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Invar and elinvar

Nobel Lecture, December 11, 1920

The anomaly of nickel steels

Discovery of the anomaly - In 1889 the General Conference on Weights and Measures met at Sèvres, the seat of the International Bureau. It performed the first great deed dictated by the motto inscribed in the pediment of the splendid edifice that is the metric system: "*A tous les temps, a tous les peuples*" (For all times, to all peoples); and this deed consisted in the approval and distribution, among the governments of the states supporting the Metre Convention, of prototype standards of hitherto unknown precision intended to propagate the metric unit throughout the whole world.

These prototypes were indeed noteworthy. They were made of a platinum-iridium alloy developed by Henri Sainte-Claire-Deville which combined all the qualities of hardness, permanence, and resistance to chemical agents which rendered it suitable for making into standards required to last for centuries. Yet their high price excluded them from the ordinary field of science; at that time a single metre actually cost 7,000 crowns - and how much more today!

A less costly answer had to be sought since between these precious prototypes and standards affording only uncertain guarantees there was a gap which nothing could fill.

I first examined this problem in 1891 and soon discovered the really excellent properties of pure nickel and still today this is the metal used to make a non-oxidizable standard, unaffected by the passage of time, rigid and of average expansibility. However, one difficulty prevented me generalizing its use. A geodesic standard 4 metres long was required, and no nickel-producing factory would undertake to supply, perfectly sound and crack-free, a suitable bar.

Subsequent studies were guided by a few strokes of good luck. In 1895, at the request of the Ordnance Technical Department (Section technique de l'artillerie) in Paris, J. R. Benoit had undertaken the study of a standard made from an iron alloy containing 22% nickel and 3% chromium and found its expansibility to be close to that of brass. It was a non-magnetic alloy and thus was doubly anomalous.

The very curious phenomena discovered by John Hopkinson had already been known for a few years, notably that after forging certain alloys of iron and nickel containing about 25% of the latter are non-magnetic and not very hard; however, once they have been cooled in, say, solid carbon dioxide, they are hard and strongly magnetic; furthermore, during this transformation, their volume has increased by about 2%.

The phenomena discovered by Hopkinson and Benoit were clearly related. But however interesting they might be for the physical chemist, they were strictly taboo for the metrologist. An alloy that is changeable, and another of high expansibility, are unsuitable for designing length standards.

The matter took on a different aspect when in 1896 I was put on the trail of a new and quite unexpected fact closely connected with those just reported. A bar of steel containing 30% nickel arrived at the International Bureau and I found its expansibility to be about one third less than that of platinum. The continuation of a study so begun augured well and I pursued it with stubborn obstinacy.

For metrology the matter of expansibility is fundamental; as a matter of fact the temperature measuring error relates to the length measurement in proportion to the expansibility of the standard and the constantly renewed efforts of metrologists to protect their measuring instruments against the interfering influence of temperature reveal clearly the importance they attach to the expansion-induced errors.

It is common knowledge, for instance, that effective measurements are possible only inside a building, the rooms of which are well protected against the changes in outside temperature, and the very presence of the observer creates an interference against which it is often necessary to take strict precautions.

Prior to the discovery of the anomaly to which I have just referred, any physicist would have sworn that there was no hope of remedy by means of metals or alloys whose expansibility was much lower than the known values because it had always been considered that the rule of mixtures was complied with in practice.

My first care was to check the direction of the expansions as a function of the composition of the alloys. This was not a vain precaution since between the non-magnetic 22% alloy and the magnetic 30% alloy a discontinuity was apt to occur. Experiments conducted on two alloys, enclosing the second, and which were reported to me by the Société de Commentry-Fourchambault & Decazeville, established the continuity.*

Classification by magnetic properties. - The accurate measurement of expansions is long and difficult. Since there could be no doubt that the anomaly involved affected all the properties of the new alloys, more readily applicable methods had to be used. It was self-evident to study the magnetic susceptibility, for if it is merely a question of ascertaining the presence or absence of ferro-magnetism, the experiments are elementary.

In its early stages this study showed me that there were two distinct transformations. The one is irreversible and this is the one discovered by Hopkinson; the other is reversible and its discovery was new. A number of observers, notably Osmond, Louis Dumas, Pierre Weiss and his pupils, Nagaoka and Honda have established its characteristics.

A very simple diagram shows at a glance the over-all pattern of the transformations of ferro-nickels referred to their magnetic properties.

Starting from iron these transformations split into two groups, AB and AC, which progressively diverge (Fig. 1a). When we cross downwards the lower curve, magnetism appears, then increases up to a certain limit. When the alloy is reheated the magnetism decreases from a given temperature and ultimately disappears at the intersection with the upper curve. On the other hand the behaviour of the single curve indicates, in alloys with a higher nickel content, both the appearance, on cooling, and the disappearance, on reheating, of the ferromagnetic properties.

The intersection of the curves for the two categories has a precise significance: additions of carbon, chromium, and manganese appreciably lower the temperature of the irreversible transformations but have far less effect on the reversible transformations. It is thus possible to follow the reversible transformation into the region of the normally irreversible alloys.

Moreover, to the right of the intersection moderate cooling leaves the magnetism completely reversible; more intense cooling sets the transformation and renders it irreversible.

Let us now assume a third axis at right angles to the other two. Along it we shall plot the susceptibility and in the solid diagram thus obtained we

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* Inspired initially by the managing director, Henry Fayol, this firm was not content to stop there; when submitting to me its analytical reports the firm supplied me with alloys numbering more than six hundred. It is due to this unstinting collaboration that my studies were able to carry on for almost a quarter of a century.

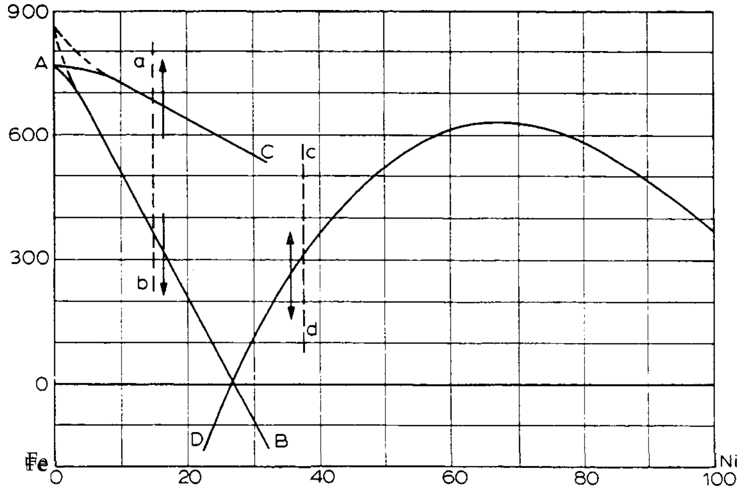
make two orthogonal sections, *ab* and *cd*. In the irreversible region the previously cooled alloy retains along ABC (Fig. 1b) the susceptibility it has acquired, which reverts to zero along CD. On cooling it will remain zero until point F is reached where it will start to rise again along line FB.

Cooling may be interrupted at any time, then the alloy reheated and it will retain the constant magnetic properties shown by the line B′C′.

In the reversible region the susceptibility is represented by the single curve ABCDEF (Fig. 1c).

All the properties of the alloys with which we are concerned are associated with these transformations, and the characteristics of those which we have just traced will also be found in the curves representing the changes in volume or elasticity modulus.

Having thus found the guide I devoted my full energies to studying the



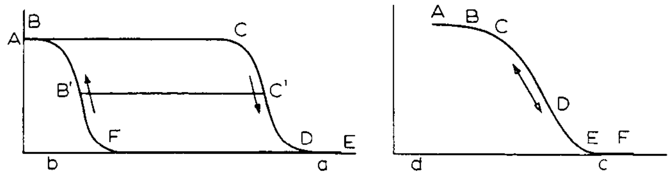


Fig. 1a. Magnetic transformation temperature of nickel steels as a function of their composition. The branches AB and AC refer to irreversible alloys, branch DE to reversible alloys.

