

DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 58

INVAR AND RELATED NICKEL STEELS

[1st Edition.]

Issued April 4, 1916



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1916

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INVAR AND RELATED NICKEL STEELS

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1. HISTORICAL AND INTRODUCTORY

The Bureau proposes to issue from time to time, as may be possible with the limited staff available for this purpose and as there may be demand for them, circulars of information concerning some of the more interesting and important classes of metals and alloys.

The present circular, issued in response to many requests received by the Bureau for information concerning invar, describes some of the most important properties of nickel steels in general, but

with particular reference to that alloy, which owes its name to its extremely small thermal expansion at ordinary temperatures.

The account is largely a compilation of results obtained during the last 25 years by various investigators, from the writings of whom figures, tables, and text have been freely taken.

Ferronickels were first made commercially in France in 1885, and our knowledge of them goes back to a publication by Stodart and Farraday in 1822.

In 1889 James Riley, of Glasgow, described before the Iron and Steel Institute his epoch-making investigation which disclosed the remarkable mechanical properties of nickel steels. His tests were made on a series of alloys containing various amounts of nickel up to 49 per cent, which had been prepared for him in France by the inventor, Marbeau. At the conclusion of Riley's lecture J. F. Hall, of Sheffield, announced that he, too, had for sometime been experimenting with nickel steels; and he supplemented Riley's statements by describing the superior qualities which these steels had exhibited when made into various articles that were subjected to severe treatment.

Later in the same year Hopkinson discovered that a sample of 25 per cent nickel steel furnished to him by Riley was practically nonmagnetizable at ordinary temperatures, the permeability being only about 1.4 and the induction proportional to the magnetizing force. It retained its nonmagnetic condition while being heated up to 700° or 800° C, and it did not recalesce on cooling from a high temperature. But when the temperature was reduced to a little below 0° C, ferromagnetic properties appeared, which were strongly intensified by further cooling. Moreover, cooling to below -50° C with solid carbon dioxide effected such a transformation that, when the specimen was returned to 13° C, it was found changed from a nonmagnetizable to a decidedly magnetizable substance; and it remained magnetizable on heating until 580° C was reached. In the neighborhood of this temperature it again became nonmagnetizable and continued so on cooling to the temperature of the room. By these experiments Hopkinson showed that the material can, at ordinary temperatures, exist in either of two quite different states, both of

which are stable. In passing he pointed out that the same kind of thing can be seen in a much less degree at a higher temperature with ordinary steel.

Early in the following year (1890) Hopkinson described the results of further experiments on wire of the same material. Among other things he showed that the heat treatment which caused such remarkable changes in permeability produced corresponding changes in the electrical resistance and in the elastic properties. For example, changing from the nonmagnetizable to the magnetizable condition changed the electrical resistivity at room temperature from 72 to 52 microhm-cm¹ and the ultimate tensile strength from 50 tons weight per square inch with 32 per cent elongation to 87 tons weight per square inch with 7.5 per cent elongation. A few months later Hopkinson brought out still another paper, in which he described the magnetic properties of a graded series of steels containing from 1 to 73 per cent nickel; and in June of the following year (1891) he pointed out that the transformations of the 22 per cent and the 25 per cent alloys from the nonmagnetizable to the magnetizable state by cooling to -100°C were accompanied by such increases in volume that the densities on return to room temperature were found lowered by about 2 per cent.

Systematic studies of the methods of manufacture of nickel steels and nickel-chrome steel, suitable for military purposes—armor plate, cannon, etc.—were carried out on an extensive scale by the metallurgical plants of Europe and America during the decade 1890 to 1900. The metallurgists and engineers associated with certain works, notably those of Hadfield in Sheffield and the French firms of Saint-Etienne and Commentry-Fourchambault d'Imphy, made a series of elaborate investigations of the properties of nickel steels, including many combinations of nickel with iron; the effects of carbon, manganese, and other elements; and the changes due to heat treatments. These studies are set forth at length in the papers of A. Abraham (*Annales des Mines*, 1898), and particularly in that of A. Dumas (*Annales des Mines*,

¹ A resistivity of 1 microhm-cm means that a rod having a cross-sectional area of 1 cm² will have a resistance of 1 microhm per centimeter of its length. The designation "microhm-cm" is now replacing the familiar "microhms per cm".

1902), metallurgist of the Société de Commentry-Fourchambault, who has made the most thorough and complete metallurgical contribution to our knowledge of nickel steels. These investigations showed that the pure ferronickels—i. e., those containing little or no carbon—were of very different properties from the nickel steels. Dumas also showed that it was not practicable to manufacture without adding manganese, which element, in proportions 0.30 to 0.70 per cent, appears necessary to obtain a forgeable material, which may be made in either the open-hearth or the crucible furnace. Dumas notes that, in general, nickel gives a fibrous texture to steel, increases its tenacity, ductility, and resistance to shock and to oxidation, and to a less degree improves its hardness.

Osmond, in a series of contemporaneous investigations on the interrelations between the composition, thermal treatment, metallography, and physical properties was able to give the first clear rational explanation of the latter in terms of the transformations in the nickel steels. This has permitted a ready classification of the nickel steels, which will be mentioned later.

During 1895 Benoît, then director of the International Bureau of Weights and Measures, in the course of calibrating a length standard of steel containing some 22 per cent nickel and 3 per cent chromium, discovered that the linear coefficient of thermal expansion at ordinary temperatures was more than 18×10^{-6} per degree centigrade, or about as great as that of average bronze—that is to say, considerably greater than that of either iron or nickel. Somewhat over a year later Guillaume found the expansion of a bar of 30 per cent nickel steel to be about one-third less than that of platinum, which has a coefficient of only 9×10^{-6} . In the hope of obtaining alloys of very small expansivity by increasing the proportion of nickel, Guillaume, with the cooperation of the Société de Commentry-Fourchambault, carried out an elaborate study of nickel steels of varied composition. This resulted in the discovery of alloys having coefficients of linear expansion at ordinary temperatures ranging from a small negative value (about -0.5×10^{-6}) to a rather large positive value (about 20×10^{-6}). The dimensions of the alloy containing about 36 per cent nickel along with small amounts of manganese, silicon, and chromium, in all about 1 per cent, were found to

remain almost invariable with ordinary atmospheric changes of temperature. For this reason, Guillaume, at the suggestion of Prof. Thury, named it "Invar." The alloy containing 46 per cent nickel and 0.15 per cent carbon, which was found to have nearly the same expansivity as the glass of incandescent electric-light bulbs, and has consequently been used to replace platinum for the sealed-in wires, was called "Platinite."

As Hopkinson had previously found from measurements of magnetic induction, so Guillaume found from measurements of thermal expansion that nickel steels do not follow the usual law of mixtures, but present marked anomalies.

These discoveries of Riley, Hopkinson, Dumas, Osmond, and Guillaume formed the starting point of many important investigations which have resulted not only in accumulating much data on the properties of nickel steels, but also in developing theories for explaining their peculiarities.

2. REVERSIBLE AND IRREVERSIBLE NICKEL STEELS

In endeavoring to form an image of what anomalies—thermal, magnetic, electrical, and mechanical—may be expected to exist in nickel steels of various compositions, the characteristics and transformations of pure iron and of medium carbon steels should be kept in mind.

Iron has two thermal transformations—one of considerable magnitude, A_3 , and a relatively minute one, A_2 —each accompanied by more or less abrupt changes in some physical properties. The addition of carbon adds a third transformation, A_1 , and lowers the position of A_3 progressively until A_2 is reached for about 0.4 per cent carbon, leaving A_2 unaltered. With further additions of carbon, A_3 becomes identical with A_1 at about 0.85 per cent carbon at 695°C on cooling. In pure iron the transformation on heating, Ac_3 , is located at 910°C , and on cooling, Ar_3 , at 898°C , while $Ar_2 = Ac_2$ is located at the constant temperature 767°C . A_2 may be called a reversible transformation and A_3 an irreversible one. The transformation A_2 is associated with the final loss of ferromagnetism on heating and its gain on cooling. Also, the electrical resistance increases very rapidly as A_2 is approached, and the resistance-temperature curve has an inflexion at A_2 .

With A_3 is associated a marked change in electrical resistance extending over an interval of about 25° , accompanied by even a drop in resistance with rising temperature if equilibrium is maintained. This is accompanied by marked crystallographic changes and abrupt changes of mechanical properties as well as of volume. The transformation due to carbon, A_1 , takes place at a temperature some 25° or more higher on heating than on cooling, when it usually occurs at about 695°C , the exact temperature, as well as the range Ac_1 – Ar_1 , depending on the other elements present and on the rate of heating or cooling.

Certain elements, such as manganese and nickel, are capable of exerting pronounced effects in modifying, retarding, extending, or even suppressing some of the above transformations with corresponding modifications of the physical properties of the material. The properties of such a complex alloy as invar will therefore be found dependent upon its previous history, and especially upon the degree of completeness with which physico-chemical equilibrium has been attained for the temperature at which the alloy is investigated.

(a) EQUILIBRIUM DIAGRAM.—In Fig. 1 is shown the equilibrium diagram of the pure iron-nickel series of alloys according to Guertler and Tammann as determined thermally, slightly modified as suggested by Tammann, taking into account the δ modification of iron above 1420° as determined by Curie and by Ruer and Schütz. It is seen that below 1420° there are four series of solid solutions, as shown in the figure, and a considerable region, below 25 per cent nickel, consisting of a heterogeneous mixture. The regions shown as dotted are uncertain. The two metals, iron and nickel, are capable of being melted in all proportions into a homogeneous solid solution of γ iron and β nickel. The nickel is seen to lower greatly the A_3 point of pure iron until in the region of the composition corresponding to invar, or from 25 per cent nickel, this transformation has been brought down to ordinary room temperatures.

The diagram applies only, of course, to the pure iron-nickel series and on the assumption that the heat changes are slow enough for the reactions to complete themselves or for the establishment of equilibrium. It is interesting to compare Fig. 1,

showing the thermal changes, with Fig. 11, the diagram of magnetic transformation. It is seen they are clearly analogous. The addition of carbon, especially if accompanied by sudden or con-

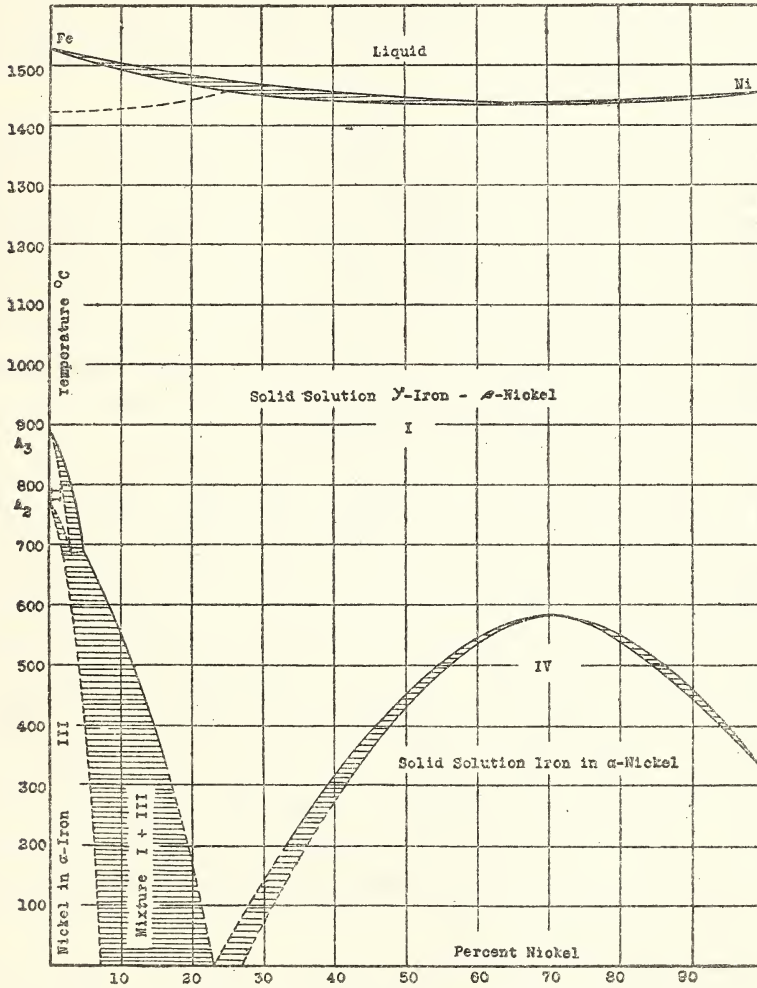


FIG. 1.—The iron-nickel equilibrium diagram

siderable changes in temperature, greatly complicates matters and may give rise to many anomalies; thus, at the same temperature the same nickel steel may be either magnetic or nonmagnetic, as noted above.

The position of the alloy "invar"—corresponding to about 36 per cent nickel—in the diagram, is seen to be such that this alloy would be expected to be subject to changes due to temperature variations, especially as the presence of carbon may still further lower and retard the transformation interval. Thus, invar at ordinary temperatures may readily be in an unstable condition located on the boundary between regions I and IV.

(b) MICROSTRUCTURE AND CONSTITUTION.—The changes produced in the microstructure of steel by the addition of varying amounts of nickel are best illustrated by the method developed by Guillet for the study of ternary steels. The effect of nickel in lowering the critical transformations of iron-carbon alloys (the Ac and Ar changes) has previously been referred to. In case the transformation has been lowered to atmospheric temperature, or nearly so, the microstructure, which in the carbon steels exists ordinarily only at high temperatures, becomes the stable form for the nickel steel at ordinary temperatures.

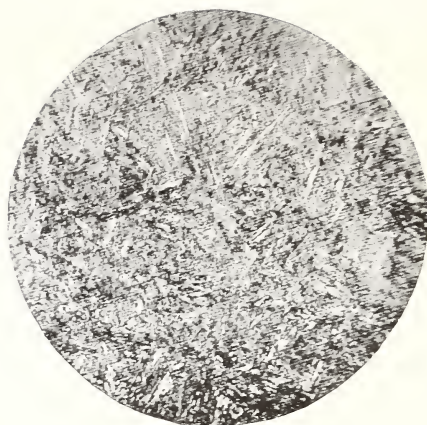
Fig. 2 shows graphically the structural conditions existing in nickel steels of varying composition after slow cooling. The diagram should not, however, be followed too closely, since there are still some points in the behavior of these steels which are not explained by it. The diagram also affords a rational basis for the classification of the nickel-steel series into groups for the study of their various properties. (See sec. 8, Mechanical properties.)

The ordinary commercial nickel steels fall within area I, "Pearlitic steels." These do not differ materially in structure from the pure carbon steels; they consist of a pearlitic matrix with excess ferrite or cementite, according to whether the particular steel is above or below the eutectoid percentage (0.85 approximately). The nickel, most probably, is dissolved in the ferrite and does not enter into combination with the carbon to form a carbide, as is the case in some alloy steels.

If the carbon content is held constant, increasing amounts of nickel cause the steel to assume, first, a martensitic structure and, finally, an austenitic one, with intermediate transition stages. Likewise, with a given nickel content, similar changes in the microstructure may be brought about by progressively increasing the percentage of carbon. While the microstructure, and hence the



1. $C = 0.12$; $Ni = 2.0$. Pearlite (dark) and ferrite (white)



2. $C = 0.12$; $Ni = 15.0$. Martensite



3. $C = 0.12$; $Ni = 30.0$. Austenitic structure; invar is very similar in appearance



4. $C = 0.80$; $Ni = 25.0$. Similar to No. 3



5. $C = 0.12$; $Ni = 25.0$. Quenched from $800^{\circ}C$; the outlines of the polyhedral austenite crystals show in the matrix of martensite



6. $C = 0.80$; $Ni = 15.0$. The steel, austenitic at ordinary temperatures, has been rendered martensitic by cooling to $-182^{\circ}C$ in liquid air; unetched

FIG. 3.—Microstructure of selected nickel steels. (Guillet)

Compare with Fig. 2 for their relation to the various structural fields of the diagram. Etching with picric acid; magnification in all cases: $300\times$. The material of Nos. 1, 2, 3, and 4 is in the "normal" condition, i. e., it has received no special thermal treatment after working

mechanical properties, can be profoundly changed by heat treatment, as in the case of pure carbon steels, the fact should be emphasized that structural conditions which are metastable for ordinary carbon steels and are produced by special heat treatment, may be the stable forms here after slow cooling if the metal has the proper proportion of nickel and carbon. Invar and the closely related alloys fall within area *III*. The microstructure shows the polyhedral crystals characteristic of austenite and of

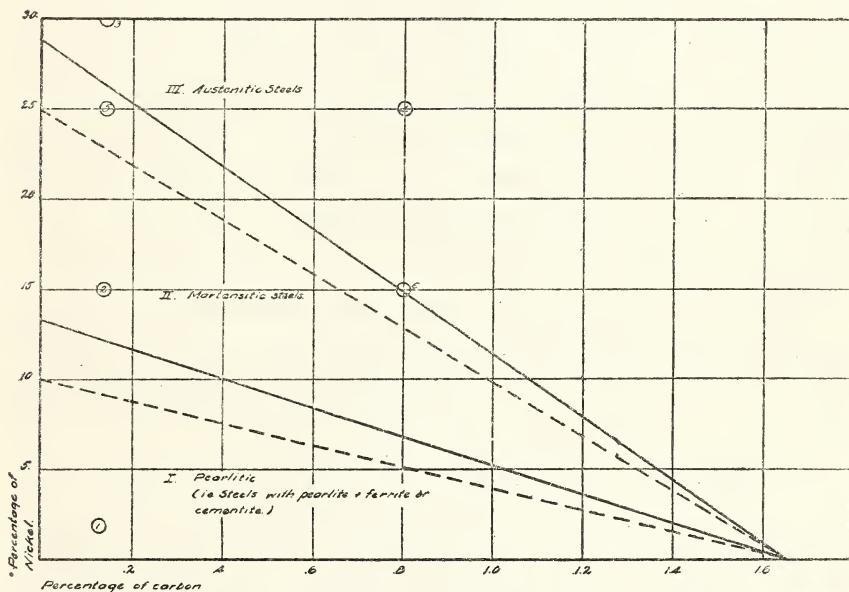


FIG. 2.—Constitutional diagram for Ni-Fe steels

solid solutions in general. The photomicrographs of several selected types (Fig. 3) show the structures for varying amounts of nickel; the position of each in the diagram is indicated by a circle inclosing the number designating the specimen.

