Society for Testing Materials, 1919, vol. xix., Part II, p.5.
- (15) Nusbaum: Proceedings of the American Society for Testing Materials, 1919, vol. xix., Part II., p. 95.
- (16) Colver-Glauert and Hilpert: Transactions of the Faraday Society, 1912, vol. viii.
- (17) Benedicks: Journal of the Iron and Steel Institute, 1908, No. II p. 222.
- (18) Whiteley: Journal of the Iron and Steel Institute, 1927, No. II, p. 293.
- (19) Honda: Science Reports of the Tohoku Imperial University, vol. vi., No. 4, Nov. 1917.
- (20) Campbell and Mohr: Journal of the Iron and Steel Institute, 1926, No. I., p. 375.
- (21) Westgren, Phragmen, and Negresco; Journal of the Iron and Steel Institute, 1928, No. I, p.383.
- (22) Yensen: Journal of the American Institute of Electrical Engineers, 1924, vol. xliii., p. 455.
- (23) Yamada: Science Reports of the Tohoku Imperial University, 1926, vol. xv., p. 851.
- (24) Sauveur and Krivobok: Journal of the Iron and Steel Institute, 1925, No. II, p. 313.
- (25) Hatfield and Others: Transactions of the Faraday Society, 1925, vol. xxi., p. 272.
- (26) Bramley and Haywood: Iron and Steel Institute, Carnegie Memoirs, 1928, vol. xvii., p. 67.
- (27) Scott: Chemical and Metallurgical Engineering, 1922, vol. xxvii, p. 1156.
- (28) Tamura: Journal of the Iron and Steel Institute, 1927, No. I, p. 747.

- (29) Brayshaw: Journal of the Iron and Steel Institute, 1921, No. I, p. 131, (see pp. 211-214).
- (30) Brearley: "The Case-Hardening of Steel" p. 156, London, 1921, Longmans, Green and Co.
- (31) Jones: Research Department, Woolwich, R.D. Report, No. 55, 1922.
- (32) Greaves: Research Department, Woolwich, R.D. Report, No. 57, 1923.
- (33) Carpenter, Hadfield, and Longmuir: "Seventh Report to the Alloys Research Committee," Proceedings of the Institution of Mechanical Engineers, 1905, p. 857.
- (34) Jones: Journal of the Iron and Steel Institute, 1923, No. I, p. 439.
- (35) Andrew, Rippon, Miller, and Wragg: Journal of the Iron and Steel Institute, 1920, No. I, p. 527.
- (36) Waterhouse: Journal of the Iron and Steel Institute, 1905, No. II, p. 376.
- (37) Dejean; Revue de Metallurgie, Memoires, 1917, vol. xiv., p.641.
- (38) Scott: Bureau of Standards, Scientific Paper, No. 376, 1920.
- (39) Kase: Science Reports of the Tohoku Imperial University, 1925, vol. xiv., p. 173.
- (40) Guillet: Bulletin de la Societe d'Encouragement, May, 1903, p. 658.
- (41) Le Chatelier: Revue de Metallurgie, 1904, vol. i., p. 334.
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