Figs. 1b, 1c. Variations in magnetic susceptibility of nickel steels as a function of temperature in the irreversible and reversible alloy regions (temperature along abscissae, susceptibilities along the ordinates).

changes in volume which constitute the main metrological factor associated with the existence of these alloys.

Changes in volume

Methods - It was during the 18th century that the expansibility of solid materials was clearly demonstrated. The famous French physicist and geodesist Bouguer once wished to exhibit its effects to a large assembly and for this purpose he suspended under the dome of the Hotel des Invalides a metal wire supporting a telescope balanced at two points. The telescope was sighted on a distant levelling rod and when, during the course of the day, the temperature rose then fell, the variations in length of the wire were revealed by the movement of the point on the rod seen in the telescope.

In that case, however, it was merely a verification and not a measurement. Various methods of determining expansions were used during the 19th century; the one which I have used almost exclusively is that of the comparator which Baron Wrede recommended to the International Bureau to be used in the form in which he himself used it and which, perfected over the years, particularly by J.R. Benoit, has resulted in the methods in use today.

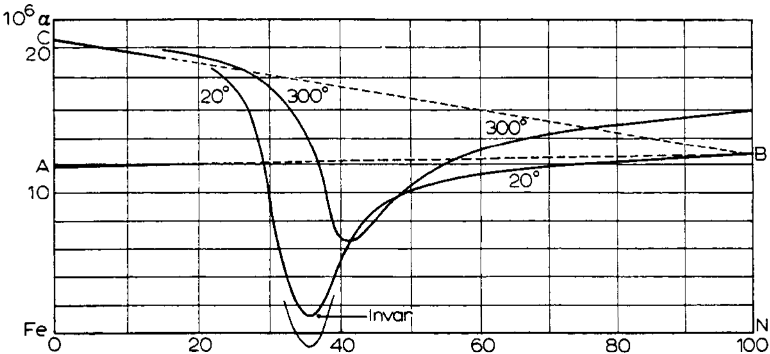
Two micrometer microscopes fixed to stone supports are vertically sighted on the marks on a rod immersed in water and measure the changes in its length when it is brought to various temperatures in succession. However, as the distance between the microscopes is not fixed, the procedure is to measure alternately the rod under test and a standard kept at a practically constant temperature in a second trough. This is termed an *absolute* method. For routine work it is replaced by the *relative* method in which the reference standard is placed in the same bath as the rod under test. The expansibility of the latter is the algebraic sum of the relative expansibility given by the experiment and of that of the standard rod determined beforehand by the absolute method. I used the comparator method in its relative form with an iridium platinum rod as the reference standard.

But the comparator method can be used only over a restricted temperature range the limits of which, in the case of my experiments, were 0° and 38° C. To attain temperatures higher than 200° C and thus better characterize the transformations, I secured the sample to be studied to a brass rod, the two being coupled at one extremity and free to expand over the remainder of their length. The relative extensions were measured at the free end with a microscope.

Later P. Chevenard designed a dilatometer whereby the relative extensions of a small sample of the metal under test (25 to 50 mm) and of a reference made of a suitably chosen alloy can be measured with high accuracy. His dilatometer, with photographic recording, enabled the whole range of temperatures from that of liquid air to 1,000° C to be covered. In their common parts our diagrams coincide, but Chevenard's go far beyond mine.

Irreversible changes - Knowledge of the irreversible changes in volume of the alloys was necessary, especially to ascertain their limit. I studied the various aspects in binary and ternary ferro-nickel alloys with chromium, copper, etc. I was only able to trace the low part of the cycle. The complete cycles were traced much later by P. Chevenard.

When a bar of an irreversible alloy is heated from a low temperature, it expands in accordance with the almost rectilinear curve ABC (Fig. 2b), then, at a certain temperature, the rate of extension falls off, then progressive con-



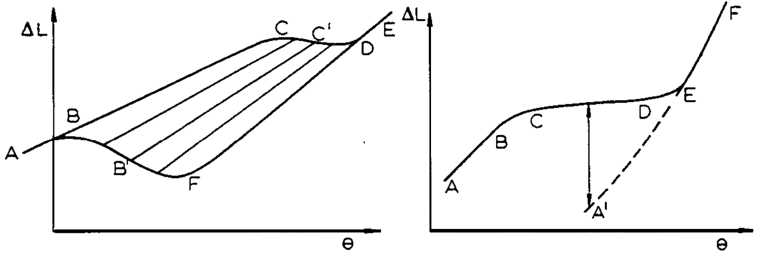


Fig. 2a. Diagram showing the expansibilities of nickel steels as a function of their composition. The two straight lines starting from A and C limit the range of the irreversible alloys, the curves represent the true expansibilities of the reversible alloys at 20°and at 300°C ($\alpha_{20}, \alpha_{300}$).

Figs. 2b, 2c. Diagrams for a reversible and an irreversible alloy.

traction sets in and continues regularly until completion of the transformation, whereupon the expansion resumes its regular course DE.

If the bar is allowed to cool it will be found to contract in accordance with EDF, at which point an expansion sets in which ceases at B and gives place to a contraction along BA.

If the cooling has been suspended at B′ and if the bar is reheated, the movement follows the line B′C′ and continues along the curve C′DE as in the preceding case. The slope of the straight line AC is between 10 and 11 x 10^{-6}, that of EF is about 18 x 10^{-6}.

The former shows the expansibilities of the ordinary irons or steels, the second those of the non-magnetic iron-nickel-chromium alloy mentioned above. Between the two all the intermediate expansibilities can be attained by suspending the transformation at any point along one of the curves CD or FB.

Along the curve ABC the iron is in a state which we shall term "cold stable"; along the curve EDF it is in the "hot stable", non-magnetic state.

Collating the expansibilities of the irreversible alloys, we find that they lie between the segments of the straight lines AB and CB in Fig. 2a, proper to their particular zone. Contrary to all appearances the rule of mixtures is obeyed but it must be applied to the association of the nickel with that of the varieties of iron present in the alloy within the limits of the zone covered, or else with a proportion of each of the two states of iron which depends on the degree attained by the transformation.

The zone which can be occupied by the high expansibilities is progressively extended to ordinary temperatures by retarding the transformation by additions of manganese, chromium, or carbon, as mentioned when discussing magnetism.

Reversible changes - The experiments with the reversible alloys were much more extensive.

A first examination consisted in determining the anomaly curve as a function of the nickel, entirely neglecting the manganese, carbon and silicon additions present in varying amounts in the alloys and which left the curve slightly ambiguous. Next I studied a series of alloys containing up to the maximum possible proportions of manganese and carbon. Having thus determined the coefficients relating to these additions for all the contents of nickel, I was able to convert the results to constant proportions of additions : 0.1% Mn, 0.4% C, and the alloys containing them I have termed *standard* alloys. Moreover, after hot rolling and cooling in air, these alloys will be referred to as being *in the natural state.*

Since the expansibility of a material is given by the equation

$$l_\theta = l_0 \; (1 + \alpha\theta + 2\beta\theta^2)$$

the expression

$$\alpha_\theta = \alpha + 2\beta\theta$$

will be termed the true coefficient at θ, which is at the same time the mean coefficient of expansion between 0°C and 2 θ ; β will be the *quadratic coefficient.*

The expansibility of most metals is well represented, over a wide range of temperatures, by an equation of the above form; for the alloys under discussion the same rule is adequately applicable over the narrow range where I used the comparator; but, when it is extended, it soon becomes apparent that a second degree equation is no longer sufficient to represent the phenomenon. Nevertheless it is convenient to retain the same form of the equation, attributing to β a value which varies with the temperature and which indicates the semi-curvature of the expansibility curve at each point.