It follows, therefore, from a consideration of Figs. 1 and 2, and is shown by experiment, that when an alloy of iron and nickel (which may contain some 0.3 per cent carbon and small percentages of manganese and silicon) cools from the neighborhood of 1000° C, its physical properties change regularly until at a certain temperature, which depends upon the composition of the alloy,

the appearance of striking anomalies marks the beginning of a transformation. With continued loss of heat the alloy rapidly assumes ferromagnetic properties, contraction almost ceases, or may even be replaced by expansion, the rate of cooling diminishes, and the modulus of elasticity, which had been gradually increasing, drops considerably. After the transformation is complete the properties again change normally with continued cooling. If more than a certain proportion of nickel is present, warming will cause a complete reversal of these changes, so that when any given temperature is again reached the alloy will resume the properties it formerly possessed when cooling through this same temperature. If, however, the proportion of nickel is less, a given property is not resumed on warming until after passing (often considerably) beyond the temperature at which the alloy possessed this property on cooling—that is to say, nickel steels may be separated into two groups, the reversible and the irreversible alloys.

Guillaume classified alloys containing more than 25 per cent nickel as reversible under ordinary conditions and those containing less than 25 per cent as irreversible. He pointed out, however, that a given alloy may under some conditions change reversibly and under other conditions irreversibly. But the curves of magnetic induction which had been published by Hopkinson in 1890 showed unmistakably that the limit of irreversibility had not been reached with even 33 per cent nickel. Much of the long-standing uncertainty in regard to this limit seems to have been cleared up, at least for the pure ferronickels, by the magnetic investigations of Weiss and his pupils Hegg and Foëx, and by the expansion and density measurements of Chevenard, which are discussed later. In 1911 Weiss and Foëx brought out several lines of evidence to prove the existence of the compound Fe_2Ni (34.45 per cent nickel), already noted as probable by Osmond in 1899, and that the pure alloys containing less than this proportion of nickel were solid solutions of Fe_2Ni and iron. Chevenard's work published in August, 1914, contributes additional evidence of a totally different character, and indicates that the dividing line between the reversible and the irreversible groups corresponds, at least fairly closely, to this compound; but Weiss and Foëx found some irreversible magnetic

properties in alloys containing as much as 40 per cent nickel. Chevenard also concludes that the reversible and the irreversible transformations have separate origins and are superposable, and that the irreversible transformation, the magnitude of which is a function of the amount of free iron in the solid solution, and which disappears when this amount becomes zero, is the transformation $\alpha \rightleftharpoons \gamma$ of the free iron, modified by the presence of the compound Fe_2Ni .

In order to form a clear idea of the complex phenomena manifested by any given property (thermal expansion, for instance) of nickel steels it is essential to note the relations between variations of the property in question and corresponding variations in other properties. With this end in view it is convenient to begin with the magnetic properties.

3. MAGNETIC PROPERTIES

The investigations of Hopkinson, referred to in section 1, form an excellent starting point for getting an insight into the anomalies of nickel steels.

Figs. 4, 5, and 6 show the characteristics found for two steels having the following compositions:

Fe	Ni	C	Mn	S	P	Si
74.31	24.5	0.27	0.85	0.01	0.04	0.02 per cent.
66.19	33.0	0.28	0.50	0.01	0.02 per cent.

Fig. 4 represents the relations between induction and magnetizing force at 13°C after the alloys had been rendered magnetic by cooling to about -50°C . Figs. 5 and 6 show the variations of induction with temperature, together with the changes produced by varying the magnetizing force.

These two alloys show marked differences in their magnetic properties. The differences are particularly striking in the case of the induction-temperature curves. Small amounts of nickel added to iron have the effect of increasing the magnitude of the irreversible anomaly until a maximum is reached with approximately 25 per cent nickel. Still further increasing the proportion of this metal greatly reduces the anomaly by lowering the temperature at which ferromagnetism disappears on heating and raising that at which it appears on cooling, until both closely approach

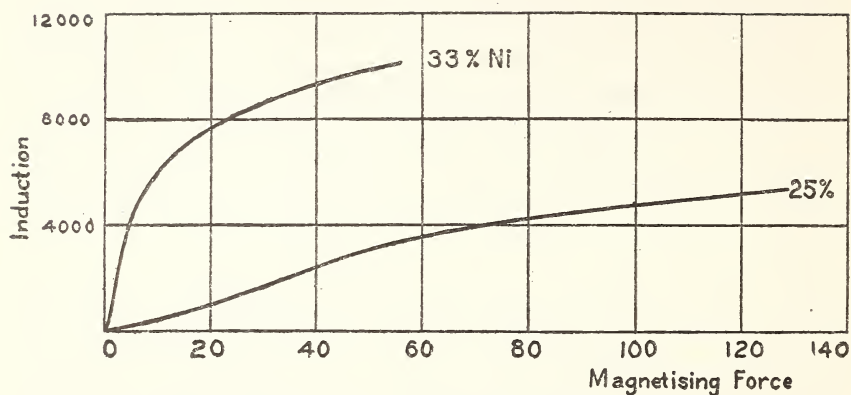


FIG. 4.—Magnetic induction in two nickel steels at 13°C. (Hopkinson)

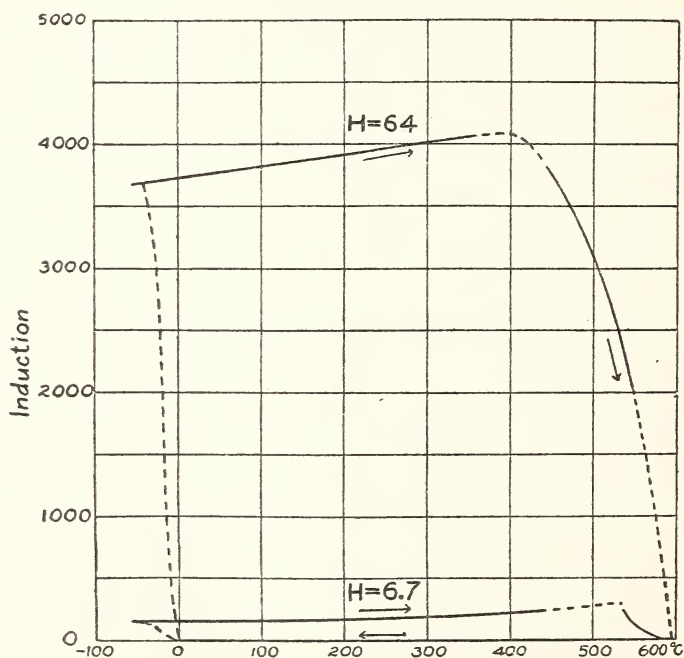


FIG. 5.—Variation of magnetic induction with temperature in a steel containing 25 per cent Ni. Magnetizing force 6.7 and 64 gauss. (Hopkinson)

each other in the neighborhood of 200°C . It is to be noted further that the 33 per cent alloy was found practically reversible when the magnetizing force was increased to 30.3 gauss.

Hopkinson also found that a steel containing 73 per cent nickel showed no material difference between the critical temperatures for heating and for cooling (600°C). He adds that "it is curious to remark that the induction for considerable forces is greater

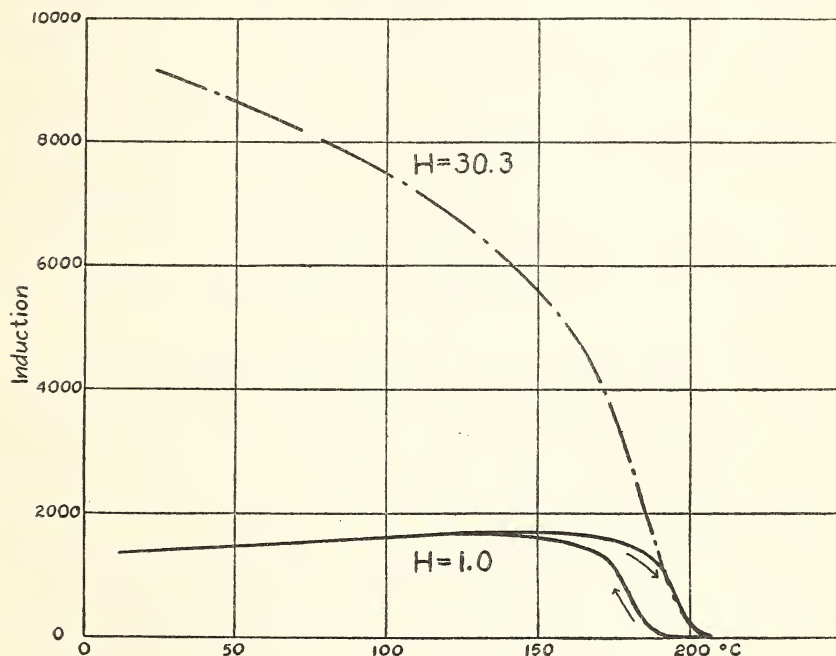


FIG. 6.—Variation of magnetic induction with temperature in a steel containing 33 per cent Ni. Magnetizing force 1.0 and 30.3 gauss. (Hopkinson)

than in the steel with 33 per cent nickel, and that it is greater than for a mechanical mixture of iron and nickel in the proportions of the analysis, however the particles might be arranged in relation to each other."

In 1897 Guillaume showed that the temperature at which ferromagnetism disappears (sometimes called the Curie point or, preferably, the critical point) in reversible nickel steels containing

28 to 40 per cent nickel could be represented approximately by the formula—

$$t = 34.1 (n - 26.7) - 0.80 (n - 26.7)^2$$

in which n represents the per cent of nickel in the alloy.

The following year E. Dumont, who studied the effect of temperatures ranging from about -80°C to $+250^{\circ}\text{C}$ and magnetizing forces from 14 to 50 gaussess upon 12 of Guillaume's alloys, pointed out that all those containing from 30 per cent up to at least 44 per cent nickel, if annealed, have induction-temperature curves similar to the curve of Fig. 6 for $H = 30.3$ gaussess, losing their magnetism gradually on heating, and that at the same number of degrees below the critical point all reversible alloys have the same permeability. At any given temperature the permeability of these alloys was found to increase with the proportion of nickel. The permeability of unannealed reversible alloys containing 39.4 per cent and 44 per cent nickel remained constant between 20° and 250°C .

In 1910 Hegg published his researches on the magnetic properties of a series of pure ferronickels (i. e., alloys free from carbon), the compositions of which varied by 10 per cent steps from pure iron to pure nickel. His measurements were made on small ellipsoids at temperatures ranging from -190°C to 760°C and with various magnetizing forces up to and beyond 10 000 gaussess. With $H = 10\,000$ gaussess he obtained the curves reproduced in Figs. 7, 8, and 9. These represent for each specimen the magnetic moment per unit mass² as a function of the absolute centigrade temperature T . Fig. 10, representing the alloy containing 50 per cent nickel, is typical of a series of figures (one for each reversible alloy) to show how the intensity of magnetization was found to change with the magnetizing force at each of a number of different temperatures.

After what has been said above, the essential features of Figs. 7, 8, and 10 are self-explanatory. Some explanation is, how-

² For technical purposes it is usual to consider the induction B or the intensity of magnetization I produced by a magnetizing force H . $I = \mathfrak{M}/V$, or the magnetic moment per unit volume; but for dealing with chemical problems Weiss has found it convenient to introduce the quantity $\sigma = \mathfrak{M}/M$, or the magnetic moment per unit mass. If the density is represented by D , then $\sigma = I/D$ and $B = H + 4\pi\sigma D$.

ever, necessary in the case of Fig. 9, representing the irreversible alloys.

The upper curves *A*, *B*, *C*, which show the successive values of the magnetization on warming, are analogous to those obtained with iron and the reversible alloys in that the disappearance of magnetism occurs gradually and appears to be almost independent of the time. Near *C* the curves commence to drop rapidly, the reversibility disappears, and the state of the alloy is a function not only of the temperature and the magnetizing force, but also

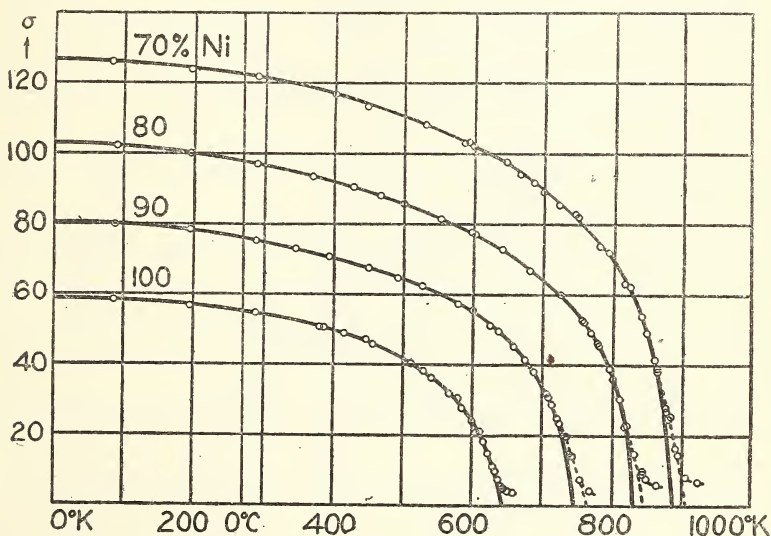


FIG. 7.—Variation of magnetic moment per unit mass with the absolute centigrade temperature K^3 of pure ferronickels. (Hegg)

of the time, which plays a preponderating rôle. On continuing the heating, the material loses its last traces of ferromagnetism at the transformation point on heating, Θ_1 .

During cooling the material retains its paramagnetic characteristics until the transformation point on cooling, Θ_2 , is passed, after which ferromagnetism appears with great rapidity. If the temperature is reduced enough to return the intensity of magnetization to the value it had before heating, the cycle will be closed. By similar treatment this can be repeated as often as desired.

³ K (from Kelvin) designates temperatures on the absolute centigrade scale; C on the ordinary centigrade scale with 0° the temperature of melting ice, or $273^\circ K$; also $T^\circ K = 273 + t^\circ C$.

While the first portions *A, B, C*, of the heating curves are very little influenced by the time and can be regarded as reversible during a series of experiments, the rapidly descending portions to the right of the lines *M N* in Fig. 9 can be perceptibly modified by the rapidity of the investigations. The nearer the temperature

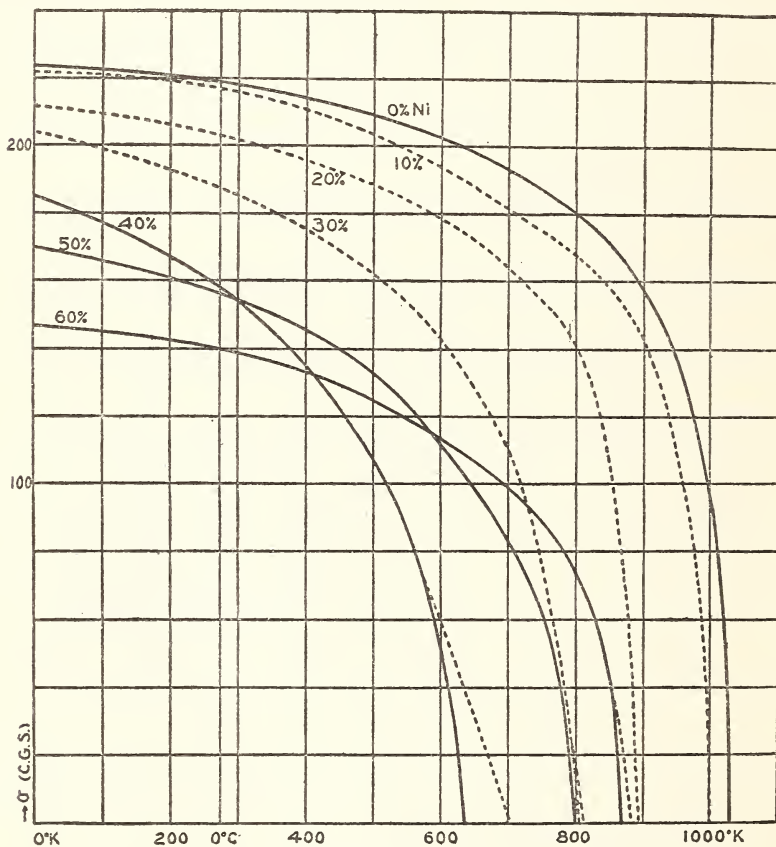


FIG. 8.—Continuation of Fig. 7. (Hegg)

is to Θ_1 and the longer it is held there the more advanced is the transformation. The return of ferromagnetism on cooling is characterized by still greater instability; the curves *E, F, G*, are not reversible, and it is very difficult to obtain the same values a second time. If on reaching any point of *E, F, G*, heating is resumed, the alloy will pass through a new cycle similar in all

respects except size to the one just described. The nearer the point at which reheating begins is to Θ_2 the smaller will it be.