For normal, reversible nickel steels the values of α_{20} and β_{20} are represented by the curves in Figs.2a and 3. The lines AB link together the values of the same coefficients for nickel and steel in the cold stable state and so reveal the magnitude of the anomaly in expansibility. For β this anomaly is undeniably positive, then negative. It appears to be likewise for α but the line CB which starts from the value of the coefficient in gamma iron and limits

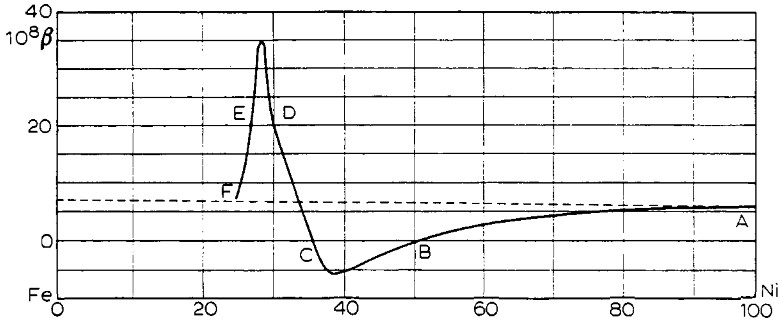


Fig. 3. Values for coefficient in reversible alloys. The letters marked on the curve correspond to those in Figs. 1c and 2c.

the zone of large expansibilities of the irreversible alloys, shows the anomaly as entirely negative. And in fact it has to be referred to this representation.

The anomaly is very great since the expansibility of the alloys varies in the ratio of about 1 to 15 and reaches a value which is only one quarter of the lowest expansibility found in one metal. From a practical standpoint, moreover, it will be noticed that the low expansibilities are achieved here by inexpensive metals and constitute a completely continuous scale in contrast with the discontinuous and costly sequence of the less expansible metals, iridium, tantalum, tungsten.

The generic name *invar,* short for invariable, has been given to the alloy whose expansibility differs little from the minimum. The coordinates of the minimum for the standard alloys in the natural state are: Ni = 35.6; $\alpha = 1.2 \times 10^{-6}$.

Great importance need not be attached to the exact value of these coordinates. Actually they relate to an alloy in which the additions have been fixed arbitrarily at about the mean amounts contained in industrial alloys, and we shall soon see that these additions have a considerable effect on the position of the minimum. Moreover, every heat treatment or mechanical treatment modifies the expansibilities, raising them in the case of annealing with slow cooling, reducing them when the cooling is rapid, and more still when the alloys are hammer hardened. By superimposing one reducing treatment on the other it is thus possible to bring the expansibility of an alloy to 1.5×10^{-6} below its value corresponding to the natural state and give it a negative value. Then, after this has been achieved, heating for a few hours at 100°C, for instance, raises it again and may bring it very close to zero. In this way a method was elaborated for making several kilometres of invar wire, the expansibility of which can be detected only by very accurate measurements. This result is of great practical importance, as we shall soon see.

The wide margin of variations of the coefficient β is sufficient to suggest that the general curve representing the true expansibility of the alloys as a function of their composition will deform rapidly when the temperature to which it corresponds is altered. Furthermore, comparison of the curves in Figs. 1a and 3 shows that the maximum of β largely corresponds, for the particular case of ordinary temperatures, to the region in which the magnetism appears or disappears. This coincidence is universal, as I was able to demonstrate in 1896, up to the limit of the temperatures which it was possible for me to attain and I immediately concluded that the complete curve for the changes in length specific to a given alloy, transfers its characteristics to the neighbouring alloys with a simple shift in the scale of temperatures. From that I deduced a rule of corresponding states which assuredly is only a coarse approximation to reality but nevertheless permits generalisation and, consequently, prediction.

It may be formulated by stating that, at a certain temperature, a given alloy is in the same state as another alloy at a temperature which differs from that at which magnetism first appears by the same margin as in the first alloy.

To apply this rule the concomitant values of α and β for the series of alloys which are considered at the same temperature will be compared as belonging to the same alloy for the series of temperatures. In this way it is possible to trace *a priori* the extension curve of a given alloy which has the general shape shown in Fig. 2c. Essentially five periods are distinguishable in this curve, the two extremes, AB and EF, with β weakly positive, giving the result obtained from the rule of nickel-iron mixtures in the cold and hot stable states, and three intermediate regions, BC and DE with β weakly negative or very strongly positive, lastly CD which is the region of inflexion where β changes from negative to positive, and where, as a result, the expansibility reaches its minimum.

Between 150° and 200° C the expansibility of invar proper starts to increase, and between 250° and 300° C its expansibility becomes normal.

Since the entire curve shifts towards the high temperatures with increasing nickel content, the alloy will be matched to the temperature range specific to the intended applications. It should not be forgotten, however, that the curve deforms slowly and that at high temperatures there are no alloys with very low expansibility.

The top curve in Fig. 2a represents, by way of an example, the expansibilities of nickel steels at 300°C as found in Chevenard's experiments. The anomaly is still very marked but the minimum has shifted considerably towards the high nickel contents as foreshadowed by the trend of the β-values.

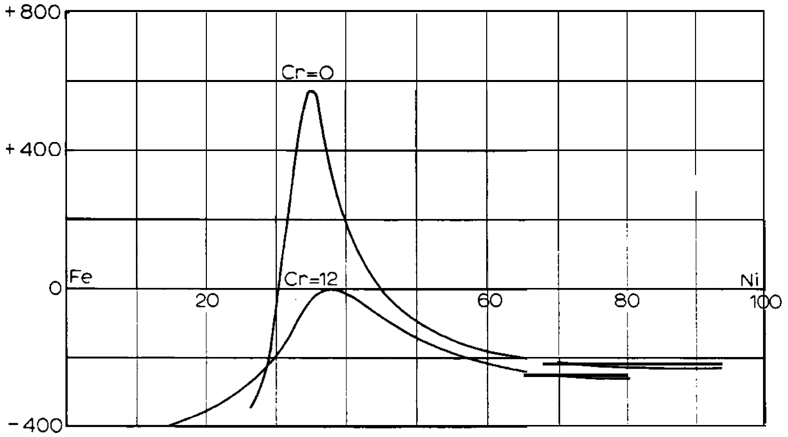
The distance between the curve FEA′ and the curve EDCBA (Fig. 2c) is the amplitude of the anomaly at each temperature.

Elastic properties

Elasticity moduli - The irreversibility and the reversibility revealed by the study of the magnetic properties of the alloys, or of the variations in their volume, recur, as was to be expected, in their elastic properties. Here again the transformations whose effects we have ascertained bring about changes which are a function of the prevailing temperature or else which are largely dependent on the thermal influences to which they have previously been exposed.

Generally speaking any expansion of materials lowers the modulus by reducing the intensity of the intermolecular reactions. The irreversible changes in volume also have this result and owing to the transformation undergone by irreversible nickel steels at low temperatures, their elasticity modulus decreases by about one tenth of its original value, the decrease being along the curve FB (Fig. 4b). Lastly, I would like to add that the system of which this curve is a part represents all the changes of the modulus in this class of alloys and its analogy with the changes in volume illustrated in Figure 2b is clearly apparent.

Compared with the values specific to iron and nickel, the curve of the moduli as a function of the content is depressed, the maximum depression



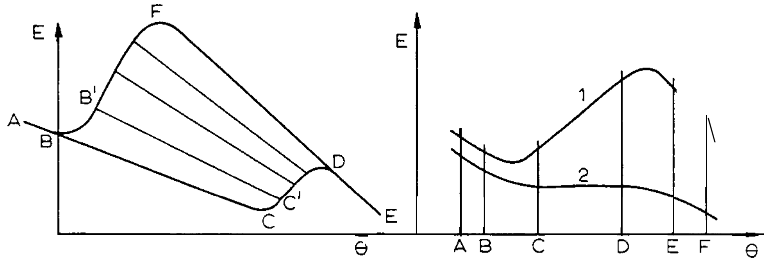


Fig. 4a. Thermoelastic coefficients of standard iron-nickel alloys and of alloys with 12% additions of chromium.

Figs. 4b, 4c. Changes in elasticity modulus of an irreversible and a reversible alloy. The letters in this diagram correspond to those in diagrams 1, 2 and 3.

occurring in the invar region, where it reaches about one quarter of the value that would be indicated by the rule of mixtures. The minimum modulus at ordinary temperature is thus close to 1.4 x 10^{12} c.g.s.units.

Variation of modulus with temperature - Interest centres mainly on studying the variations of the modulus with temperature, whether flexion or torsion is involved.

In the case of the latter I merely performed a rapid examination which showed me how, by an adaptation, it was possible to deduce the thermal coefficients from those which govern the flexion. P. Chevenard went into it very thoroughly. In all cases the torsional pendulum method was used.

To study the thermoelastic coefficient in the case of flexion the instrument chosen is the chronometer, this being readily available, very small, and yielding directly a result that can be used in practice. Its drawback is that successful manufacture and fitting of the balance spring require an expert. For this study I had the valuable assistance of a skilled regulator, Paul Perret, who had taken the initiative in offering me his services soon after my initial publications on invar; later, the experiments were conducted under my control by the technical laboratories of the Sociétè des Fabriques de Spiraux Réunies.

The balance spring is made of the alloy under examination and mounted on a balance of a known metal and the assembly constitutes the regulator of the chronometer.

The thermal changes in the period of oscillation of the balance driven by the balance spring involve the expansions and the variations in bending modulus simultaneously.

Contrary to a very widespread idea, the expansion of the balance spring alone would reduce the oscillation period, i.e. the chronometer would be fast at high temperatures, the reason being that the transverse dimensional changes occur four times, and the changes in length only once, in determining the elastic moment. For its part, the expansion of the balance causes the chronometer to go slowly at high temperatures in accordance with the generally accepted idea. In the case of a steel balance spring and a brass balance the effects of the expansion largely cancel out each other. But a chronometer so equipped loses 11 seconds a day for each degree rise in temperature; this loss is due almost entirely to the temperature-induced change in modulus, the coefficient of which is negative.

For the reversible alloys the values of the thermoelastic coefficient, $dE/d\theta$, exhibit equally as strange an anomaly as that of the expansibility. The trend is shown by the top curve (Cr = 0) in Fig. 4a. Beginning at a negative, i.e. normal value, the thermoelastic coefficient climbs very steeply, concurrently with increasing nickel content, crosses the zero axis, continues to climb, passes through a pronounced maximum in the invar region, then turns down and carries on more slowly to the value proper to nickel. Thus, for a whole category of alloys, the thermoelastic coefficient is positive; when bent at ordinary temperature, these alloys tend to straighten out when heated.

If not Young's modulus but the coefficient of deformability of the alloys had been plotted as a function of temperature, the sign would have altered and the curve, starting from positive values, would have exhibited a minimum. Its shape would then not have been very different from that of the expansibility curve and the common origin of the two anomalies would have been evident.

Owing to the low elastic limit of the metals at high temperatures the study of their bending deformations is very delicate there. Nevertheless, the application of the rule of corresponding states enables us to presume the characteristic of the modulus. Its general trend is shown by curve 1, Fig. 4c, where the minimum and maximum relate to the two points at which the over-all curve intersects the zero axis; the regions AB, etc..., which have already appeared in the study of the magnetic properties and expansibility, also occur in this curve.

Ternary alloys

The alloys whose properties have just been described are not pure mixtures of iron and nickel free from additions. They are, in fact, complexes in which solely the main constituents are entirely predominant since they form more than 99% of the total mass of the alloy. The additions are close to the indispensable minimum although it is possible to raise the quantity to a second limit and thus obtain ternary or quaternary alloys proper whose properties it is interesting to know.

Apart from the importance of this study considered from the physico-chemical point of view, these alloys may possess properties which render them particularly suitable for practical problems. Thus a sufficient addition of manganese makes the alloys suitable for casting, whereas chromium or carbon, or the two together, raise the elastic limit and make them better for manufacturing into springs.

My studies dealt in most detail with iron-nickel-manganese alloys and they

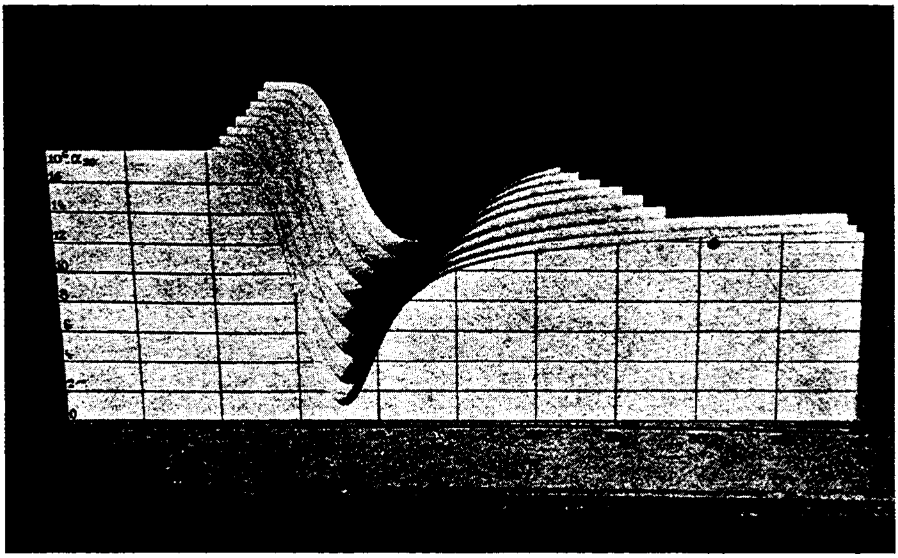


Fig. 5. Triangular diagram of the iron-nickel-manganese alloys.

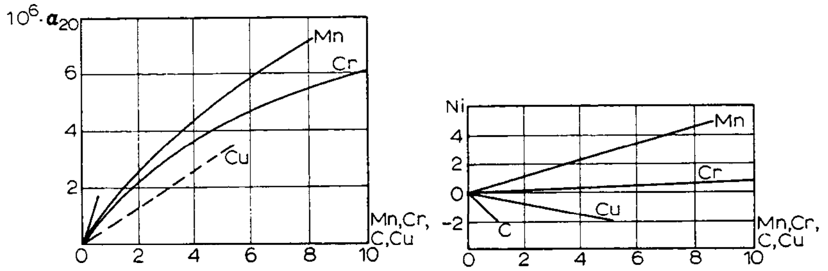
were sufficiently thorough to enable a family of curves Fig. 5 to be plotted on the principle of Guthrie's triangular diagrams.

The first curve is that of the standard alloys containing 0.4% manganese, the others refer to whole per cents, from 1 to 8. This three-dimensional diagram shows that the minimum rises rapidly, at the same time shifting towards the higher nickel contents.

Studies of the action of chromium, copper and carbon, although less extensive, have enabled an accurate plot to be obtained showing the trend of both value and position of the minimum. The two diagrams Figs. 6a and 6b illustrate this trend. Slight extrapolation to higher manganese content shows that when this metal is present to the extent of 10%, in the alloy of least expansibility, it reduces the anomaly by about a half.

The curves in Fig. 7 represent the true expansibilities at 20°C for the limit contents of the additional constituent. The study of their action was of very special significance in connection with a practical problem, the solution of which I was searching for. Essentially the problem was to improve the conditions under which it was possible to prepare an alloy with a zero thermoelastic coefficient, an alloy with invariable elasticity modulus to which I had given the name *elinvar* in advance to define the programme of its preparation.