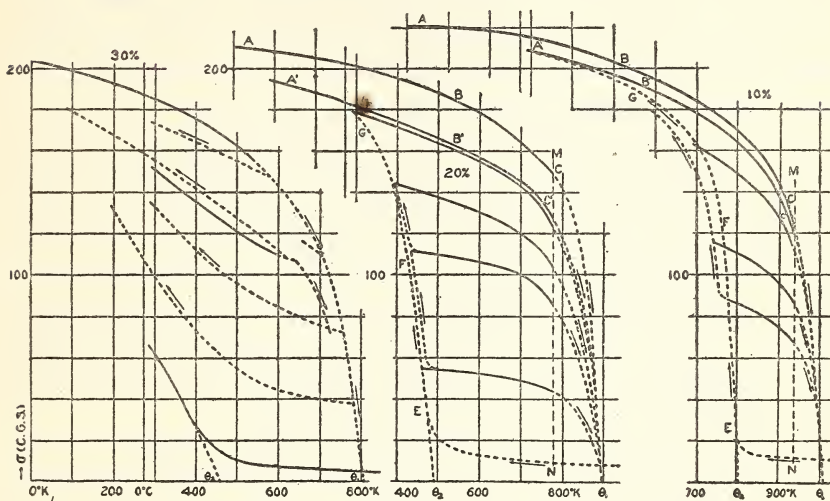


FIG. 9.—Continuation of Fig. 8. Irreversible alloys. (Hegg)

Among the properties common to all the curves A , B , C , A' , B' , C' , etc., the most important is their almost complete reversibility up to the region bounded by MN . The more rapidly the experiments are made the less do these curves differ from those obtained with the reversible alloys. For the sake of clearness the reversible portions of Fig. 9 are drawn with full lines and the irreversible portions with dotted lines, the arrows indicating the directions in which the latter are traversed.

Another quite unexpected

property noted by Hegg was that if lines corresponding to any two different temperatures were drawn parallel to the axis of σ across the reversible curves for a given alloy, the ordinates cut off by these curves would be very nearly proportional. From

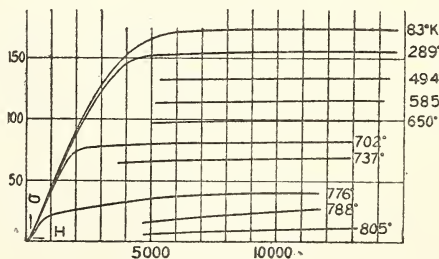


FIG. 10.—Variation of magnetic moment per unit mass with magnetizing force in an alloy containing 50 per cent Ni and 50 per cent Fe at different absolute centigrade temperatures. (Hegg)

this he concludes that a part of the material is in the paramagnetic state, and up to a certain temperature $M N$ offers such a stability that the reversibility is not altered. It is, then, only in the region between $M N$ and the point Θ_1 that the ferromagnetic material not yet transformed would undergo at constant temperature partial or complete transformation to any great extent.

If, however, the alloy is maintained at a sufficiently low temperature, the excess of paramagnetic material will very gradually be transformed into the ferromagnetic state. For example, the alloy containing 30 per cent nickel, after having been heated beyond the transformation point, was measured at room temperature. Three weeks later its permeability was found to be 5 per cent greater. Thus, ageing a nickel steel at low temperature increases its ferromagnetic properties, while annealing at a temperature near the transformation point decreases them.

In Fig. 11 the abscissas indicate percentages of nickel (0 per cent corresponding to pure iron and 100 per cent to pure nickel) and the ordinates the temperatures on the absolute centigrade scale which Hegg found for the transformation points Θ . These were determined by extrapolating to the axis of temperatures the curves representing I^2 when the magnetizing force was 10 000 gauss. For comparison with the work of earlier observers Hegg adds values obtained by A. Dumas magnetically, by Guertler and Tammann with the ordinary time-temperature cooling curve method, and by Boudouard thermoelectrically. The magnetic observations of Osmond and the thermal observations of Ruer and Schüz are also here included. It is to be noted that the transformation points Θ_1 and Θ_2 for the irreversible alloys lie on two straight lines which, if produced, intersect on the line corresponding to pure iron and $\Theta = \Theta_1 = \Theta_2 = (820^\circ + 273^\circ) K$; but the transformation point for pure iron was found to be $(758^\circ + 273^\circ) K$. Some of the discrepancies noted are not due to experimental errors, but to the effects of carbon and manganese on the location of the critical points.

Experiments of Weiss and Foëx made on the identical samples that Hegg used throw additional light upon the nature of the ferronickels. Weiss has pointed out that the two magnetic constants which are particularly characteristic for the solid homogeneous solutions of ferromagnetic bodies are σ_0 , the satu-

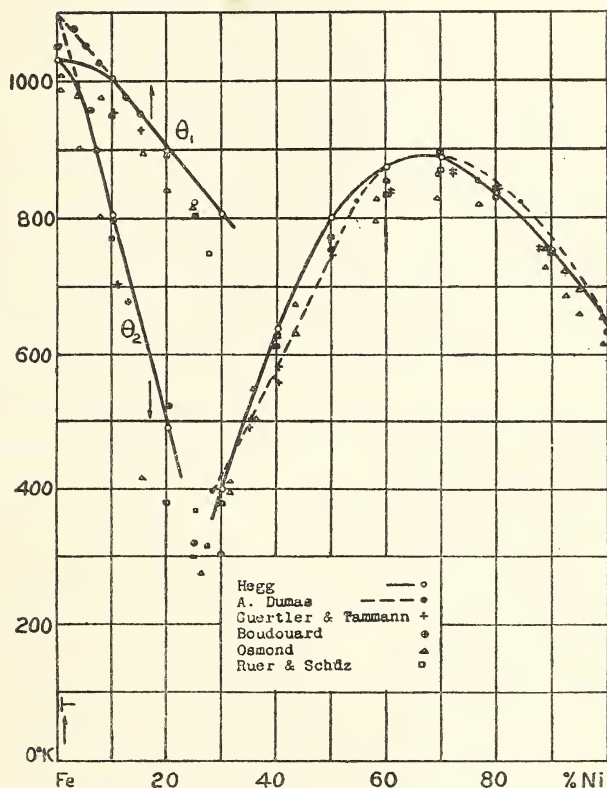


FIG. 11.—Absolute centigrade temperatures of magnetic transformation (Curie points) for pure ferronickels. (Hegg)

ration value of the magnetic moment per unit mass at the absolute zero of temperature, and C , the Curie constant.⁴ From the

⁴ In the case of paramagnetic bodies the susceptibility per unit mass χ is, for many substances and over wide temperature intervals, approximately inversely proportional to the absolute temperature T . The constant $C = \chi T$ is known as the Curie constant. If $\kappa = I/H = \mathfrak{M}/VH$ is the susceptibility as usually expressed in terms of magnetic moment per unit volume (see note 2, p. 16), then $\chi = \sigma/H = \kappa/D$.

kinetic theory of ferromagnetism Weiss has deduced the relation

$$C = \chi (T - \Theta)$$

in which Θ is the temperature of the Curie transformation point and T the temperature of the experiment. C is nothing but the

Curie constant which the substance would have if it were to become paramagnetic by the suppression of actions between the molecules. In a great many cases the linear variation of $1/\chi$ with temperature has been observed within intervals of several hundreds of degrees. Weiss has further shown that in the case of homogeneous solid solutions both σ_0 and C will vary as linear

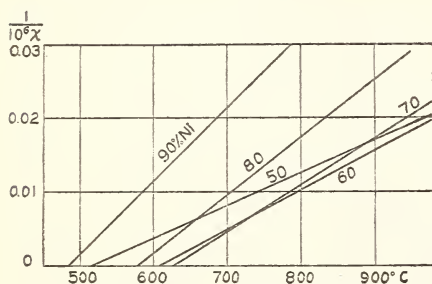


FIG. 12.—Reciprocals of susceptibilities per unit mass of pure ferronickels as functions of the temperature. (Weiss and Foëx)

functions of the composition. Honda and others have shown, however, that Curie's law can not be considered generally true and is never exactly true.

Figs. 12 and 13 represent the values of $1/\chi$ as functions of the temperature which Weiss and Foëx found from measurements on Hegg's ferronickels at temperatures above the Curie points. Each alloy containing more than 40 per cent nickel yielded a straight line from which both Θ and C could be determined by means of the relation $1/\chi = (T - \Theta)/C$.

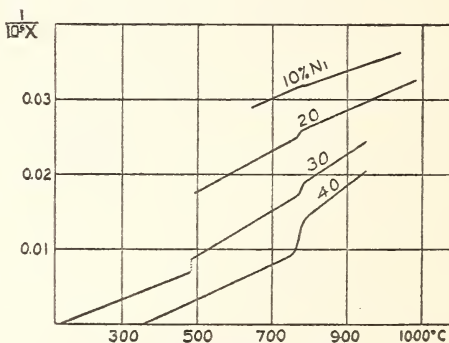


FIG. 13.—Continuation of Fig. 12. (Weiss and Foëx)

The alloy containing 40 per cent nickel presents some interesting features. On cooling from high temperatures $1/\chi$ at first followed a straight line giving a Curie constant of 0.0256. A second series of

measurements made with increasing temperatures gave a series of points which, except for a small and almost constant deviation, followed the same line. Since the deviation could be explained by lack of adjustment when the attraction was a maximum, the first portion appears to be reversible. The Curie point corresponding to this is $\Theta = (423^\circ + 273^\circ)K$ approximately, with $C = 0.0251$. On cooling from $790^\circ C$ to $730^\circ C$ a transformation takes place, after which follows another straight line for which $C = 0.047$ and $\Theta = (335^\circ + 273^\circ)K$. Below $730^\circ C$ the phenomenon is irreversible. On warming, the points fall below those obtained on cooling, the heating curve tending to join the cooling curve as $730^\circ C$ is approached. But the phenomenon is complicated by its variable dependence on the time in the irreversible regions. In the transformation region the alloy is still reversible. The last series of experiments gave a third line, not represented in the figure, which was reversible within a small region and characterized by $C = 0.091$ and $\Theta = (300^\circ + 273^\circ)K$.

The alloys containing 10, 20, and 30 per cent nickel resembled the 40 per cent alloy in many respects (Fig. 13). All showed the same irreversibilities and the same type of transformation at about $790^\circ C$; and all gave several Curie temperatures Θ and Curie constants C corresponding to restricted temperature intervals.

The lower broken line in Fig. 14 represents the Curie constants C derived by Weiss and Foëx from Fig. 12 and from the high temperature portions of Fig. 13. The upper one shows Hegg's values of σ_0 , the magnetic moment per unit mass at saturation, obtained by extrapolating to absolute zero the results of measurements carried down to liquid air temperatures. The results for both C and σ_0 point strikingly toward the existence of the compound Fe_2Ni . Weiss and Foëx draw the following conclusion: "The ferronickels form two uninterrupted series of solid solutions, the first between Fe and Fe_2Ni , the second between Fe_2Ni and Ni." The location of Fe_2Ni appears also to be associated with the transition region from irreversible to reversible nickel steels as shown in Fig. 11.

Table 1 contains some of the numerical data given by Hegg and by Weiss and Foëx which are plotted in Figs. 11 and 14. The values for the temperatures of the Curie points deduced by the

latter investigators from lines representing $1/\chi$ as functions of T are not included because they differ considerably from those obtained by the more direct methods of other observers even in the case of the reversible alloys, while they contain such fictitious results as temperatures below the absolute zero in the case of the irreversible alloys and γ iron.

Magnetostrictive effects in iron, nickel, and nickel steels have been studied by the Japanese physicists Nagaoka, Honda, and Shimizu, the alloys investigated containing various amounts of nickel ranging from 24 to 70 per cent.

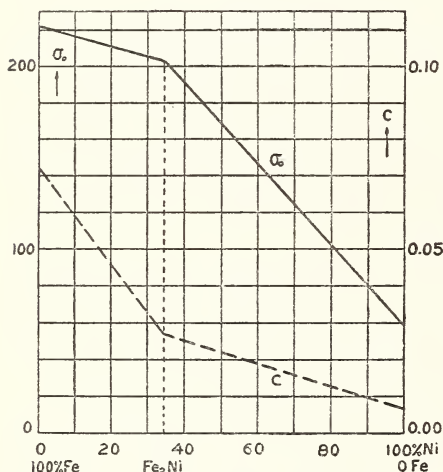


FIG. 14.—Curie constants and saturation magnetic moments of ferronickels. (Weiss and Foëx)

In all the nickel steels examined, longitudinal magnetization produced increase of length (the Joule effect), and, reciprocally, mechanical elongation produced increase of magnetization. A specimen after annealing elongated more than when in the hard-drawn state. The elongation caused by magnetizing a wire under tension was reduced and in some cases even changed to a contraction by increasing the load.

The effect of cooling on the magnetic elongation was similar to its effect on the intensity of magnetization. In steels containing more than 28.7 per cent nickel the elongation was diminished in weak fields and increased in strong fields by cooling in liquid air. In steels containing less nickel the initial decrease of elongation vanished. The ratio of the elongation in liquid air to that at ordinary temperatures increased in strong fields with decrease of nickel content. With a magnetizing force of 500 gauss it amounted to 1.6 with 36 per cent nickel, 3.7 with 28.3 per cent, and 160 with 24.4 per cent. The elongations before and after cooling reversible nickel steels were the same, but the

elongations of irreversible steels were always greater after cooling. A 25 per cent nickel steel did not elongate appreciably at either ordinary temperatures or that of liquid air.

Because of its bearing on the use of nickel steels in constructing measuring apparatus the length changes produced by fields as weak as that of the earth were investigated and found to be generally less than 10^{-7} .

The increases in volume of magnetized ellipsoids were found to be practically proportional to the magnetizing forces for each alloy tried. In the alloys of small thermal expansivity the effect observed was far greater than anything that had ever been found in other ferromagnetic substances.

The torsion produced in nickel steels by the combined action of longitudinal and circular magnetic fields (the Wiedemann effect) was found similar to that previously observed in the case of iron.

Reference to magnetostrictive and other experiments at the Bureau of Standards is given in section 6 (j).

4. ELECTRICAL PROPERTIES

Guillaume failed to find any marked differences in the electrical resistivities of his various nickel steels, all those studied ranging between 80 and 90 microhm/cm at ordinary temperatures.

For temperature changes between 20° and 150° C he also failed to find any anomalies in the resistance corresponding to the anomalies in other properties. The results he obtained for several alloys are given in Table 2.

That the nickel steels do, however, show anomalies in the change of electrical resistance with temperature was pointed out by Hopkinson in 1890, as mentioned on page 5. Fig. 15, which is reproduced from Hopkinson's paper, shows the irreversibility of his 25 per cent alloy over a region which coincides fairly closely with the region in which he found such remarkable irreversibility in magnetic properties. Boudouard (1903) located transformation regions by resistance changes in three steels containing from 3 per cent to 3.7 per cent nickel. Schleicher and Guertler (1914) have also found anomalies in the resistance changes with temperature. The three alloys which they examined, containing 25.2,

30.6, and 35.26 per cent nickel, behaved very irregularly in passing through the critical regions.

Numerous investigators besides Guillaume have measured with commercial accuracy the electrical resistivity of nickel steels at

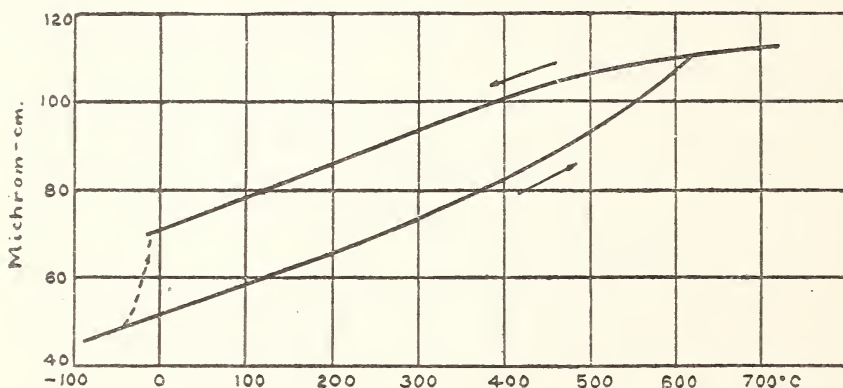


FIG. 15.—Variation of electrical resistivity with temperature in an irreversible steel containing 25 per cent Ni. (Hopkinson)

room temperatures. Since, however, the results have been complicated by the presence of irregularly varying elements in addition to iron and nickel, it is difficult to see just what effect follows

directly from changing the proportion of the latter metal.

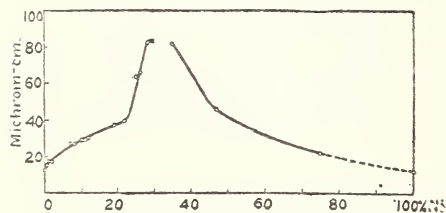


FIG. 16.—Electrical resistivity of pure ferro-nickels. (Burgess and Aston)

A graded series of very pure ferronickels, made by melting together electrolytic iron and electrolytic nickel, was examined by C. F. Burgess and James Aston. Table 3 contains the results of resistance measurements which they published in

January, 1910. Fig. 16 represents them plotted as a function of the per cent of nickel present. The point for 100 per cent nickel is taken from a standard handbook (not mentioned). They ask: "Might not the maximum point in this curve of resistance be at 34 per cent of nickel, corresponding to the compound Fe_2Ni ?" This is very probable and is strengthened in view of the magnetic observa-

tions of Osmond and of Weiss and Foëx noted above, of the expansion measurements of Chevenard, and the thermal observations of Guertler and Tammann.