The binary alloys provide a double solution to the problem. However,



Figs. 6a, 6b. Trend of minimum for nickel steels containing varying additions of manganese, chromium, copper and carbon.

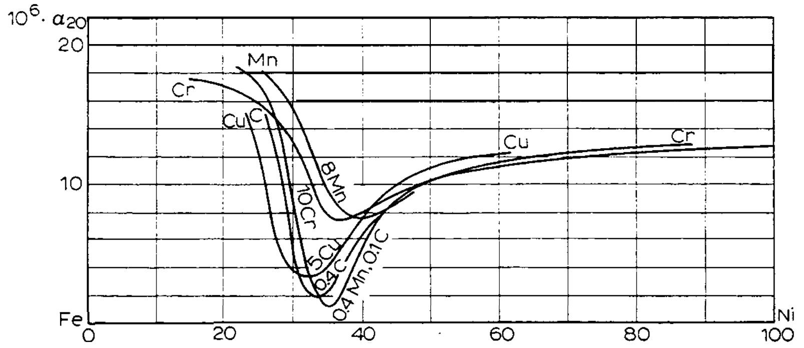


Fig. 7. True expansibilities at 20°C of nickel steels with additions of manganese, chromium, copper and carbon to the limits attained by the experiments.

on the one hand the thermoelastic coefficient curve cuts the zero axis at a very steep angle so that the smallest errors in composition, and even mere defects in the homogeneity of the alloy, lead to a property different from that sought; on the other hand the zero value is nothing other than the minimum or maximum of a variation curve and this value exists practically only over a small range of temperature.

Yet if we consider the raising of the expansibility minimum in ternary alloys and the analogy between the elastic and expansibility anomalies, we can be certain beforehand that suitable additions will give a thermoelastic coefficient curve tangential to the zero axis and, hence, leading to the ready preparation of elinvar. Furthermore, the rule of corresponding states shows that the whole of the modulus values for one and the same alloy will exhibit neither a maximum nor a minimum, but rather an inflexion, probably very extensive and almost horizontal.

These two conditions are indicated in the bottom curve (Cr = 12) in Fig. 4a and in curve 2 of Fig. 4c (region CD); they characterize elinvar.

Direct experiments have established the amount of the additions needed to make elinvar. The elastic limit conditions directed research mainly towards the hardening additions: chromium tungsten and carbon. The number of solutions is infinite since to reduce the anomaly the additions can replace one another continuously. In his torsion experiments, Chevenard found true elinvar with a 12% addition of chromium, the other auxiliary substances being kept close to the indispensable minimum.

Progressive or transient changes

The quite remarkable properties of nickel steels hold much promise for metrology. However, the hopes that had been founded on their use were for long restricted by a real defect which they have, notably a slight instability detected by accurate measurements of the length of test bars repeated over the years or else performed after a variety of heat treatments.

The character of these changes varies from one alloy to another and to describe it effectively it must be related to a particular alloy.

A bar of invar, for example, cooled in air from the forging temperature and kept at ambient temperature extends over the years at rather a fast rate to begin with, then at a progressively slower rate such that after twenty years very accurate measurements can only positively detect the change that occurs in one year.

If the cooling had been interrupted by a period at 100°C, the bar would have extended at an incomparably higher rate than at ordinary temperatures and, after about a hundred hours, the movement would almost have ceased to be perceptible. Generally speaking, the rapid initial rate is an exponential function of the temperature, such that each time the temperature increases by 20°C, the rate increases by a factor of about 7. This movement thus obeys the laws formerly established by Arrhenius.

From almost nothing at 100°C the movement re-ensues when the bar is brought to ordinary temperature but it is much less than in the absence of an intermediate stage. If after a few months or years have elapsed the bar is reheated to 100°C it can be seen to contract rapidly and revert to its length after the first heating.

Thus, at each temperature, the length of the bar tends towards a limit value; between 0° and 100°C these values lie practically on a curve, the ordinates (negative) of which are proportional to the square of the temperature, starting from common zero. This rule continues beyond 100°C, then the rate of change decreases and when the alloy passes into the non-magnetic state, it undergoes only very slight changes.

The difference between the ultimate lengths of the bars at 0° and 100°C is of the order of 30 millionths for standard invar. The first extension, at 100°C, after the forging temperature, has about the same value. However, the magnitude of these changes is a steep function of the nickel content. Thus, when this content is increased from that corresponding to invar the magnitude of the changes diminishes rapidly and there is no change when the nickel content attains 42%; the change then reverses, passes through a negative minimum then continues to increase and ceases perceptibly when the nickel content reaches 70%.

A number of very significant results recently emerged from my study of ternary alloys in the region of instability.

I found, one after another, that the presence of manganese and of chromium reduces the instability while the presence of carbon aggravates it. By means of experiments in which, through the offices of the Aciéries d'Imphy, the carbon additions were made with the ultimate degree of accuracy, I found that the instability is proportional to the carbon and that consequently alloys from which all carbon had been removed would be perfectly stable. However, ferric alloys cannot be altogether freed from carbon and it might be thought that invar will always retain a slight degree of instability.

The cause of this instability appeared to me to be probably in the transformations of cementite (Fe_3C), a compound which forms almost always when iron and carbon occur together and which, again, undergoes transformations with accompanying change in volume.

The answer to the instability problems will thus be to eliminate the cementite. The method is simple, consisting in introducing into the alloy a constituent having a strong affinity for carbon, e.g. chromium, tungsten or vanadium.

Reducing the carbon content to the minimum lowers the expansibility; the supplementary constituent raises it slightly. The matter is novel and the best conditions have not yet been established nor, more especially, achieved. But even now it has been possible to obtain alloy castings, whose expansibility remained that of a good quality invar and whose instability was reduced to one tenth of that of standard invar.

The slow changes in the elastic properties of the alloys, associated with those of their dimensions, have not been studied systematically. However, it may be taken as almost certain that they obey analogous laws in the sense that any increase in volume entails a reduction in the modulus. The ratio of the relative changes in these two properties, either in the transformation of the irreversible alloys, or else in just the expansion of normal metals and alloys, is of an order of magnitude between 20 and 30, i.e. an increase in length is accompanied by a relative decrease in modulus greater by a factor of twenty to thirty.

In the absence of a direct investigation it is possible with a certain degree of probability to guess the form of the laws governing the progressive or transient changes in elastic properties, and even the order of magnitude of their parameters.

Applications

The unusual properties of nickel steels afford an approach by entirely new methods to the generally simple solution of technical and scientific problems hitherto regarded as difficult or complex.

The elasticity or expansion anomalies, and even the magnetic transformations of these alloys, have led to certain applications, the enumeration of which will be sufficient to make them immediately evident.

The presence in a magnetic circuit of a component made of an alloy with approximately the composition at which magnetism disappears rapidly alters the properties of that circuit as a function of temperature. If, say, this component is the armature of a magnet, the mutual attraction will decrease with increasing temperature until it disappears altogether. This circuit can thus be applied as an automatic temperature limiter; for that purpose it is sufficient to load the armature with an appropriate mechanical component. With the alloy piece it is also possible to make a shunt across the magnetic field, the value of which decreases with increasing temperature such that the field proper tends to reinforce itself. Proceeding from this idea E. Meylan has equipped measuring instruments with temperature compensation for field variations.

Furthermore, along the expansibility curve there is a region close to 45% Ni in which the successive alloys have the expansibility of all the usual types of glass. These alloys could be used to make constant-grip optical mountings, or else conductor wires for incandescent lamps. In the latter case the wire, from which the large quantity of occluded gas has first been removed by prolonged heating in vacuo, readily fuses to the glass. The *platinite* so formed has, for this purpose, almost completely supplanted platinum which is thus freed for other applications. The saving achieved in this way is approximately one hundred million crowns.

Elinvar, for its part, is suitable for making monofilar suspensions or, with a slight change in composition, for making tuning-forks, the period of which is independent of temperature. This information, which I announced in 1898, was confirmed in 1912 by Félix Robin who worked extensively on the study of nickel steel thermoelasticity.

This rapid survey clearly demonstrates the diversity of the problems which can be solved with the aid of nickel steels.

We shall now study in detail very refined applications, the method or scientific importance of which prompt a closer examination.

Measurement of length

General - To determine the limits to which nickel steels can be used in constructing instruments for the measurement of length, it is necessary to know those of their properties which will have to be involved in each specific case.

These alloys take a wonderful polish; provided the manganese or carbon addition is not too close to the minimum they are generally free from pitting. Perfectly clean traces can be made on them. They are slightly oxidizable and are able to withstand several hours' immersion in cold water. After a few years in a moist atmosphere the polished surfaces are unimpaired or else covered with a very fine film which can be removed simply by rubbing gently with a soft leather; on the other hand acid vapours attack nickel steels quite rapidly and their action must carefully be avoided.

I should mention, however, that the alloys suitable for all the length measuring applications of invar are not exactly the same. Lengths are measured by means of rulers, the marked surfaces of which are observed through a microscope, or else by means of freely suspended wires, as we shall shortly see. The absence of pitting is an essential quality of the metals used for marked standards; for wires a high elastic limit is required. In the first case the manganese content will be increased, in the second a slight amount of chromium will be introduced into the alloy. Carbon would be useful for both but we have seen that it is the cause of instability; hence it must be used as little as possible.

Although on the one hand it is true that the finished wires must have a high elastic limit, their manufacture on the other hand requires high malleability. These properties appear contradictory to a certain degree. Nevertheless the invar type alloys achieve them in the sense that in the annealed state they are highly extensible but they harden rapidly when mechanically deformed so that if the initial length of an annealed wire has been doubled by drawing, it is capable of quite large elastic deformations.

The instability of nickel steels imposes, as has been stated, a limit to the field of applications for which one might initially be tempted to use them. However, providing that a measuring standard made of, say, invar can from time to time be checked against a perfectly stable standard, it may with almost complete reliability be used as an interpolation instrument; in all cases where its temperature is difficult to determine or cannot be determined with accuracy its value becomes paramount.

The detailed study of the laws governing the changes undergone by invar and the alloys close to it have in the past enabled the results to be freed from most of the effects of these changes. And, for the future, the prospect of making a perfectly stable invar removes most of the objections that might be raised to the use of low expansion alloys in very high precision measurements.

Geodetic base-lines - Every geodetic grid relies on one or more base-lines, each comprising a length marked out on the ground between fixed limits, the intervening distance being as large as permitted by the circumstances and generally of the order of about ten kilometres and measured with the maximum accuracy.

The determination of this distance, in the open air and under frequently ill-defined conditions of temperature, calls for careful precautions which geodesists have persistently striven to elaborate during the last century. During the first three-quarters of the century they tried mainly to improve accuracy largely regardless of the cost of the operations. Then a reaction set in; it was realized that there was more to be gained, as regards dividing the work between measuring angles and measuring lengths, by increasing the number of base-lines or extending them at the cost of a slight loss in measuring accuracy.

E. Jäderin, who assembled and codified the sparse methods, invented new processes and developed a complete technique, was the chief proponent of this reaction which gave rise to a new conception of the organisation of geodetic grids.

In traditional geodesy the measuring instrument was the rigid rod (generally 4 metres long) in conjunction with microscopes sighted on the end-marks to fix their distance on the ground; then, after the rod had been moved a distance of its own length, the position of a third microscope was fixed by reference to the second, and so on. The method was accurate but costly. To avoid the action of radiation the instruments and the observers were accommodated in mobile huts. The instruments themselves were heavy and certain preparatory steps were required before they could be placed in position on the ground. The full team required for the measurements thus totalled about sixty men and, on days when everything went off smoothly, one hundred lengths, i.e. 400 metres, could be measured.

The measuring instrument proposed by Jäderin is a wire under tension at constant load and which is used to determine the relative distances of a series of lightweight marks that are readily transported and placed in position.

The length given to the wire by Jäderin is normally 24 metres, which reduces to one sixth the number of spans. The ground no longer needs preparation; with longer wires, if need be, ravines or rivers can be crossed (the longest wire used so far was 168 metres), all with 12 to 15 men; in short it is much more economical to use and its rate of measurement is quite different from that of the ruler and microscopes.

Temperature remained a very difficult point, of course.

Jäderin had seen, quite rightly, that the best procedure was to apply the principle adopted by Borda and Lavoisier, namely to measure each of the spans in succession by means of a steel wire and a brass wire, the difference between them giving at each moment the common temperature. However, the method developed before the discovery of invar was substantially less accurate than the ruler and microscope method, since the temperature remained unreliable; but the method as a whole was there in the rational form of a much better balance between the number of base-lines and the number of triangles.

Immediately he knew of the existence of invar, Jäderin, who was busy preparing for the measurement of base-lines for the Swedish-Russian Spitzbergen Expedition requested me to supply him with the necessary wire. I had already given the matter my attention and had had the Aciéries d'Imphy prepare wires suitable for base-line measurements, which wires had been used in a number of preliminary experiments. The effect of drawing on the expansibility was already partly known and it was possible to supply the Expedition with wires that were practically non-expanding.

The success of the Spitzbergen measurements in 1899 was quite remarkable. A letter from Jäderin dated Treurenberg Bay, September 13, 1899 actually states the following:

"I am now pleased to inform you that our base-line measurements carried out this summer were completely successful. In both the outward and return directions we measured a base-line of 10,024 metres. So far we have made only a single provisional calculation which shows a discrepancy of merely 19 mm. We made no allowance for the expansion of the wires."

And the letter closed with these words which, through their infinite melancholy, seem to me full of fine courage:

"The last of our boats leaves tomorrow for Stockholm and until June 1900 we shall be left completely separated from the world. Only once post has arrived for us; part of it seems to have gone astray."

This message from the ends of the inhabitable world was for me the most powerful and the most valued encouragement. Benoit and I performed our own experiments with greater urgency and when, a year later, the Geodetic Association met in Paris, while the results submitted by the Swedish-Russian Expedition created a tremendous sensation, we were able to assert that a very high accuracy ought to be attained by an even greater perfection of the method, to which we were prepared to devote our utmost efforts. The Association passed a resolution to that effect and the committee vested with the permanent authority over the International Bureau finally entered this project on its programme.

A wall base-line which was built at once has been used since 1901 for studies which have been continuously in progress ever since.

The observations which we have made in about twenty years now number some hundreds of thousands. However, our labours have been amply rewarded since we have been able to define the conditions under which invar wires which have first been specially treated, then determined at the Bureau or in any standardization laboratory, can be transported in the form of a coil to the base-line area, then uncoiled and used without their characteristics altering.

By eliminating temperature-induced errors from measurements altogether, the use of invar wire appreciably raised the accuracy of the method. To take advantage of the method's potentialities Benoit and I were led to make a partly new equipment which now ensures that in the measurement of each span - normally 24 metres - errors of the order of a hundred thousandth of the measured length will never be made. In accordance with the principle of the addition of errors, a length of 100 spans will thus not be subject to errors of the order of one millionth as a result of the observations.

A great many base-line measurements have been carried out in recent years using invar wire. The checks obtained either by the determinations performed in the outward and return directions or else by successive measurements with different wires have revealed that an accuracy of one millionth is quite common. Since the equipment is very easily installed it is now possible to use sites which would have been quite unsuitable with the old instruments comprising rigid rulers and microscopes. Moreover, in view of the speedy installation and the long spans coupled with the light weight and ready transportability of the equipment, it has been possible to reduce the number of personnel to about one fifth, and increase the speed tenfold; a well-trained team is capable of measuring up to 5 km in a day. Thus, the over-all saving in the measurement of base-lines is about 98%.