The thermoelectric properties of the ferronickels do not appear to have been subjected to systematic quantitative investigation. Boudouard, however, in 1904, located transformation regions by means of thermal electromotive forces due to temperature differences between the ends of 10-cm bars that resulted from the natural temperature gradient along the axis of the electric furnace in which the bars were heated.

5. THERMAL EXPANSION ⁵

At the same time that an irreversible nickel steel gradually assumes ferromagnetic properties on cooling, it gradually undergoes a change in volume—a change which is also irreversible. Fig. 17 illustrates the behavior of a bar containing 15 per cent nickel which was investigated by Guillaume. On cooling from cherry red it contracted at first, following the nearly straight line *A B*. Near 130° C a rapid expansion began, which soon reached

⁵ The term "thermal expansivity" is used in this circular to designate the expansion per unit length of a material, whether this characteristic is expressed by means of a numerical coefficient, an equation, or a curve.

If L_0 represents the distance between two points of a body at 0°C and L the distance between the same two points at some other temperature t° , it is often convenient to express the expansivity by an equation of the form—

$$\frac{L-L_0}{L_0} = at + bt^2 + ct^3 + \dots \quad (1)$$

It is more common, especially among technical men, to use the *mean zero coefficient of linear expansion* between two limiting temperatures t_1 and t_2 , defined as

$$\bar{\alpha}_{1/2} = \frac{1}{L_0} \cdot \frac{L_2 - L_1}{t_2 - t_1} \quad (2)$$

Again, when one is concerned with the rate at which a length changes at a particular temperature t , it may be desirable to use the *true zero coefficient of linear expansion at t°* , defined as the limit approached by $\bar{\alpha}_{1/2}$ as both t_1 and t_2 approach t , which, in the notation of the differential calculus, is

$$\alpha = \frac{1}{L_0} \frac{dL}{dt} \quad (3)$$

The expression "coefficient of expansion" is often used so indiscriminately that it is difficult to make out whether the user has in mind $\bar{\alpha}_{1/2}$ or α or something else. For small temperature ranges and the accuracy ordinarily required it is immaterial; but the expansion frequently deviates enough from a linear function of the temperature change to make discrimination a matter of importance. If the expansivity is expressed by some such equation as (1), it is a matter of simple algebra to derive whatever coefficient may be needed for a given purpose; but the behavior of the alloys described in this circular is so complicated that even such equations are not feasible except within restricted temperature ranges, so that curves must be resorted to.

as high a value as 40 microns⁶ per meter per degree. If the bar was then reheated, it did not contract according to the curve it followed on cooling, but it expanded according to some such line as *D C*. Cooling again caused the bar to return to *D* and then continue along the curve toward *E*. At low temperatures under certain circumstances the contraction along such a line as *C D* might continue perhaps 15° C beyond the curve *B E*, and then be followed by a sudden change which brought the bar to the same length it would have reached at the existing temperature if

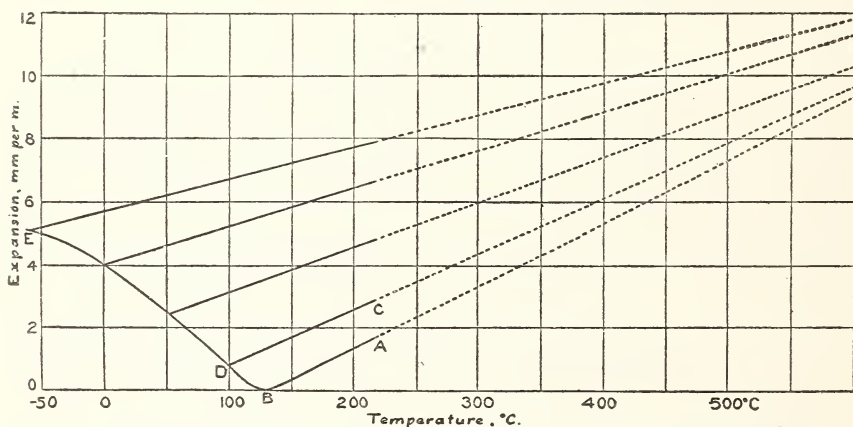


FIG. 17.—Variation of length with temperature in an irreversible steel containing 15 per cent nickel. (Guillaume)

it had followed the curve *B E* immediately after reaching *D*—a phenomenon analogous to the undercooling of a saturated solution or of a liquid that has passed below its normal freezing temperature.

Since by appropriate cooling the changes of length with temperature may be made to follow any such line as *C D*, it is evident that the coefficient of expansion, which is proportional to the slope, may, for the very same bar, be caused to assume any desired value between the limits allowable by the transformation. These limits may include values ranging all the way from 10 millionths to 20 millionths. In the case of the 15 per cent nickel steel, illustrated in Fig. 17, lowering the temperature to -60° C was not sufficient to complete the transformation into the state which is stable at very low temperatures.

⁶ 1 micron = 1μ = 0.001 mm.

All the irreversible nickel steels exhibit the phenomena just described, which correspond strikingly with the magnetic anomalies discussed in section 3. They differ from one another only in the magnitude of the changes and in the particular temperature regions within which the transformations occur.

The expansion phenomena exhibited by the reversible nickel steels appear to be quite different. By applying the principle of corresponding states to the results of measuring different alloys within a moderate temperature range, Guillaume concluded that the thermal expansion of a reversible nickel steel would be represented by a curve having the general characteristics of Fig. 18. Expansion measurements carried up to 900°C , which were published by Charpy and Grenet in 1902, supported this conclusion.

On cooling a reversible alloy from a high temperature there is, first, a normal contraction following a nearly straight line FE , the inclination of which always corresponds to an expansivity greater than that of iron or of a mixture of iron

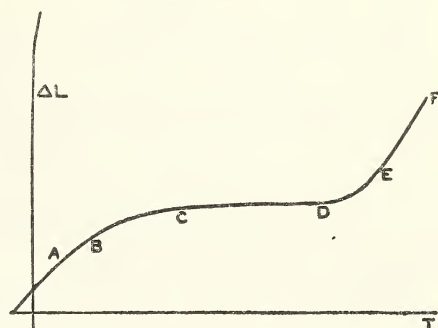


FIG. 18.—Typical curve representing the variation of length with temperature in a reversible nickel steel. (Guillaume)

and nickel at ordinary temperatures, and is reduced by increasing the proportion of nickel except for small nickel contents. Then, within the temperature range which is characterized by the appearance of magnetic properties, there is a region of rapid change, ED , which is soon followed by a regular region DC of very small slope. At still lower temperatures this is followed by another region of rapid change, CB , and then by a regular one BA , the slope of which corresponds to the expansivity of a mixture of iron and nickel at ordinary temperatures.

At ordinary atmospheric temperatures the expansivity of an alloy containing very little more than 25 per cent nickel would be represented, roughly, by EF ; between about 27 and 32 per cent by DE ; up to 36 or 37 per cent by CD ; up to 48 or 50 per

cent by $B C$; and above this, especially above 60 per cent, by $A B$ or the portion below A .

At higher temperatures each region corresponds to alloys containing greater proportions of nickel. The complete curve from

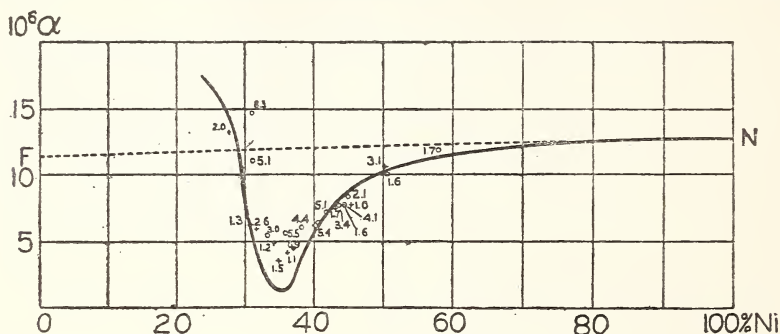


FIG. 19.—True coefficients of linear expansion at $20^{\circ} C$ of nickel steels. (Guillaume)
Curve, normal alloys; o, alloys containing the designated per cent of manganese; +, alloys containing chromium

A to F gradually deforms somewhat and shifts as a whole parallel to the axis of temperatures, following step by step the curve of magnetic transformation, Fig. 11.

Tables 4 and 5 show how Guillaume found the thermal expansivity of nickel steels to change with the composition and with

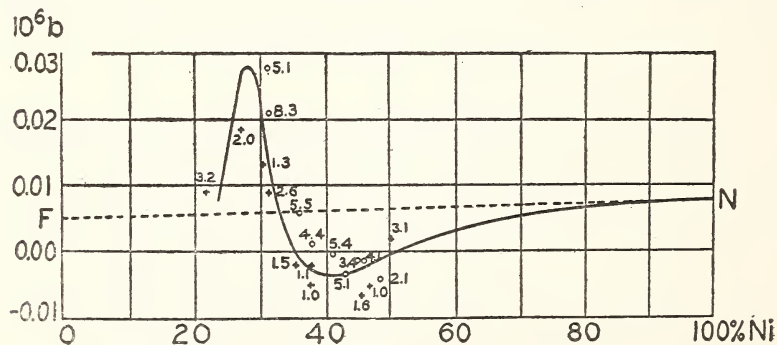


FIG. 20.—Values of the quadratic coefficient in the formulas for the linear expansivity of nickel steels. (Guillaume)

Curve, normal alloys; o, alloys rich in manganese; +, alloys rich in chromium

the temperature. Figs. 19, 20, and 21 show how varying the composition affected the true coefficient of linear expansion at $20^{\circ} C$. These tables and curves describe alloys cooled in the air

after a simple hot forging. They contain the usual quantities of manganese, silicon, and carbon, in all about 1 per cent. Guillaume states that these additions, of which he considers manganese (about 0.5 per cent) the most essential, are necessary to render the alloys workable; but that they produce a noticeable effect upon the expansivity. By reducing them to a minimum and by giving the alloys a certain course of thermal and mechanical treatment the expansivity has been lowered; and, in the case of alloys containing about 36 per cent nickel, the expansivity has been rendered zero and even negative. The straight line FN in Fig. 19, which joins the expansivity of iron with that of nickel at 20° , and which represents the results to which the law of mixtures would lead, shows clearly the magnitude of the anomaly. The corresponding line FN in Fig. 18 has a similar significance.

The small circles in Figs. 19 and 20 show results obtained with alloys containing an abnormally large proportion of manganese, the percentage of which is indicated near each circle. The crosses refer to alloys containing chromium.

Fig. 21 shows how the addition of 1 per cent manganese or of chromium affected the expansivity.

With the normal quantities of carbon and manganese present it is difficult to reduce the expansivity below 1.2 or even 1.5 millionths per degree centigrade. One can indeed go below this with alloys containing very little manganese; but lack of manganese introduces serious metallurgical difficulties. However, by the exercise of great care in carrying out a certain series of operations, it has been possible to realize a mean coefficient of linear

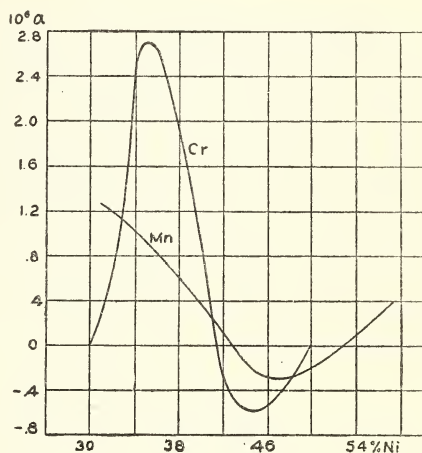


FIG. 21.—Effect upon the linear expansivity of nickel steels produced by adding 1 per cent manganese or chromium. (Guillaume)

expansion between zero and t° with the negative value (deduced from measurements between 0° and 38° C) of

$$(-0.552 + 0.00377 t) 10^{-6}$$

Moreover, by carefully adjusting the conditions to secure only part of the maximum possible reduction in expansivity, several hundred meters of wire had been produced as early as 1903 with an expansivity of

$$(+0.028 - 0.00232 t) 10^{-6}$$

A wire of this alloy, 1 km long, would contract in passing from 0° to 20° C by an amount less than 0.4 mm. Used for the measurement of geodetic base lines, it would render entirely superfluous the determination of its temperature, an operation which in the past has formed one of the great difficulties in accurate surveying. The following table, giving side by side the elongations in microns of a meter of platinum, a meter of this wire, and a meter of bessemer steel ⁷ when warmed from zero to the temperature indicated, shows what perfection has been attained in the industrial production of invar.

Temperature, in degrees centigrade	Platinum	Invar	Steel
10	88.6	+0.05	121
20	177.6	-0.36	242
30	266.9	-1.26	364

The processes by which these remarkable results were obtained are, however, applicable to small quantities only.

By means of expansion measurements at temperatures ranging from -195° C to over 700° C and density measurements at ordinary temperatures Chevenard has extended the work of Guillaume and has accomplished much in the way of giving us organized knowledge of the peculiarities of nickel steels of low carbon content. His experiments, published in 1914, were conducted on a graded series of 26 forged alloys containing from 0 per cent to 98

⁷ Containing 0.06 per cent C, 0.079 per cent S, 0.093 per cent P, 0.39 per cent Mn, and 0.011 per cent Si. Expansion determined at the Bureau of Standards.

per cent nickel. These contained less than 0.05 per cent carbon, less than 0.10 per cent silicon, and a total of foreign elements which hardly exceeded 0.50 to 0.70 per cent. Chevenard, as well as Guillaume, states that the most important of the additional elements is manganese, and that a minimum amount is indispensable for mechanical working, as was previously noted by Dumas.

Before measuring expansions Chevenard took the precaution to have all his specimens cooled sufficiently to transform them completely into the state which is stable at very low temperatures. Some of them were cooled with liquid hydrogen to -253°C (20°K) by Kamerlingh Onnes in the cryogenic laboratory at Leyden. After these had returned to room temperature they were found to have been permanently elongated by the following amounts:

Percent Ni	Millimeters per meter
25.9	7.6
29.2	5.5
30.6	5.0
31.9	1.2
33.5	0.3
34.1	Imperceptible.
35.4	Imperceptible.

The change in dimensions of the 31.9 per cent alloy was found to be exactly the same if the cooling was carried to only -195°C instead of -253° . Consequently, the transformation of this alloy, which begins at about -125° , is entirely completed at -195° ; so that the vanishing of the irreversible elongation can not be ascribed to failure to effect complete transformation. From this, Chevenard, bearing in mind the results obtained magnetically by Weiss and his pupils, concludes that the limit of the irreversible alloys corresponds to the compound Fe_2Ni (34.45 per cent nickel).

This conclusion is further supported by the curves of Figs. 22 and 23, which represent the elongations found by Chevenard on changing the temperature of his irreversible steels in the directions indicated by the arrows. When the iron is very pure the two temperatures A_c and A_r (which mark the beginning of the trans-

formation on heating and on cooling) differ but few degrees. The addition of nickel produces, on the one hand, a lowering of the

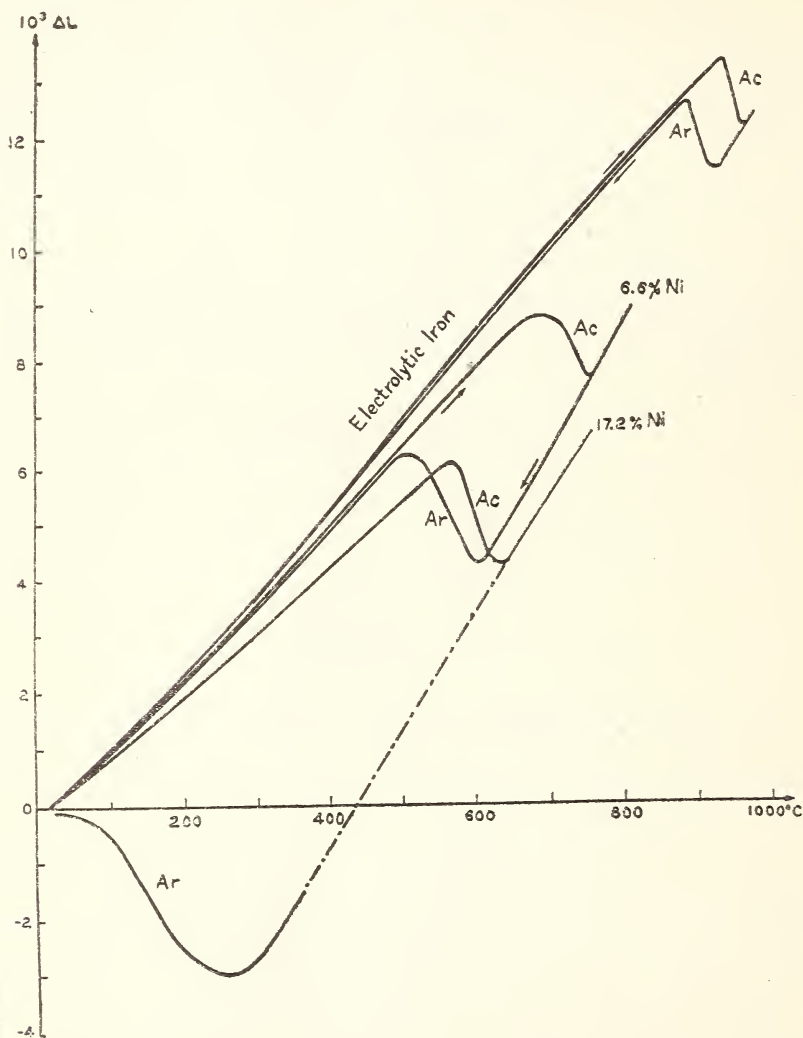


FIG. 22.—Variation of length with temperature in electrolytic iron and in irreversible nickel steels having compositions between Fe and Fe_2Ni . (Chevenard)

transformation Ac , and, on the other, a considerable increase in the difference $Ac-Ar$. For a given alloy this difference depends

upon the conditions of cooling, principally on the rate of temperature change; but if the experiment is repeated with slower and slower rates, the difference $Ac-Ar$ will be found to approach