The increase in the number of base-lines and their greater length strongly reduce the effects of errors in the measurement of angles and the requirements which traditional geodesy was obliged to impose on them can be relaxed; the result is a second appreciable saving.

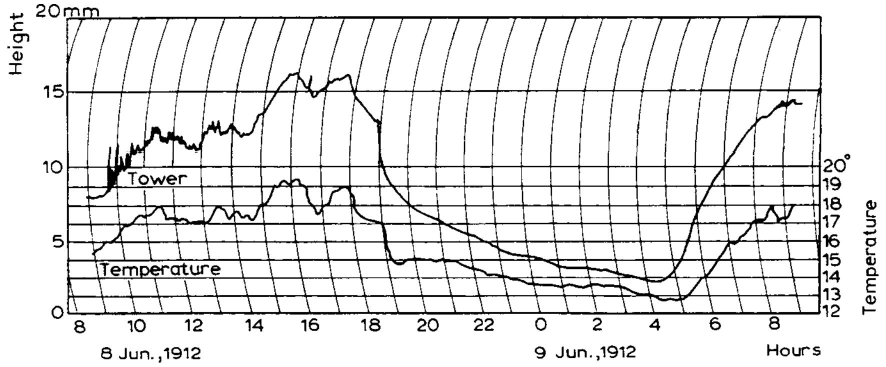
Non-expanding transmissions - From the point of view of the principle I shall confine myself almost entirely to the matter which has just been discussed by mentioning transmission over a fixed distance by means of an invar wire.

Its specialist applications are many. On railways, for example, there are a great many transmissions between a manoeuvre in a signal box and a movement received by a signal on the track. The expansion of the control wires disturbs the transmission: in the case of a rather severe temperature drop it may cause the signal to operate prematurely, and if the temperature increases rapidly, the expansion may completely neutralize the manoeuvre. Invar wire has afforded a means of overcoming these drawbacks and of guarding against the resultant dangers; however, its use has not been very widely adopted since, except for in special cases, the price of the alloy is considered prohibitive.

In contrast, no such limitation is involved in the acceptance testing of metal structures where a wire, fixed at one end to the structure itself, faithfully transmits its movement to a recording instrument.

The study, interesting in itself, of the vertical movements of the Eiffel Tower, plainly demonstrates the variety of applications of which this technique is capable.

Invar wire has greatly facilitated this operation. A wire of this type, fixed at its lower end to a peg in the ground, was attached at the other to a lever mounted on the second platform of the Tower and which actuated a recording instrument; a damping device integral with the lever compelled the latter to return slowly to the position assigned to it by the straight wire when it had momentarily been bent by a gust of wind. The experiment showed that, however violent the movement of the air, moments of calm occur from time to time which are sufficiently long to allow the lever to return to its rest position. Thus, its limit positions indicated the true movements of the



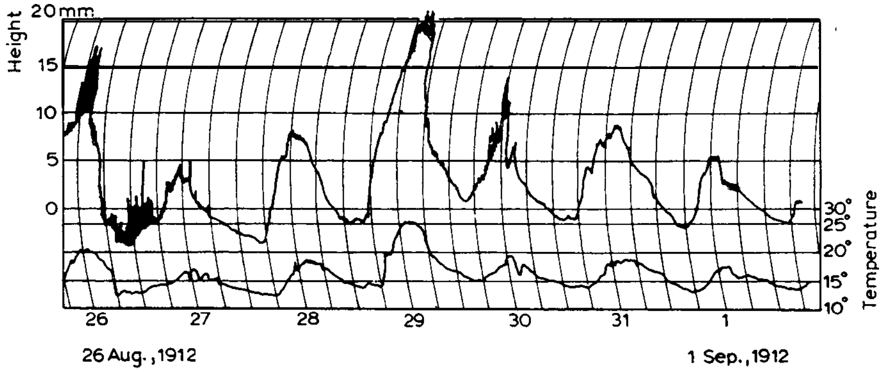


Fig. 8. Daily movements of the Eiffel Tower (a downpour at 19 hours caused a sudden temperature drop).

Fig. 9. Movements of the Tower under variable summer conditions (stormy week).

Tower, while a kind of tail, starting from the envelope, recorded the gusts of wind.

Figs. 8 and 9 show two examples of the movements observed. The first was obtained using a recording drum which rotated once per day, the other with one rotating once weekly. The lower curves are those of the thermograph.

When inspecting the two series of curves it is impossible not to be struck by their extraordinary similarity, which is such that each small inflection of one has its counterpart in the other. Thus the Eiffel Tower appears as a gigantic thermometer of high sensitivity, notwithstanding its enormous mass.

Measurement of time

Once time measuring instruments had become sufficiently accurate it became evident that their action was affected by temperature and attempts were made to guard against this by fitting them with devices known as compensators, the effectiveness of which had been demonstrated by a century and a half of experience, although they complicate the already complex mechanisms of clocks and watches.

Reference has been made earlier to the causes of the temperature-induced changes in the functioning of watches; they are very different from those specific to clocks, so that the two problems have to be treated separately.

The compensated pendulum in clocks - Of the various compensating devices invented to offset the influence of temperature on clock pendulums, the most widespread by far a few years ago was Graham's, which took advantage of the upward expansion of mercury in a vessel suspended from the pendulum rod to cancel out the effects of the rod's downward expansion.

Invar which has been treated in various ways is capable of all possible expansions between two limits close to zero and a bob of any desired metal will, when attached to the nut of the previously selected rod, correct the extensions of the rod by its upward expansion.

The advantages are many. Apart from the presence in the oscillating system of a liquid, Graham's pendulum has the drawback of being actually compensated only provided that the temperature is uniform from top to bottom of the clock case, a condition which is fully satisfied only in competently constructed installations.

It will be noticed that for this specific application, the instability of ordinary invar does not matter since the state of a clock must be checked from time to time, so that a slow change in its daily rate entails no error in the time measurement. After a few year's operations, this change will be reduced to two or three hundredths of a second per year.

The compensating spring of watches - A watch fitted with a steel balance spring and a brass balance loses, as we have seen, about 11 seconds per degree per day, almost the whole of this change being attributable to the variation in Young's modulus of the metal from which the spring is made. A correcting mechanism for watches is thus indicated.

In Ferdinand Berthoud's "marine clocks" this mechanism comprised a bimetallic plate which automatically modified the active length of the spring. In 1775 Arnold invented the compensating balance which was soon perfected by Earnshaw and which consists of a diametral arm, from the two extremities of which project semi-circular, bimetallic plates, steel inside, brass outside, which curve in towards the axis when the temperature rises, so reducing the moment of inertia of the assembly in the mean ratio of the change undergone by the elasticity modulus of the balance spring.

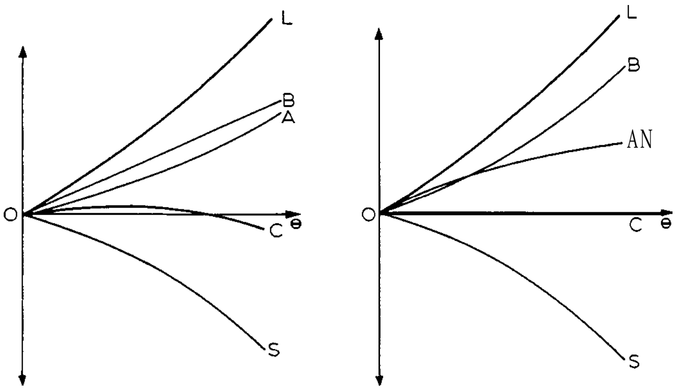
If the steel of the spring is replaced by a nickel steel of composition such that the maximum or minimum modulus occurs at ordinary temperatures, the watch, fitted with a monometallic balance, will function alike at two temperatures at either side of the ambient, e.g. 0° and 30° C, and between the two will gain or lose most at 15° C. The trend of the curve is such that the maximum gain (the loss occurs with alloys having a low elastic limit) will be 20 to 25 seconds per day compared to the running at extreme temperatures, this being twelve or fifteen times less than the discrepancies observed in the case of the steel balance spring. This progress has been considered so important by watchmakers that almost three million watches are equipped annually with the compensator spring.