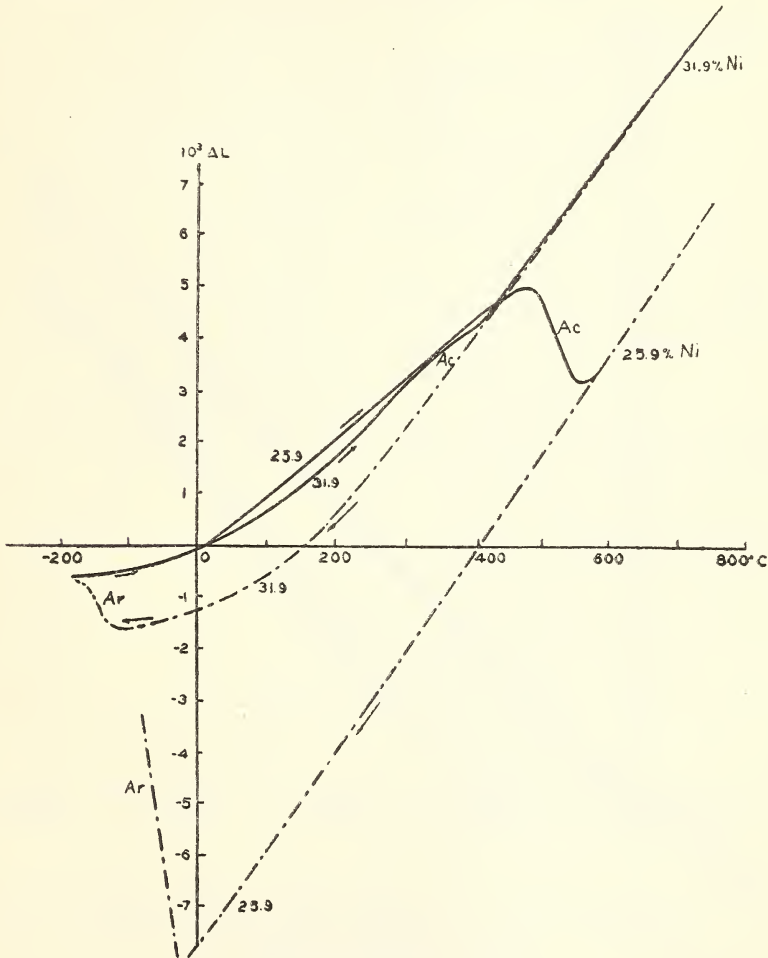


FIG. 23.—Continuation of Fig. 21. (Chevenard)

a finite limit which is the true thermal hysteresis of the transformation.

When the proportion of nickel exceeds 25 per cent, the point Ar falls below ordinary room temperatures (Fig. 23). Consequently,

nickel steels containing more than 25 per cent habitually show the characteristics of the state which is stable at high temperatures, and behave quite differently from the steels containing less nickel, which are normally in the state that is stable at low temperatures.

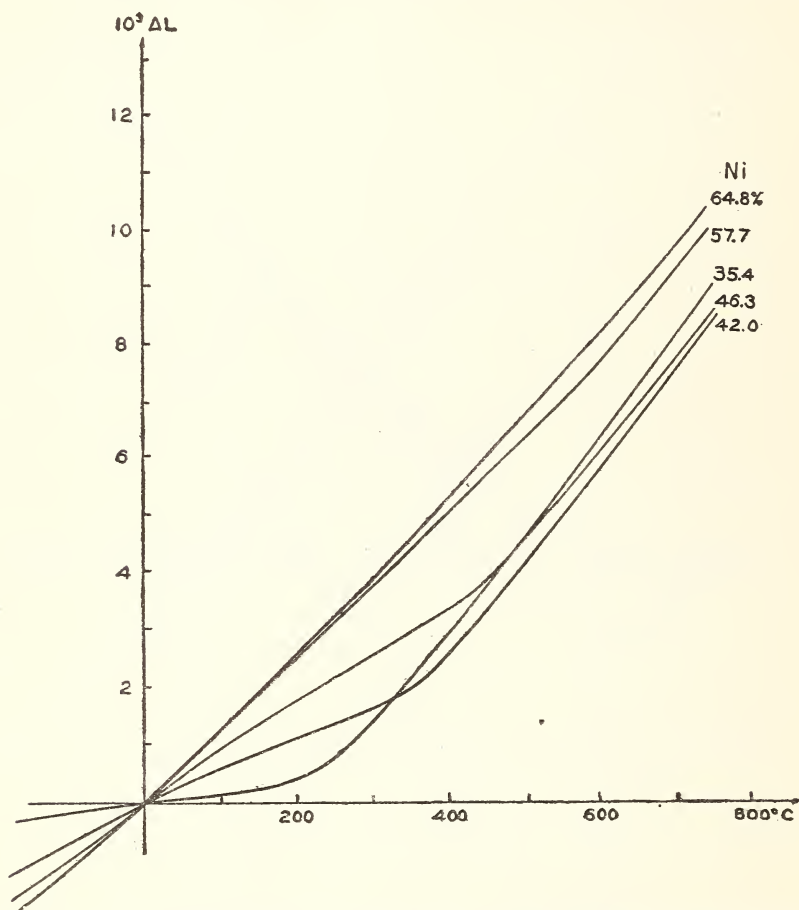


FIG. 24.—Continuation of Fig. 22. Reversible nickel steels with compositions between Fe_2Ni and FeNi_2 . (Chevenard)

In the 31.9 per cent alloy the transformation point A_r is at -125°C . Comparison of the curves for the two alloys represented by Fig. 23 shows that as the proportion of nickel approaches that in the compound Fe_2Ni the length change accompanying the irreversible transformation diminishes and appears to approach zero as a limit.

The alloys comprised between the limits Fe_2Ni (34.45 per cent Ni) and FeNi_2 (67.75 per cent Ni) were found to be reversible and to follow expansion curves having the general characteristics of Fig. 18 discussed above. Fig. 24 reproduces a group of such curves. It is seen that the alloy of composition approximating invar (35.4 per cent Ni) behaves normally as to expansion above 200°C , and, in fact, has very closely the constants of Bessemer steel. The variation in the true coefficient of expansion of each alloy is represented by Fig. 25, which shows clearly how the anomaly changes progressively with the composition. The corresponding

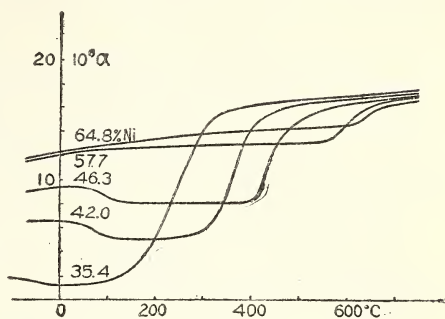


FIG. 25.—Variation of the true coefficient of linear expansion with the temperature in the nickel steels represented in Fig. 23. (Chevenard)

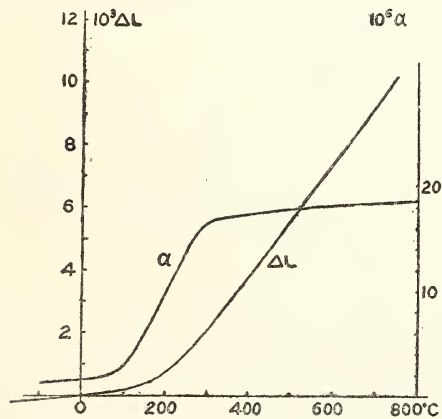


FIG. 26.—Variation of length and of the true coefficient of linear expansion with temperature in a reversible steel containing 34.1 per cent Ni. (Chevenard)

curves for the alloy containing 34.1 per cent nickel (very nearly Fe_2Ni) are given separately in Fig. 26. This alloy is the only one of the group that does not show a bend corresponding to BC in Fig. 18; that is to say, its true coefficient of expansion always decreases with cooling until at least -150°C . The bend BC appears in the alloy of 35.4 per cent, and the curve of the true coefficient has a minimum—the minimum of invar.

From these results it appears that the reversible anomaly gradually disappears as the alloy approaches the composition corresponding to FeNi_2 , which contains 67.75 per cent nickel.

Various observers have noticed peculiarities in the thermal expansion of nickel at temperatures above 300°C . Colby (1910) examined three specimens of different origin and found that all

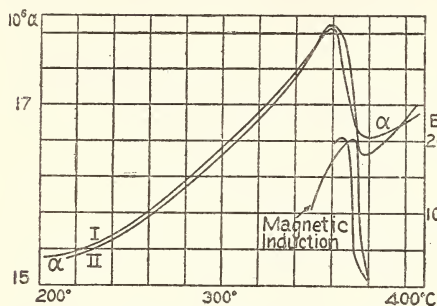


FIG. 27.—Variation of the true coefficient of linear expansion and of magnetic induction with temperature within the critical region of electrolytic Ni. (Colby)

showed abrupt changes in the value of the true coefficient of expansion as ferromagnetic properties disappeared on heating. The curves which he obtained with a sample prepared electrolytically are reproduced in Fig. 27. Chevenard's measurements indicate that the ferronickels comprised between the limits FeNi_2 and Ni show expansion anomalies of the same sort, decreasing with the addition of iron to pure nickel until they disappear completely when the composition FeNi_2 is reached. He found that the change with temperature in the true expansion coefficient of such an alloy was represented by two straight-line segments meeting on the ordinate through the Curie point, as shown in Fig. 28; and he points out that in the whole series of ferronickels, the one having the composition FeNi_2 is the only one the expansion of which can be represented by a single parabolic function of the temperature between 0° and 800°C .

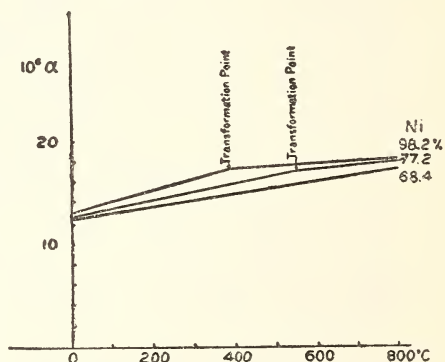


FIG. 28.—Variation of the true coefficient of linear expansion with the temperature in reversible nickel steels having compositions between FeNi_2 and Ni. (Chevenard)

Fig. 29 is a résumé of Chevenard's expansion measurements on nickel steels. Each curve shows how varying the proportion of nickel affects the true coefficient of linear expansion at the temperature indicated. The alloys containing less than 34.45 per cent nickel are represented in the state that is stable at high tem-

peratures, in which state their properties are reversible. The curve for 0°C differs but little from Fig. 19, which Guillaume derived from measurements of far greater precision.

The curve for 700°C begins at the point corresponding to 5 per cent nickel, because alloys containing less than this amount do not exist at 700°C in the state which is stable at high temperatures. Nevertheless, it is interesting to note that if this curve, which is almost a straight line, is prolonged backward, it will

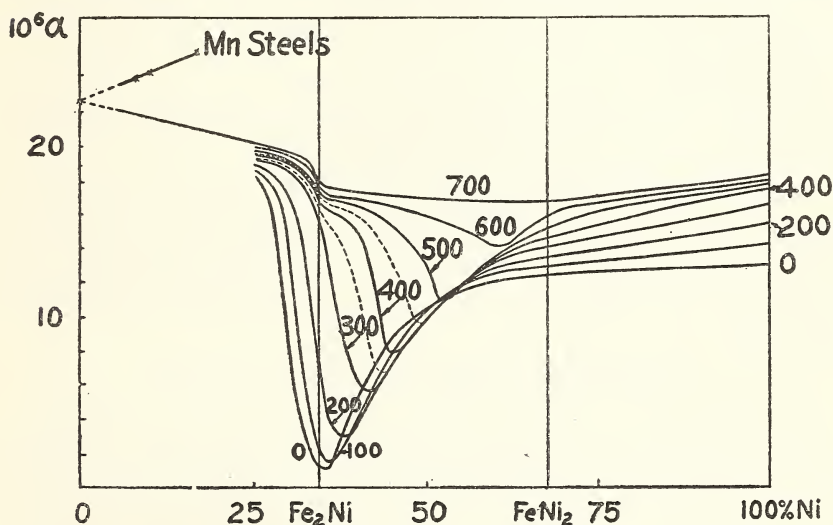


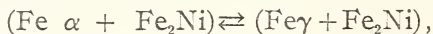
FIG. 29.—Variations in the true coefficient of linear expansion of Ni steels at various temperatures. (Chevenard)

cut the ordinate corresponding to pure iron in the same point as the prolongation of the line through the results of measurements on nickel steels containing considerable amounts of manganese. Chevenard refers to this point as indicating (hypothetically) the expansion coefficient of γ iron at 700°C .

The expansion investigations of Chevenard, supplemented by his measurements on density (which will be treated in a later section), led him to the following general conclusions concerning the ferronickels: The irreversible phenomena are associated with the transformation of iron; the reversible anomaly with a modification of the compound Fe_2Ni . While the external manifesta-

tions of these phenomena show such common features as reduction of volume and increase of rigidity on warming, nevertheless, there is an essential difference between the two.

According to Chevenard, the *irreversible transformation* consists in a reaction between the two solid solutions



each of which can exist within a certain temperature region. The two members of the reaction are two different phases; and the passage from one state to the other is accompanied by change in crystalline structure.

The *anomaly*, on the other hand, consists of a progressive and reversible modification of the properties of the alloys, which is spread over a large temperature interval.

The reversible anomaly reaches a maximum in the neighborhood of the compound Fe_2Ni , and gradually disappears on approaching the composition FeNi_2 , which forms the boundary between the anomalous reversible alloys and those showing the peculiarities of nickel.

6. CONSTANCY IN THE DIMENSIONS OF INVAR

(a) TRANSITORY LENGTH VARIATIONS FOLLOWING TEMPERATURE CHANGES.—In outlining the principal characteristics of the thermal expansion of nickel steels certain secondary phenomena were left out of consideration, although important in the practical application of reversible alloys where precision is a requisite. In reality the expansion does not follow rigorously a unique curve of the type shown in Fig. 18. After effects, similar to those observed in glass, are quite pronounced, so that the length of a bar at a given temperature depends, at least in the beginning, on the temperatures to which it has previously been subjected, and also on the rapidity with which the final temperature has been attained.

Consider, for example, a forged bar in the state corresponding to the region CD of Fig. 18, and suppose that its dimensions be measured from time to time while it is maintained constantly at any given temperature. If the bar had previously been exposed to a higher temperature, it will, after completing the main contraction accompanying the attainment of temperature equilibrium,

slowly elongate somewhat in the course of time. If, on the other hand, the bar has been brought to the given temperature from a lower one, it will contract. The duration of such length changes is always greater when the final temperature is reached by cooling than when it is reached by heating. In either case the higher the temperature the greater the speed with which the changes occur. Guillaume found that a meter of invar brought to 100°C immediately after forging elongates at the rate of about 0.067 micron per minute, whereas if brought to 100°C after a long rest at room temperature it contracts at the rate of 0.8 to 0.9 micron per minute. At 15°C the elongation is 0.07 to 0.08μ per day after forging and 0.03μ per day after annealing to 40°C . Again, after a long rest at room temperature (10 to 20°C) the contraction that occurs after assuming a higher temperature is complete in about half an hour at 100° , but continues for several days at 40° .

(b) PERMANENT CHANGES IN LENGTH AT CONSTANT TEMPERATURE.—In addition to these transitory length variations that follow change of temperature there are other changes that continue for a long time while the temperature remains constant. Thus, a bar of invar left to itself at any constant temperature gradually elongates slightly, at first rapidly, then more and more slowly, following an exponential function of the time as it approaches asymptotically a definite length. The rate at which this limiting length is approached increases with the temperature. In order to reduce these secular changes to a minimum Guillaume employs an ageing process or heat treatment which he calls *étuvage* (steaming or stewing) to differentiate it from the ordinary process of annealing (*recuit*). After the bars have been forged they are subjected to a series of very slowly decreasing temperatures, starting, for example, at 100°C and ending at 20° or 25° after an interval of two or three months.

(c) HEAT TREATMENT OF FORGED BARS.—The effects of heat-treating forged bars are shown in Tables 6, 7, and 8 and in Fig. 30. The upper curve of this figure represents the elongations observed during a period of 4500 days in a bar of invar simply cooled in the air after forging at red heat and then maintained almost constantly below 20°C . The lower curve represents the changes in a similar bar which had previously been reheated to

150° and then cooled in 50 days to 40°. Other experiments have shown that a bar of the same alloy cooled gradually for several weeks more down to 25° elongates afterwards according to the same curve, but starting from the point of which the coordinates are 100 days and 3 microns per meter. A curve which is almost the same has been found for bars that have been quenched or drawn, and even for wires, kept at the temperature of the laboratory after very slow cooling from 100° to 25°. On the other hand, rest at a higher temperature has continued the effect of the previous heatings and accelerated the elongation. In this way,

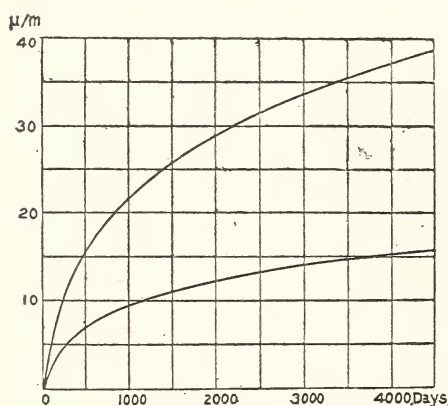


FIG. 30.—Elongations in microns per meter of invar with time. (Guillaume)

Upper curve, forged bar not treated; lower curve, forged bar cooled in 50 days from 150° to 40° C.

invar wires used for geodetic measurements in equatorial Africa have been found elongated after several years by three or four millionths of their length beyond what would be predicted according to the curve.

That the thermal expansivity of nickel steels is increased somewhat by the process of very slow cooling appears on examining the last column of Table 8. But after this treatment has once been completed, the

expansivity appears to remain constant for a long period, as is seen in the case of bars Nos. 6 and 7. Quenching, on the other hand, has been found to lower the expansivity of invar.

(d) BEHAVIOR OF DRAWN BARS.—Guillaume has found the behavior of drawn bars somewhat different from that of forged ones. The first reheating to 100° C caused an elongation for several hours followed by a contraction. At lower temperatures they behaved as forged bars, even if the contraction at 100° had hardly commenced. A drawn bar kept for a long time at the temperature of the laboratory and then brought to 100° shortened for perhaps half an hour, then elongated for several hours, and finally

shortened again for more than 100 hours. Thus one can observe successively in the same bar three distinct variations, differing in magnitude and in duration, of which the first two resemble those observed in forged bars, while the third is peculiar to drawn bars.

(e) **ELONGATION OF INVAR WITH TIME.**—Table 9 gives the elongations which a drawn forged bar of invar undergoes in the course of time counted from the completion of a gradual cooling lasting three months, starting at 100° C and finishing at 25° C. But in applying these corrections to the length of a geodetic wire or tape, the time is never counted from this point, since a wire or tape is rarely in suitable condition for calibrating until four or five months later. If, for example, calibration takes place 200 days after the cooling process is completed, a year still later the length indicated by the calibration equation should be corrected by adding $4.7 - 2.5 = 2.2$ microns per meter. Benoît and Guillaume have found the corrections in Table 9 to hold for wires kept in the laboratory; but, after use in the field under extremes of climate, these values should be considered only as provisional, and the equation of the wire should be checked by a new direct determination.

(f) **RANGE OF TRANSITORY LENGTH VARIATIONS FOLLOWING TEMPERATURE CHANGES.**—The transitory length changes discussed at the beginning of this section are similar to variations which occur in reaching a state of chemical equilibrium that depends upon the temperature. As there stated, the higher the temperature the more rapidly is this equilibrium attained. These variations leave the expansion of a bar of invar indeterminate between two extreme limits, namely, that corresponding to sudden attainment of the final temperature, and that corresponding to a rest at this temperature which is theoretically of infinite duration. For a temperature t between 0° and 100° C the difference between these two limits has been found to be well represented by the empirical formula—

$$\Delta L/L = -0.00325 \times 10^{-6} t^2$$

Fig. 31 represents the results of measurements together with those given by the interpolation formula. The latter are also collected in Table 10.

(g) RAPIDITY OF INVAR TRANSFORMATIONS.—Observations made upon the speed of transformation of invar lead to this practical rule: At ordinary temperatures consider daily variations as sudden and seasonal variations as infinitely slow. For example, if invar were employed in a base measurement, the mean temperature of the weeks immediately preceding would be considered as attained slowly, whereas the equation for thermal expansion is based on rapid changes; so that if the mean temperature of the season were 20°C while the equation of the invar had been determined after a long rest at 12° , the length should be corrected by -1.3 ± 0.4 or $-0.6 \pm 0.3 = -0.9$ micron per meter for all the

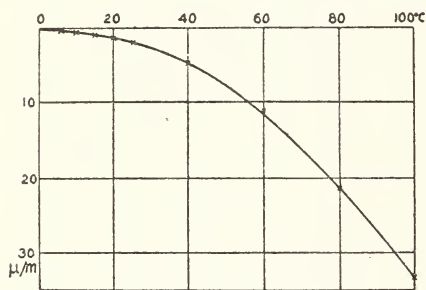


FIG. 31.—Temporary variations, in microns per meter, in the length of invar following rapid change in temperature. (Guillaume)

observations during the course of several days. Then, in addition, each separate measurement should be corrected for the temperature existing at the time of observation by applying the expansion formula determined during the calibration. Inspection of Table 10 shows that an uncertainty of 5 or 6 degrees in the temperature assumed for the season does not ordinarily affect a length determination by one part in a million. Except under very unusual conditions, then, one can apply these corrections with a certainty entirely sufficient for the needs of geodesy.

(h) EFFECT OF COMPOSITION ON INSTABILITY.—Guillaume has found that at a given temperature the instability of a nickel steel is greater the nearer this temperature is to that at which the alloy loses its magnetic properties. At ordinary temperatures the stability as regards variations produced either by time or by temperature change is increased by adding nickel up to a maximum of about 43 per cent. On exceeding this amount the direction of the length change becomes reversed, the contraction with time increasing slightly on adding still more nickel, but never becoming very great. A bar containing 43.6 per cent was measured immediately after forging and was then submitted to a gradual cooling

from 100° C to 30° C, which lasted three months. After this treatment its length was found only 0.7 micron per meter shorter than immediately after forging. A meter of 44.2 per cent nickel steel was shortened 2.6 microns by 66 hours at 100° immediately after forging. It then contracted 0.4 micron more during 2000 days and 1.1 micron during 4000 days at room temperature. A meter containing 56.2 per cent nickel was shortened 8.8 microns by 130 hours at 100° and subsequently 2.5 microns by 2000 days at room temperature.

The alloy of 42 per cent nickel is preferred for constructing standards of length because of greater stability than is possessed by invar, resistance to oxidation, and a thermal expansivity appreciably less than that of platinum. The alloy of 56 per cent, having an expansivity about the same as that of ordinary steel, and at the same time being more stable and less subject to corrosion, can be used in industrial measuring machines to avoid temperature corrections in testing the dimensions of steel parts.

(i) REPRODUCIBILITY OF THE PROPERTIES OF INVARI.—As to the uniformity of invar, it may be said that different wires from the same melt, and subjected to treatments that are apparently identical, show measurable differences in thermal expansivity; but the average deviation of these from the average does not amount to more than $\pm 0.03 \times 10^{-6}$; so that, if the same expansion formula is adopted for all the wires or bars from the same melt, it will require on the average a difference of 30° C between the temperature of calibration and that of use to introduce an error of one part in a million. This is more than is required for actual geodetic operations. Since the conditions for producing small expansivity are now well established, wires are regularly made which, after heat treatment, show an expansivity that does not exceed $\pm 0.1 \times 10^{-6}$ per degree. Thus, a precision of one part in a million does not require a knowledge of the temperature closer than about 10°.

(j) INVESTIGATION OF NICKEL STEELS BY THE BUREAU OF STANDARDS.—In cooperation with the Midvale Steel Company, the Bureau of Standards is conducting an investigation for the purpose of producing American steels of specified thermal expan-

sivity, combined with stability of dimensions and other desirable properties. At present steels of small expansivity are being studied to determine the effect of various thermal, magnetic, and mechanical treatments as well as of slight variations in the constituents. This has already resulted in the production of specimens which, as far as small expansivity is concerned, compare favorably with good French invar; but as yet sufficient time has not elapsed to show how stable they can be made in regard to length.

Expansion measurements have been made at many temperatures distributed between -150°C and $+620^{\circ}\text{C}$. In conformity with the experience of Guillaume it has been found that cold-drawing and quenching lower somewhat the expansivity at room temperatures while annealing raises it. Also, the curve representing the expansion on heating was found to lie above that representing the contraction on return to room temperature, except in the case of a cold-drawn specimen, in which the relation was reversed. At any temperature, however, above that at which the alloy assumes ferromagnetic properties on cooling the length was always found to be the same whether the temperature in question was reached by warming or by cooling.

The effects of cold drawing, annealing, and quenching are apparent from the following figures, which give in millionths per degree centigrade preliminary values of the true coefficient of linear expansion at 20°C found on warming specimens of the alloy marked No. 6 in Table 14 after they had been subjected to the treatments indicated:

Treatment	A	Annealed B	Quenched C
Rolled.....	1.2	1.7	0.7
Cold drawn.....	0.3	1.2	0.7

Additional significant figures are not given here because even those that are given may be expected to vary a few units in the last place with different specimens that are supposed to have the same composition and to have undergone the same treatment.

Even after warming the specimens just described to 100° C the coefficients at 20° C were found to have changed, and in some cases greatly changed.

Magnetostriction measurements have also been made at various temperatures extending from -75° C to over 300° C, and the expansion measurements have been carried up to 620° C. Observations made by Nagaoka, Honda, and Shimizu have been confirmed and extended. (See sec. 3.) It will suffice to mention here that complete magnetostriction cycles showing hysteresis, similar to those first observed by Nagaoka in the case of iron, have been taken at a series of temperatures up to that at which the magnetostriction vanishes, and that magnetic elongations exceeding 45 microns per meter have been measured. This appears to be the largest longitudinal magnetostriction effect on record. The greatest elongations in nickel steels noted by Honda and Shimizu were less than 31 microns per meter, and were observed in steels containing 36 and 46 per cent nickel when cooled in liquid air. Even the maximum contraction recorded by Nagaoka and Honda for nickel was only about 38 microns per meter.

An account of the investigations now under way at the Bureau of Standards on the properties of nickel steels it is hoped to publish shortly as a scientific paper of the Bureau.

7. DENSITY

Table 11 contains values of the density in grams per cubic centimeter which Guillaume found for some specimens of his nickel steels, which, as has been pointed out above, contained small amounts of other elements. The values which Hegg found for a series of pure ferronickels are contained in Table 1.

Chevenard determined the densities of the nickel steels described on page 32, taking great care to make sure that the specimens were free from bubbles, cracks, or other imperfections that might lead to errors. Internal strains were removed by annealing from a high temperature, and two specimens were taken from each melt. His results are reproduced by Fig. 32, in which the abscissas represent the percentages of nickel and the ordinates the specific volumes in cubic centimeters per gram (reciprocals of densities) at three different temperatures: 0° absolute, 0° C, and 750° C. His

determinations of thermal expansivity (see sec. 5) were used to compute these values from the values actually measured.

The specific volume curve for 0°C has two separate branches. The first, A_0B_0 , which represents alloys in the state that is stable

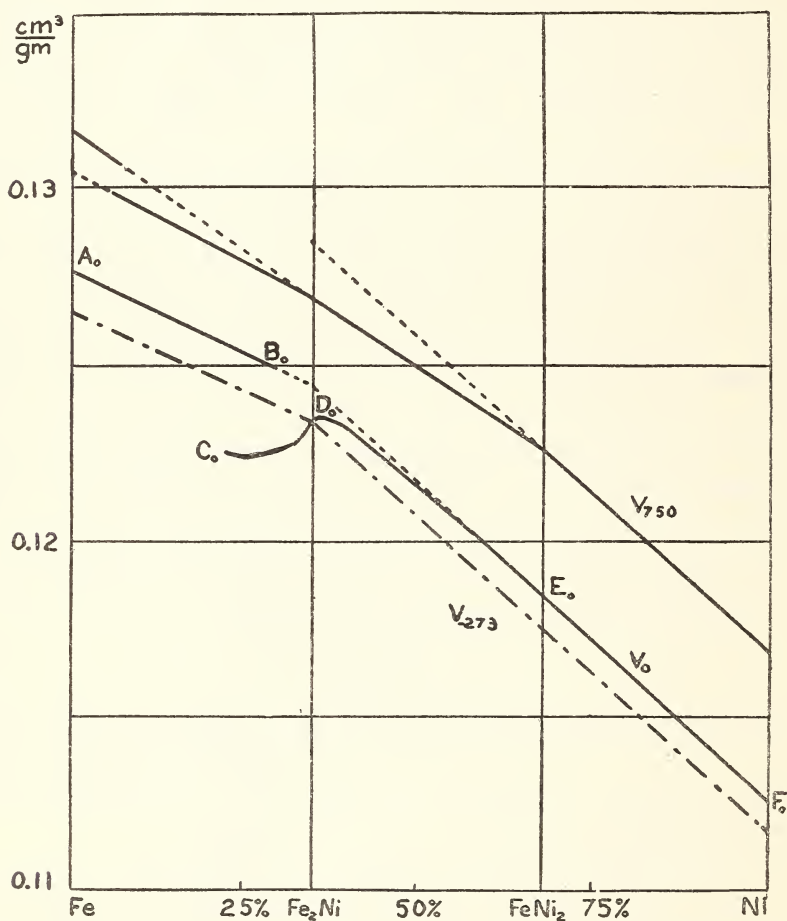


FIG. 32.—Specific volumes of nickel steels at 0°K , 0°C , and 750°C . (Chevenard)

at low temperatures, is straight. The second, $C_0D_0E_0F_0$, representing alloys in the state that is stable at high temperatures, begins with a marked anomaly (corresponding to the reversible expansion anomaly discussed in sec. 5), which gradually disappears as the composition of FeNi_2 is approached. Those alloys,

which can exist at 0°C in both states, are represented by points on both branches.

The curves for both 0° absolute (by extrapolation from measurements carried to -195°C) and for 750°C are broken lines showing no trace of the anomaly. It is significant to note that the changes of direction occur at points corresponding to Fe_2Ni and FeNi_2 .

8. MECHANICAL PROPERTIES

(a) STRENGTH, ELASTIC LIMIT, ELONGATION, REDUCTION OF AREA.—The mechanical properties of nickel steels are dependent not alone on the nickel content and the treatment which they have received; but small amounts of other elements usually found in steels, such as carbon and manganese, affect the properties appreciably. This may readily be seen when nickel steels are divided into groups according to their mechanical properties or their metallographic structures and depending on the carbon and nickel contents. Guillet gives the following division:

Per cent carbon	Per cent Ni		
	Group I	Group 2	Group 3
0.12.....	0-10	10-27	+27
0.25.....	0- 7	7-25	+25
0.80.....	0- 5	5-15	+15

In his discussion of the properties of nickel steels Giesen has a similar division but gives slightly higher percentages of nickel as the limits of each group.

The properties of the first group are similar to those of carbon steels with the strength and hardness slightly increased by the nickel.

The alloys of the second group have about the same properties as quenched high-carbon steels, having high tensile strength and elastic limit and low elongations.

The third group, including invar, have a medium breaking strength, low elastic limit, and are very ductile, though difficult to forge.

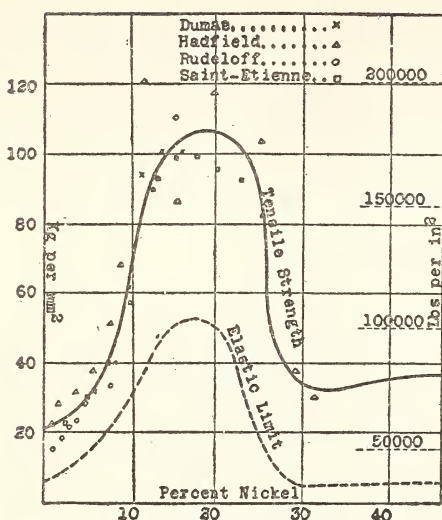


FIG. 33.—Tensile strength and elastic limit of nickel steels

tion with nickel content is dotted and might not seem to follow the plotted results of all observers. The values obtained for the elongation of annealed nickel steel by Les Aciéries de Saint-Étienne⁸ do not agree closely with those of other investigators, and the explanation of this difference is not apparent. The results of other observers on annealed nickel steel and a consideration of results on quenched nickel steels would indicate that the curve for elongation is as shown.

It is evident from a consideration of the groups of

Quenching increases the tensile strength and elastic limit of steels of the first and second groups. The only noticeable effect of quenching on alloys of the third group is a slight raising of the elastic limit.

Figs. 33 and 34 show the results of observations on the tensile strength, elastic limit, elongation, and reduction of area of annealed nickel steel with about 0.20 per cent carbon.