Correction of secondary error of chronometers by the integral balance - Arnold and Earnshaw's balance does not compensate entirely the action of temperature on the rate of watches. Ferdinand Berthoud noticed in 1775 a "secondary error" which Dent found in 1832 for the balance, and which consists in the fact that a watch equipped with a steel balance spring compensated by a steel-brass balance gains 2 to 3 seconds per day at 15° C, if it functions correctly at 0°C and 30°C.

Considerable efforts were made with a view to eliminating Dent's error.

We shall see how a rational application of a nickel steel afforded a very simple means to achieve that.

The reason for Dent's error lies in the following fact: the elasticity modulus of the balance spring varies with temperature in accordance with a pronounced curve OS (Fig. 10a). The action of the balance, for its part, is controlled by the difference in expansibility between the brass OL and the steel OA, expressed by functions in which the coefficients β are very approximately the same. Their difference OB will hence be linear and the algebraic sum of OS and OB, i.e. OC, will leave a quadratic remainder.



Figs. 10a, 10b. Diagrams showing the cause of the secondary error of chronometers and the principle of its correction.

Let us now replace OA by a curve OAN (Fig. 10b) representing the expansibility of a nickel steel with negative β. The difference with OL will be a curve OB which can be made symmetrical with OS and thus a zero algebraic sum is obtained at all its points.

In 1899 I made the design calculations for such a balance, the low expansion constituent of which was a steel containing 45% Ni, and in 1900 two Swiss chronometer makers, P. D. Nardin and P. Ditisheim, achieved complete temperature compensation by its aid.

From then on the new balance has replaced the old practically everywhere in precision chronometers. Rate logs thus became obsolete, not only owing to the elimination of the secondary error but because once chronometers no longer had this error it became important to attempt to correct the lesser defects. In fact, the rates of the best chronometers today are four to five times less erratic than twenty years ago.

The complete solution to the problem of compensation by the elinvar balance spring - For more than ten years I thought that the use of nickel steels had led to all the fundamental improvements in compensating mechanisms of which they were capable. Yet, in about 1912, a faint inkling occurred to me of a means to achieve perhaps the ultimate solution to the compensation problem. When studying ternary alloys I had just had a glimpse of the simultaneous reduction in the anomaly of expansibility and thermoelasticity.

A series of experiments was embarked on during the following year using two series of alloys with varying nickel contents and with 5% and 10% additions of chromium. The maximum thermoelastic coefficient in this second series was already very close to that of elinvar and only a very slight modification of the composition was needed to produce an alloy forming balance springs which in conjunction with monometallic balance wheels vouchsafed that the watches in which they were fitted ran almost the same at various temperatures and were almost free from the secondary error. The problem was hence very close to its solution. Then, after a pause, the experiments could be resumed; they recently resulted in the manufacture of balance springs which, in conjunction with a suitably chosen monometallic balance, constitute a regulating device almost entirely immune to temperature changes.

Such a simple solution as this to a long standing problem is regarded as revolutionary by the most competent chronometer makers. However, its very simplicity, if its retention is insisted upon, conceals a further slight defect.

The particular and immense advantage of the new combination is that of leading very close to perfection at the first attempt by the association of a balance spring having a low, constant thermoelastic coefficient with a balance of suitable expansibility. For industrial manufacture the balance metal will be matched as closely as possible to the requirements of the balance spring; the range of expansions between invar and brass affords ample scope for doing so. Nevertheless once the combination has been found it is not, at least in its immediate form, suitable for those progressive and meticulous small alterations which make the task of the regulator an art at once so difficult and so exciting.

To reduce the scope of this reservation to its correct proportions forthwith, I should state that at the present time it is very common for the combination of a balance spring and monometallic balance to be manufactured. the temperature-induced error of which is less than one hundredth of that which would occur were a steel spring used.

Currently the situation is that whereas the compensating spring used to be restricted to use in ordinary watches, it is now becoming established in the precision watch sector; at present it is still only barred from precision chronometry. However it has only just appeared and it would be presumptuous to think that it has reached the limit of its perfection at the first attempt.

The simplicity of the new compensating mechanism entails many advantages. Bimetallic plates invariably upset regulators slightly who see in them a possible cause of instability; deformations by centrifugal force necessitate ensuring that the large and small arcs are isochronous by slight alterations to the shape of the balance spring; lastly the rectangular shape and the presence of setting screws cause air to be entrained, so giving rise to a "barometric coefficient" whose value is sufficiently high for the changes in atmospheric pressure to constitute in certain circumstances the essential cause of rate variations in the present state of chronometry. On the other hand it is easy to taper the cross-section of a monometallic balance wheel, reducing as far as possible the entrainment of air. These various points enhance the relative advantages of the new balance spring and should justify relaxing the stipulations governing the ultimate limits of compensation.

Conclusion

Let us now glance back to the origins of the studies of which the results have just been reported. The point at issue was essentially to look for a metal having qualities which would enable it to be used to make standards of length that are inexpensive while satisfying metrological requirements. An initial solution had been found which required only slight refinement and it was during the search for this slight refinement that an unsuspected anomaly came to light which was a direct manifestation of the struggle between the various states of iron to which the association of nickel gives an unexpected shape, creating a class of alloys whose properties, unique so far, satisfy in a quite unhoped-for manner the wishes which metrologists would have formulated had it not been assumed that such properties could not exist in metals.

Then the problem broadened: from the measurement of length, which was the only aim of the original programme, the measurement of time arose of its own accord as a direct and to some extent obvious consequence, so true is it that in metrology everything is related and that a carefully executed measurement invariably entails generalizations.

The whole of the research programme required the constant collaboration of a factory and a laboratory. The great advantage of cooperation of this type is nowadays commonly appreciated and it would be superfluous to insist on it except to highlight a particular feature.

When in the spring of 1896, the Société de Commentry-Fourchambault & Decazeville undertook to assist a programme of research which, failing such assistance, would not have advanced beyond its initial stages, they did so without the directors imagining that they would be rewarded with anything but the satisfaction of having lent effective assistance to a task of scientific exploration. But the meticulous examination to which the alloys were subjected, and the increasingly stringent requirements imposed on the company as regards the compositions as well as the treatments, led, in the jointly explored field, to the creation of a kind of precision metallurgy, the result of which has been the manufacture of products considered impossible a few years ago.

That has been a new and unexpected outcome of the scope of precision measurements. Demanding unflagging and occasionally laborious effort of those who apply themselves to it, precision measurement research could not long be pursued without the guidance and illumination of an ideal of perfection. For the research worker himself, this ideal stimulated by a belief in the utility - even afar off - of every unselfish effort is his mainstay at all times and the counsellor of every initiative.

The highest approval which you have just conferred on my work highlights a task stretching back a quarter of a century and for that reason I feel obliged right here to express my deepest gratitude to the illustrious members of the Nobel Committee and of the Swedish Academy of Sciences, as well as to the memory of Alfred Nobel. From generation to generation my descendants will look with pride on the magnificent diploma and the Nobel medal, treasured testimony of your kindness and esteem. But also I wish to express my gratitude to you on behalf of the International Bureau which I have served for thirty-seven years and whose existence reflects at this moment the dramatic changes occurring in the world. Next I am grateful to you on behalf of metrology on which the conferment of a Nobel Prize casts a bright lustre well-fitted to commend it as a vocation. Lastly my gratitude is on behalf of the two countries with which my life is associated: Switzerland, of which I am a citizen and which I left equipped for life, and France, where I have known so many esteemed friendships.