The probable curve showing the variation of elonga-

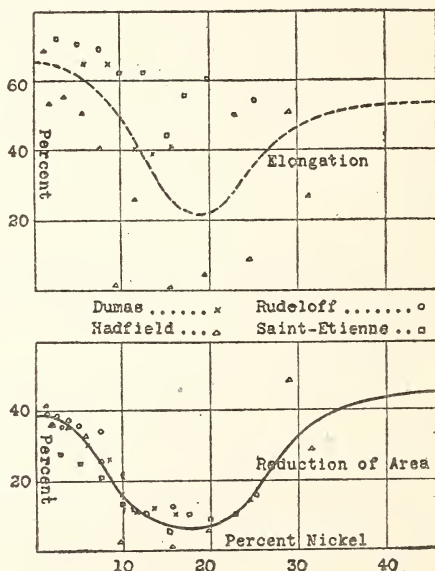


FIG. 34.—Elongation and reduction of area of nickel steels

⁸ See Dumas *Annales des Mines, Mémoires* 1, p. 377 (1902).

nickel steels that the greatest variation of properties with small additions in carbon would occur with a nickel content less than 27 per cent. However, the changes in alloys of the third group, including invar, are not small. The following are the results obtained by Dumas on steels containing about 29 per cent nickel:

Per cent carbon	Tensile strength		Elastic limit		Elongation	Reduction of area
	Kilograms per square millimeter	Pounds per square inch	Kilograms per square millimeter	Pounds per square inch		
0.11.....	52	74,000	34	48,000	Per cent 34.0	Per cent 64.0
0.32.....	68	97,000	45	64,000	33.0	57.0

Guillet made some tests on forged bars of nickel steel containing up to 30 per cent nickel and with 0.12, 0.25, and 0.80 per cent carbon. The results for a 30 per cent nickel steel were:

Per cent carbon	Tensile strength		Elastic limit		Elongation	Reduction of area
	Kilograms per square millimeter	Pounds per square inch	Kilograms per square millimeter	Pounds per square inch		
0.12.....	45	64,000	29	41,000	Per cent 29.5	Per cent 63.9
0.25.....	56	79,000	33	47,000	32.0	71.3
0.80.....	80	114,000	48	68,000	32.5	50.0

The investigation of Giesen included steels which approach more nearly the composition of invar. His work was on nickel steels with nickel content up to 35 per cent, carbon 0.15, 0.30, and 0.95 per cent, and the maximum amounts of other elements contained were Mn 0.131 per cent, Si 0.10 per cent, and S 0.0073 per cent. He described the specimens as being naturally hard. The steels with 35 per cent nickel gave the following results:

Per cent carbon	Tensile strength		Elastic limit		Elongation	Reduction of area
	Kilograms per square millimeter	Pounds per square inch	Kilograms per square millimeter	Pounds per square inch		
0.15.....	50	71,000	42	60,000	Per cent 35.5	Per cent 71.8
0.30.....	81	115,000	48	68,000	38.3	78.6
0.95.....	79	112,000	61	87,000	39.1	62.7

The effect of small changes in the amount of other elements than carbon contained in nickel steel has not been so thoroughly investigated, but it has been found that vanadium exerts almost as much influence as carbon, and, like carbon, it is more active with low content of nickel. The action of manganese and chromium is not felt with small changes in the percentage of either element. The addition of a few per cent of chromium to steels of the third group increases the tensile strength and elastic limit, but slightly lowers the elongation. Chromium has also been found to increase

the resistance to wear of nickel steels.

In Table 14 are shown results obtained by the Midvale Steel Co. on several nickel steels made by this firm. The elastic limits given in Table 14 are the apparent elastic limits as determined by the Johnson method. (T. B. Johnson, *Materials of Construction*, p. 18.) Physical properties are those obtained from material rolled to 1 inch round and subjected to various treatments.

(b) **HARDNESS AND ABRASION.**—The hardness of nickel-iron alloys varies somewhat as the tensile strength varies, in

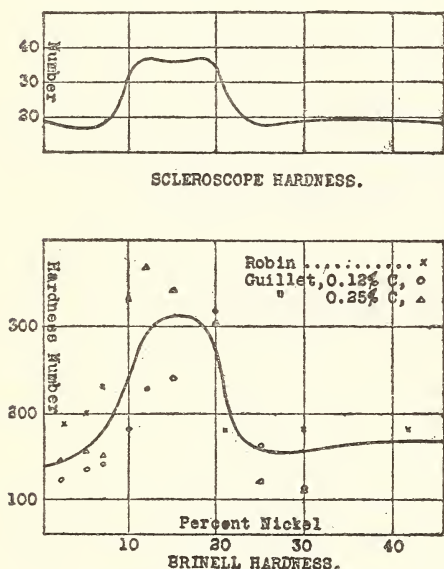


FIG. 35.—Hardness of nickel steels

that it reaches a maximum and then decreases rapidly to a nearly constant value.

Some results on hardness are shown graphically in Fig. 35. The work of Roush with the Shore scleroscope was on forged alloys of nearly pure nickel and electrolytic iron, so it can not be compared to results on commercial steels, although we might expect the curve to be similar. The results shown on the curve for Brinell tests are for untreated steels.

Robin has done considerable work on the wear of steels with abrasives. He found that the resistance to wear of nickel steels of the first group diminished with increase of nickel content; that of the second group was very low; and of the third group higher, being particularly high considering their low hardness value as measured by other methods.

(c) ELASTICITY AND ITS CHANGE WITH TEMPERATURE.—Guillaume found that during transformation the nickel steels present anomalies in the elastic modulus which correspond closely to the anomalies in thermal expansion. At temperatures both below and above the limits of the transformation region these alloys behave nor-

mally; that is to say, the elasticity decreases with rising temperature; but during transformation rapid changes in the opposite direction occur as indicated roughly by Figs. 36 and 37, which are self-explanatory after what has already been said in section 5.

Table 12 gives the results found by Guillaume at room tempera-

ture for the elastic modulus of some nickel steels. Table 13 and Fig. 38 show how the modulus has been found to change with the temperature. In the few cases investigated the temperature at which the elasticity of any given alloy reached its maximum value appeared to be about 10°C below that at which ferromagnetic properties began to appear on cooling. The anomalous change in elasticity with temperature has been employed to

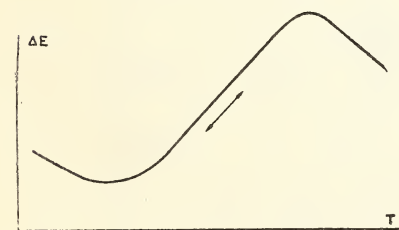


FIG. 37.—Typical curve representing variations in the modulus of elasticity of a reversible nickel steel with temperature. (Guillaume)

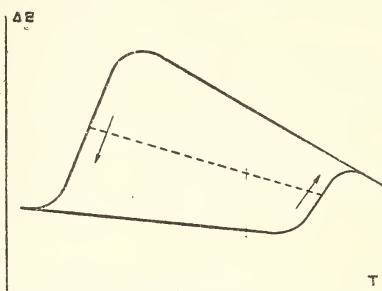


FIG. 36.—Typical curve representing variations in the modulus of elasticity of an irreversible nickel steel with temperature. (Guillaume)

advantage in constructing chronometers of precision.

Cold working and annealing modify the elastic properties appreciably; so that the values given above must be regarded as hold-

ing strictly only for the particular specimens investigated. The elastic modulus of invar forged hot is about 15 000 kg wt/mm²;

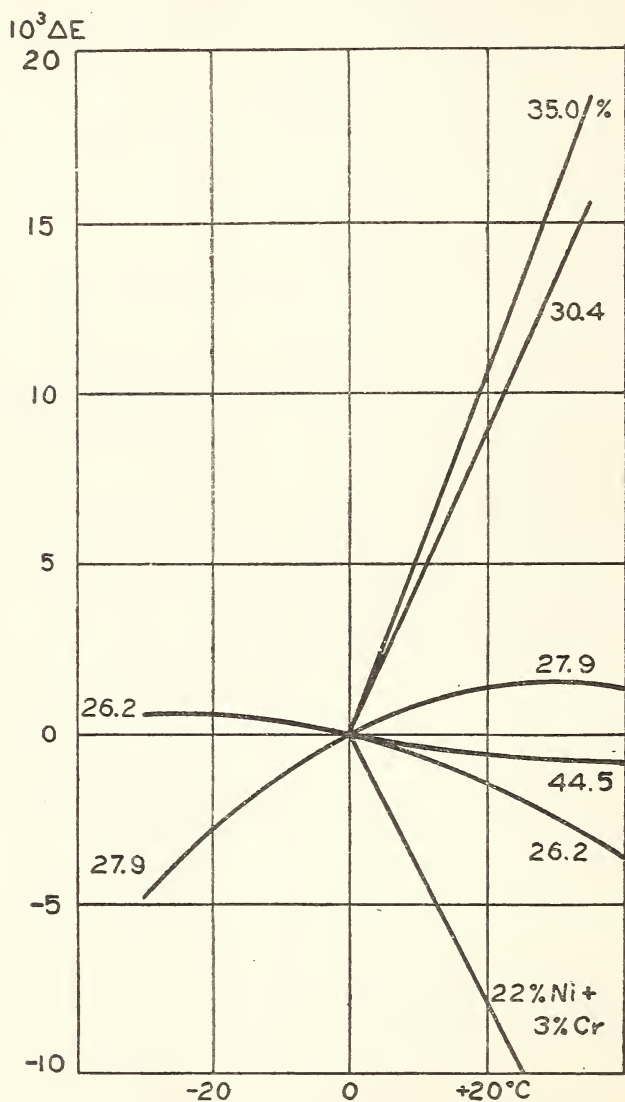


FIG. 38.—Variations of the elastic moduli of nickel steels with temperature. (Guillaume)

drawn into a large rod it reaches 15 500 kg wt/mm²; in a very hard drawn wire it may attain 16 000 kg wt/mm².

Like all the other high nickel steels, invar is very ductile and very strong. It is easily rolled into sheets or drawn into wire, but it wears cutting tools rapidly. When annealed it can undergo large deformations without rupture. On the other hand, by hard rolling or drawing it can be rendered sufficiently elastic for making fair springs.

(d) **POLISH.**—After the surface layers, which are always a little cracked in rough bars of nickel steels, have been thoroughly removed the remaining metal is perfectly sound and takes a beautiful polish, showing no pits under a magnification of 80 diameters. Very regular lines a few microns wide may be ruled on these surfaces.

9. RESISTANCE TO CORROSION

Resistance to attack by water increases with the proportion of nickel. Alloys containing even 36 per cent are so resistant that a divided length standard may be left to itself for months in an atmosphere saturated with moisture without showing rust spots. In expansion measurements bars have remained hours in warm water and were never dried on removal from the bath. Afterwards they were placed in steam for a long time without showing deterioration of the fine lines ruled on the polished surfaces. Rough surfaces, on the other hand, became covered with a slightly adherent layer of rust on exposure to steam for a few days. It is important to avoid the commencement of an attack. A spot of ink produces a slight tarnish which increases after wetting. All the alloys are very rapidly attacked by hydrochloric acid. A soldered joint improperly washed may start extensive corrosion.

While the resistance of invar to oxidation is very much greater than that of ordinary steel, nevertheless it is not perfect. Therefore it is prudent to cover an invar instrument with vaseline if it is to be left for a long time in a moist atmosphere. This precaution is necessary in tropical climates, where invar tapes and wires ought never to be left ungreaed except during actual use. The slight rust spots which may appear in time can generally be removed by rubbing with a greasy rag.

10. SUMMARY OF PROPERTIES OF INVAR

Invar is a nickel-steel containing about 36 per cent nickel together with about 0.5 per cent each of carbon and manganese, with metallurgically negligible quantities of sulphur, phosphorus, and other elements. It is made either in the open-hearth furnace or by the crucible method. It melts sharply at about 1425°C . Above some 200°C to its melting point, invar may be considered to consist of a homogeneous solid solution of iron, nickel, and carbon. Below 200°C and at a temperature dependent on its history and exact composition it undergoes a reversible transformation of such a nature that for any sample the transformation may be incomplete. This condition of thermochemical instability gives rise to both slowly changing and quickly changing values of its physical properties—changes which are particularly manifested in the expansion.

The alloy invar can be forged, rolled, turned, filed, and drawn into wires; and it takes a beautiful polish, giving an excellent surface on which fine lines may be ruled. In general, it should be worked slowly. It will withstand without spotting the corrosive action of water, even when immersed for several days. Its density is about 8.0 gm per cm^3 ; its electrical resistivity is of the order of 80 microhm/cm , or about 8 times that of pure iron; and its temperature coefficient of electrical resistance about $0.0012\text{ per degree centigrade}$. It is ferromagnetic, but becomes paramagnetic in the neighborhood of 165°C .

The mean coefficient of linear expansion between 0 and 40°C is of the order of one millionth for the ordinary invar, and samples have been prepared with even small negative coefficients; the amounts of carbon and manganese present appear to exercise considerable influence on the expansion. Small quantities have been manufactured with a coefficient $(+0.028 - 0.00232\text{ } t) 10^{-6}$, equivalent to a change in length of 0.4 mm in 1 km between 0 and 20°C . This was for one alloy containing $0.06\text{ per cent carbon}$ and $0.39\text{ per cent manganese}$, the other elements being negligible. Above 200°C the expansion of invar is nearly that of Bessemer steel.

Invar is subject to changes in length due to "after effects" following cooling from a high temperature, and to changes in

length following even slight alterations in temperature. For example, at 15° C the elongation of 1 m is 0.07 to 0.08 μ per day after forging and 0.03 μ after annealing to 40° C. After a long rest at room temperatures (10 to 20° C) the contraction setting in after bringing the metal to a higher temperature is completed in about one-half hour at 100° C and only after several days at 40° C. The range of transitory length variations following temperature changes is given approximately by the formula—

$$\Delta L/L = -0.00325 \cdot 10^{-8} t^2$$

which holds for temperatures between 0° and 100° C.

Invar also gradually elongates with time, forged and drawn material behaving somewhat differently in this respect, so that there is a determinable, seasonal correction to be applied to its length when used as a length standard. This effect may be reduced, but not entirely eliminated, by special heat treatments consisting in an annealing process extending over several weeks carried out at successively decreasing temperatures.

Invar also shows marked magnetostriction phenomena, or changes of length accompanying changes in strong magnetic fields.

The invar from a single melt will not, in general, be of absolutely uniform properties throughout, the expansion variations not being more than $\pm 0.03 \cdot 10^{-6}$, so that, in determining lengths to one part in ten million, it appears safe to use the same expansion formula for all the pieces from a given melt.

The mechanical properties are about as follows: Tensile strength 35 to 60 kg per square millimeter, or 50 000 to 85 000 pounds per square inch; elastic limit 5 to 21 kg per square millimeter, or 7000 to 30 000 pounds per square inch; elongation 40 to 50 per cent; reduction of area 40 to 65 per cent; scleroscope hardness 19; and Brinell hardness 160.

11. APPLICATIONS

The applications of nickel steels depend naturally upon their properties, or to the group (see sec. 8) to which they belong; and the properties of each group suggest possible applications of those steels within that group. The steels of the first group, usually containing less than 5 per cent nickel, have a high elastic

limit and high tensile strength. They are used for armor plate, guns, large axles, automobile parts, and structural purposes. Steels with a larger nickel content are very hard, take a good polish, resist oxidation, and have a higher elastic limit and tensile strength than carbon steels of the same hardness; so they may replace carbon steels where hardness is the property desired.

Further increase of nickel lowers the elastic limit and tensile strength, but greatly increases the elongation. Nickel steels of this third group are very resistant to shock, and may be used in machine parts which are designed to receive violent shocks. Steels of this group cover a wide range of expansion coefficients and anomalous variations of the elastic modulus. They are used in the manufacture of clocks, watches, and scientific instruments; and also for measures of length, measuring tapes, etc.

Invar is being used extensively for length measures. It has proved to be an excellent material for tapes. The United States Coast and Geodetic Survey has found invar tapes far superior to steel tapes, it being possible to measure a base line more rapidly and with greater accuracy than with steel tapes. The advantage arises mainly from the low expansion of invar, measurements being made in daylight with very small corrections for temperature. This Bureau has found that invar tapes which have been properly manufactured vary less than one part in 500 000 after six months' use in the field. There have been cases where invar tapes changed length between calibrations, but in practically every instance the cause could be traced to lack of proper treatment during the production or use of the tape.

French investigators have constructed length measures of invar in the form of wires instead of tapes. Tapes are more trouble to handle in a breeze, but wires twist and introduce errors in measurement which are not evident. The United States Coast and Geodetic Survey have found that wind caused little delay in the use of tapes, while the errors due to twist in wires were appreciable.

The low expansion of invar has been used to advantage in the construction of instruments requiring fixed distances between points to be independent of temperature, such as the bar between microscopes of a comparator for length standards. Nickel steels with low expansion have also been used for boiler tubes.

Industrial measuring machines constructed of 56 per cent nickel steel avoid temperature corrections in testing the dimensions of steel gauges and machine parts, since this alloy has about the same thermal expansivity as ordinary steel. In addition, it is more stable and less subject to corrosion.

Platinite, a nickel steel with about 46 per cent nickel, has the same expansion as platinum and has taken the place of platinum for sealing-in leads in electric-light bulbs. Nickel steel with the same expansion as glass, is also used in mounting lenses of optical instruments, diminishing the possibility of strain in the glass.

The application of invar and related nickel steels to the construction of clocks and watches has resulted in a great increase in the accuracy of instruments for measuring time. Invar, or a nickel steel with a low expansion coefficient, has made possible the compensated clock pendulum without mercury, resulting in convenient design and greater accuracy.

The use of nickel steel with a low coefficient of expansion in balance wheels of chronometers has made possible good compensation over a fairly wide range of temperature instead of for two definite temperatures.

The abnormal variation of elastic modulus with temperature has been utilized in the manufacture of watches by making the hair spring of a nickel steel with a little chromium to raise the elastic limit. A fair degree of compensation is obtained quite cheaply in this manner.

Clocks with torsion pendulums require little driving power and are constructed to run 400 days on a single winding. Compensation is obtained by making the torsion pendulum of nickel steel.

The high electrical resistance of 25 per cent nickel steel has also been of commercial importance. The steel called ferronickel is employed in the construction of rheostats

12. SOURCES OF SUPPLY

The alloys sold under the trade-marks "Invar," "Dilver," and "Platinite"⁹ are protected by patents and are manufactured only

⁹ Invar, expansion coefficient between -100° and $+150^{\circ}$ C almost zero; Dilver, expansion coefficient nearly that of ordinary glass, or 8×10^{-6} per degree centigrade; Platinite, expansion coefficient nearly that of platinum.

by the Société Anonyme de Commentry-Fourchambault et Decazeville, 84, rue de Lille, Paris (7^e). This company, which has been the pioneer in the scientific development of high nickel steels, manufactures on order pieces of any desired composition, pattern, or size.

Steels containing from 1.5 to 95 per cent nickel are manufactured in America for a great variety of purposes, e. g., gun tubes and other gun parts, pneumatic hammers and air drills, turbine blades, gas-engine valves, ignition tubes, spark plugs, axles, shafts, steering knuckles, gears, and other parts of automobiles, aeroplanes, and machinery subjected to severe stresses.

The following firms have informed this Bureau that they are makers of nickel steels:

Carpenter Steel Co., Reading, Pa. Makes steels with from 25 to 30 per cent nickel, but does not make steel of specified low thermal expansivity.

Crucible Steel Co. of America, Pittsburgh, Pa. 5 to 95 per cent nickel; expansivity to specifications.

Midvale Steel Co., Philadelphia, Pa. 1.5 to 95 per cent nickel; chrome-nickel steels; expansivity to specifications.

The dealers listed below also have informed the Bureau of Standards that they can supply nickel steels of minimum thermal expansivity:

J. H. Agar Baugh, 92 Hatton Gardens, London, E. C., England. Invar tape and invar pendulum rods.

Bausch & Lomb Optical Co., Rochester, N. Y. Invar rods, sheet, flat, T-section, L-section.

H. Boker & Co. (Inc.), 101 Duane Street, New York, N. Y. German product sold under trade name "G-Nickel."

International Nickel Co., 43 Exchange Place, New York, N. Y. Invar in various shapes.

Keuffel & Esser Co., Hoboken, N. J. Invar tapes.

Richards & Co. (Inc.), 200-206 Causeway, Boston, Mass. Various grades, shapes, and sizes.

Clemens Riefler, 29 Karlsplatz, Munich, Germany. Nickel-steel pendulum rods and bobs.

The price of 36 per cent nickel steel ranges from less than \$0.50 to as high as \$5 per pound, depending on source, quality, shape, size, quantity, and other factors. That made in America, though not at present guaranteed to meet the exacting requirements of precise measuring instruments, is far cheaper than the imported artificially aged invar, and should be satisfactory for many purposes.

TABLE 1
Magnetic Properties of Ferronickels

Per cent Ni	Hegg (1910)					Curie constants C (Weiss & Foëx, 1911)
	Density D, in grams per cubic centimeter	Transformation temperatures centigrade (Curie points)		Saturation values at 0° absolute magnetic moment per unit mass (B—H) ₀ .		
		θ or θ_1	θ_2	σ°	$= 4\pi\sigma_0 D$	
		Degrees	Degrees			
0.....	7. 875	758	223. 2	22 090	0. 072
10.....	7. 89	730	532	221. 0	21 910	. 0577
20.....	8. 02	625	218	210. 8	21 240	. 0460
30.....	8. 06	533	127	203. 6	20 620	. 0315
40.....	7. 63?	365	184. 2	17 660	. 0251
50.....	8. 05	527	169. 2	17 120	. 0227
60.....	8. 29	599	146. 8	15 290	. 0185
70.....	8. 39	613	127. 1	13 400	. 0157
80.....	8. 52	562	103. 1	11 040	. 0126
90.....	8. 60	480	80. 6	8710	. 0100
100.....	8. 86	374	58. 8	6550	. 0056

TABLE 2
Change in Electrical Resistance with Temperature (Guillaume)

Per cent nickel	Mean coefficients of variation between 0 and t° C	Per cent nickel	Mean coefficients of variation between 0 and t° C
22.0+3 Cr.....	(784-0.13 t) 10 ⁻⁶	30.4.....	(897-0.43 t) 10 ⁻⁶
26.2.....	(844+0.01 t) 10 ⁻⁶	35.0.....	(1561-1.69 t) 10 ⁻⁶
28.7.....	(700-0.20 t) 10 ⁻⁶	35.7.....	(1161-1.68 t) 10 ⁻⁶

TABLE 3
Electrical Resistivity of Ferronickels (C. F. Burgess and James Aston, 1910)

Per cent Ni	Microhm- cm	Relative resistance	Per cent Ni	Microhm- cm	Relative resistance
0.....	12.1	1.00	13.11 ^a	34.8	2.62
0.27.....	13.1	1.08	19.21.....	36.2	2.99
0.56.....	15.4	1.27	22.11.....	38.7	3.20
1.07.....	16.9	1.40	25.20.....	63.2	5.22
1.93.....	16.4	1.36	26.40.....	65.5	5.41
7.05.....	26.9	2.22	28.42.....	82.0	6.77
8.17.....	26.7	2.20	35.09.....	81.1	6.70
10.20.....	28.6	2.36	47.08.....	44.7	3.69
11.29.....	29.4	2.43	75.06.....	22.1	1.83
12.07.....	30.3	2.50	100.00.....	12.4	1.02

^a Contains 0.888 per cent C

TABLE 4

Expansion of Nickel Steels—Mean Coefficients of Linear Expansion Between 0° and t° C; Applicable Between 0° and 38° (Guillaume)

Per cent Ni	Mean coefficients of linear expansion $\times 10^6$	Per cent Ni	Mean coefficients of linear expansion $\times 10^6$
0.....	10.354+0.00523 t	44.4.....	8.508-0.00251 t
5.0.....	10.529+0.00580 t	48.7.....	9.901-0.00067 t
19.0.....	11.427+0.00362 t	50.7.....	9.824+0.00243 t
26.2.....	13.103+0.02123 t	53.2.....	10.045+0.00031 t
27.9.....	11.288+0.02889 t	70.3.....	11.890+0.00387 t
28.7.....	10.387+0.03004 t	100.0.....	12.661+0.00550 t
30.4.....	4.570+0.01194 t	12.2+1 Cr.....	11.714+0.00508 t
31.4.....	3.395+0.00885 t	16.8+1 Cr.....	11.436+0.00170 t
34.6.....	1.373+0.00237 t	16.2+2.5 Cr.....	19.496+0.00432 t
35.6.....	0.877+0.00127 t	21.3+3 Cr.....	18.180+0.00426 t
37.3.....	3.457-0.00647 t	34.8+1.5 Cr.....	3.580-0.00132 t
39.4.....	5.357-0.00448 t	35.7+1.7 Cr.....	3.373+0.00165 t
43.6.....	7.992-0.00273 t	36.4+0.9 Cr.....	4.433-0.00392 t

TABLE 5

Expansion of Nickel Steels—True Coefficients of Linear Expansion at t° C (Guillaume)

Per cent Ni	Limits of application	True coefficients of linear expansion $\times 10^6$
	Degrees	
30.4.....	0-110	4.570+0.0235 (t-0)
	110-164	7.15 +0.104 (t-110)
	164-220	12.60 +0.008 (t-164)
31.4.....	0-122	3.395+0.0150 (t-0)
	122-182	5.25 +0.128 (t-122)
	182-220	13.00 +0.036 (t-182)
34.6.....	0-142	1.373+0.0047 (t-0)
	142-220	2.05 +0.065 (t-142)
37.3.....	0-150	3.457-0.0072 (t-0)
	150-220	2.37 +0.011 (t-150)

TABLE 6

Elongations on Heat Treating a 35.5 Per Cent Nickel Steel Bar (Guillaume)

Temperature °C	Time	Elongations in microns per meter—				
		Total	At 100°	At 60°	At 40°	At 6°-20°
	Hours					
150.....	40	8.1				
100.....	1	12.2	4.1			
100.....	7	19.3	11.2			
100.....	47	25.3	17.2			
100.....	79	28.1	20.0			
60.....	45	33.8		5.7		
60.....	111	36.7		8.6		
60.....	202	39.7		11.6		
60.....	318	40.5		12.4		
40.....	88	42.7			2.2	
40.....	229	44.3			3.8	
40.....	395	46.1			5.6	
40.....	509	46.7			6.2	
40.....	698	47.0			6.5	
	Days					
11.....	3	47.5				0.5
11.....	17	47.4				0.4
11.....	33	48.8				1.8
11-18.....	74	49.3				2.3
18-20.....	118	50.0				3.0
20-14.....	176	51.6				4.6
14-8.....	244	52.6				5.6
6-8.....	300	52.8				5.8
6-8.....	333	53.5				6.5
8-9.....	375	53.1				6.1

TABLE 7

Elongations on Heat Treating a 35.5 Per Cent Nickel Steel Bar (Guillaume)

Temperature °C	Time	Elongations in μ per meter	
		Total	At 6° to 20°
	Hours		
100.....	4	12.3	
100.....	21	22.4	
100.....	71	26.7	
100.....	118	26.7	
100.....	150	28.1	

TABLE 7—Continued

Elongations on Heat Treating a 35.5 Per Cent Nickel Steel Bar (Guillaume)—Con.

Temperature °C	Time	Elongations in μ per meter	
		Total	At 6° to 20°
	Days		
10.....	5	28.3	0.2
10.....	14	28.7	0.6
10.....	30	29.5	1.4
10-11.....	54	30.2	2.1
10-15.....	92	32.0	3.9
16-20.....	145	32.8	4.7
20-14.....	223	35.3	7.2
14-8.....	343	36.8	8.7
6-8.....	385	37.7	9.6

TABLE 8

Length Variations in Hot-Forged Bars of Invar (Guillaume)

Number	Nickel	Treatment of bar	Elongation in millionths	True coefficients of linear expansion at 20° C $\times 10^6$
	Per cent			
1.....	35.2	Forged hot.....		1.27
		4536 days at room temperature.....	38	1.32
2.....	35.5	Forged hot.....		1.21
		Skin removed; 150 hours at 100°, 4820 days at room temperature.....	65	1.32
3.....	35.5	Forged hot.....		1.18
		Skin removed; 40 hours at 150°, gradually cooled in 50 days to 40°, 4802 days at room temperature.....	66	1.31
4.....	35.5	Forged hot; 55 hours at 100°, 150 hours at 60°.....		1.67
		62 hours at 100°, cooled in 73 days to 25°, 4015 days at room temperature.....	34	1.73
5.....	35.6	Quenched; 55 hours at 100°, 187 hours at 60°.....		1.36
		4564 days at room temperature.....	26	1.42
6.....	35.5	Quenched; 55 hours at 100°, 189 hours at 60°.....		1.28
		479 hours at 60°, 856 hours at 40°, 690 days at room temperature, planned to H-section.....		1.31
		4145 days at room temperature.....		1.32
7.....	35.5	Forged hot; 66 hours at 100°.....		1.30
		739 hours at 60°, cooled in 102 days to 25°, planed to H-section, 320 days to room temperature.....		1.35
		4145 days at room temperature.....		1.33
8.....	43.0	Forged hot.....		7.33
		108 hours at 100°, 4496 days at room temperature.....		7.47

TABLE 9

Elongation of Invar with Time After Cooling Three Months from 100° to 25° C
(Benoit and Guillaume)

Days after completion of treatment	Elongation in microns per meter	Days after completion of treatment	Elongation in microns per meter	Days after completion of treatment	Elongation in microns per meter
0.....	0.0	1000.....	6.6	2000.....	9.3
100.....	1.5	1100.....	6.9	2100.....	9.5
200.....	2.5	1200.....	7.2	2200.....	9.7
300.....	3.2	1300.....	7.5	2300.....	9.8
400.....	3.9	1400.....	7.8	2400.....	10.0
500.....	4.4	1500.....	8.1	2500.....	10.1
600.....	4.9	1600.....	8.4	2600.....	10.3
700.....	5.4	1700.....	8.7	2700.....	10.5
800.....	5.8	1800.....	8.9	2800.....	10.6
900.....	6.2	1900.....	9.1	2900.....	10.8

TABLE 10

Temporary Length Variations of Invar Following Rapid Change in Temperature
 $\Delta L/L = -0.00325 \times 10^{-6} t^2$ (Benoit and Guillaume)

Temperature, °C	10 ⁶ ΔL/L Starting from—		Temperature, °C	10 ⁶ ΔL/L Starting from—		Temperature, °C	10 ⁶ ΔL/L Starting from—	
	0°	15°		0°	15°		0°	15°
0.....	0.0	+0.7	10.....	-0.3	+0.4	20.....	-1.3	-0.6
1.....	0.0	+0.7	11.....	-0.4	+0.3	21.....	-1.4	-0.7
2.....	0.0	+0.7	12.....	-0.4	+0.3	22.....	-1.5	-0.8
3.....	0.0	+0.7	13.....	-0.5	+0.2	23.....	-1.7	-1.0
4.....	0.0	+0.7	14.....	-0.6	+0.1	24.....	-1.8	-1.1
5.....	-0.1	+0.6	15.....	-0.7	+0.0	25.....	-2.0	-1.3
6.....	-0.1	+0.6	16.....	-0.8	-0.1	26.....	-2.2	-1.5
7.....	-0.1	+0.6	17.....	-0.9	-0.2	27.....	-2.3	-1.6
8.....	-0.2	+0.5	18.....	-1.0	-0.3	28.....	-2.5	-1.8
9.....	-0.2	+0.5	19.....	-1.1	-0.4	29.....	-2.7	-2.0

TABLE 11

Densities of Nickel Steels (Guillaume)

Per cent Ni	Density in grams per cubic centimeter	Per cent Ni	Density in grams per cubic centimeter	Per cent Ni	Density in grams per cubic centimeter	Per cent Ni	Density in grams per cubic centimeter
5.0.....	7.787	24.1 ^b	8.014	34.6.....	8.066	100.0.....	8.750
15.0.....	7.903	26.2.....	8.096	37.2.....	8.005	12.2 Ni+1 Cr	7.892
19.0.....	7.913	30.4.....	8.049	39.4.....	8.076		
24.1 ^a	8.111	31.4.....	8.008	44.3.....	8.120		

^a Nonmagnetic.^b Magnetic, but transformation apparently incomplete.

TABLE 12

Elastic Moduli of Nickel Steels (Guillaume)

Per cent nickel	Modulus of elasticity in metric ^a tons weight per square millimeter	Per cent nickel	Modulus of elasticity in metric ^a tons weight per square millimeter	Per cent nickel	Modulus of elasticity in metric ^a tons weight per square millimeter
5.0.....	21.7	31.4.....	15.5	12.2+1 Cr.....	19.0
15.0.....	19.1	34.6.....	15.4	16.2+2.5 Cr.....	19.6
19.0.....	17.7	35.2.....	14.9	16.8+1 Cr.....	18.3
24.1 ^b	19.3	37.2.....	14.6	34.8+1.5 Cr.....	15.5
24.1 ^c	17.4	39.4.....	15.1	35.7+1.7 Cr.....	15.7
26.2.....	18.5	44.3.....	16.3	36.4+0.9 Cr.....	15.7
27.9.....	18.1	70.0.....	19.8		
30.4.....	16.0	100.0.....	21.6		

^a A metric ton is 1000 kg.^b Nonmagnetic.^c Magnetic; transformation apparently incomplete.

TABLE 13

Change in Elastic Modulus with Temperature (Guillaume)

Per cent Ni	Magnetic state	Coefficient of elasticity in metric tons weight per square millimeter at t °C
22.0+3 Cr.....	Not magnetic.....	19.67 (1-394×10 ⁻⁶ t)
26.2.....	Very slightly magnetic.....	18.54 [1-(51.6t+0.95 t ²) 10 ⁻⁶]
27.9.....	Slightly magnetic.....	18.06 [1+(104. t-1.72 t ²) 10 ⁻⁶]
30.4.....	Magnetic.....	15.96 (1+389×10 ⁻⁶ t)
35.0.....	Very magnetic.....	15.04 (1+464×10 ⁻⁶ t)
44.5.....	do.....	16.40 [1-(43.6 t-0.62 t ²) 10 ⁻⁶]

TABLE 14
Nickel Steels from Midvale Steel Co.

No.	Composition			Treatment	Physical properties			
	C	Mn	Ni		T. S.	E. L.	Ext.	Cont.
1.....	0.20	1.50	26.00	A	78 500	12 000	50.0	70.7
				C	76 000	15 000	49.5	70.5
2.....	.15	1.50	30.00	A	90 000	27 000	39.5	69.7
				B	84 500	28 000	46.5	68.5
				C	81 500	23 000	44.2	70.5
3.....	.40	2.00	30.00	A	105 000	45 000	47.0	66.6
				B	101 500	35 000	46.7	66.4
				C	91 000	25 000	45.7	69.3
4.....	.12	2.30	32.27	A	82 000	30 000	37.5	65.6
				B	77 500	22 000	43.0	66.2
				C	73 000	18 600	39.5	64.7
5.....	.22	1.50	35.05	A	89 000	30 000	40.6	67.5
				B	85 000	30 000	42.0	67.3
				C	82 000	27 500	41.0	65.0
6.....	.08	.50	36.00	A	76 500	36 500	36.3	65.6
				B	72 500	24 000	39.2	67.5
				C	70 500	20 000	38.0	58.3
7.....	.37	1.50	45.00	A	107 000	40 000	40.0	51.1
				B	94 500	35 000	43.7	51.1
				C	73 000	19 500	38.0	46.3
8.....	.35	1.50	43.00	Cold drawn	100 000	52 500	16.2	46.0
9.....	.17	1.25	50.66	A	99 000	48 500	38.5	67.7

Treatment A is the bar as rolled; B the bar after being annealed (i. e., slowly cooled) from above 790° C.; C the bar quenched, but not drawn, from above 760° C. The exact temperatures are not given.

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