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Expansion Properties of Low-expansion Fe-Ni-Co Alloys

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(New York Meeting, February, 1930)

Invar is the preëminent low-expansion metal by virtue of the fact that it can be prepared with a zero coefficient of expansion at atmospheric temperature. This fact suggests that there is little room for improvement in the expansion properties of the low-expansion nickel steels. The inference is true, however, only so far as the expansion at and near atmospheric temperature is concerned, because the expansivity of invar starts to increase rapidly on heating above 100° C. and soon reaches the value of copper. Guillaume[1] met this situation by increasing the nickel content above that of invar. By that expedient, alloys having low expansivity under higher temperatures were obtained, but not without a large increase in minimum expansivity. The increase in minimum expansivity with increasing nickel content severely limits the technical applications of these alloys at high temperatures.

Prospects of improving the expansion characteristics of the nickel steels is offered by alloying. Search for an advantageous alloying addition by analogy with other alloy systems, however, is not productive because the low-expansion characteristic is unique with that system. The rule of mixtures usually gives a fair value of the expansivity of other solid-solution alloys, but in the iron-nickel systems gives a value of 18×10^{-6} per deg. C. whereas the actual value is 1×10^{-6} per deg. C. Apparently suitable additions are not to be deduced from such ingenuous considerations.

Recognition of the fact that the temperature range of low expansivity in nickel steels is terminated with loss of magnetism affords a more promising basis for the selection of an advantageous element. One may expect from that fact that additions of nonmagnetic elements to the iron-nickel alloys are detrimental to the low-expansion characteristic. Indeed, carbon, manganese, silicon, copper and chromium are detrimental to the expansion properties and no nonmagnetic element is reported to be beneficial. From the same viewpoint, the addition of a magnetic metal offers prospects of improvement. As two of the three ferromagnetic elements are already present in the

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[1] U. S. Bureau of Standards *Circular* 58 gives an excellent review of the history and properties of the low expansion nickel steels.

low-expansion alloys, there remains only cobalt as a promising addition thereto. Brace[2] made this addition and found a marked improvement in the expansion properties.

The introduction of cobalt into the iron-nickel alloys brought complications not met in the simpler system. Investigation of these complications showed that a certain minimum content of nickel is required to preserve the low-expansion characteristic over a favorable temperature range when cobalt is present in considerable quantity. With incomplete knowledge of the limiting nickel content, a series of alloys was prepared with a high constant nickel content and cobalt variable. Study of the expansion properties of this group of alloys showed the general effects of cobalt and permitted an explicit statement of the problem of determining optimum compositions, as given in the following section. Subsequent sections are devoted to the experimental solution of the problem and to the determination of the relation of the expansion properties to composition.

The apparatus used for measuring expansion makes use of the differential expansion between the test specimen and a fused silica tube. Differential length changes are measured by means of a dial indicator sensitive to 0.0001 in. The test method has already been described[3] except for one improvement. This was the substitution of a pin bearing at the contact end of the mechanical length-change indicator for the previous ball-and-socket contact between the lever arm and the silica rod which transmits motion of the upper end of the specimen to the indicator. The readings of the length-change indicator were converted into true unit expansion by the relation:

$$E = \frac{Mx}{L} + NT$$

where E is the true unit expansion between 0° C. and the temperature of observation T. x is the corresponding increment in dial reading, L is the length of the specimen, M a correction for transverse expansion of the specimen having the value 0.95 and N a correction for the expansion of the silica tube having the value 0.53×10^{-6} per degree Centigrade.

The alloys tested were prepared by melting 13-lb. charges of electrolytic iron and nickel with other elements in a high-frequency induction furnace. The charges were melted in magnesia-lined graphite crucibles and protected from excessive oxidation by a top on the furnace. Manganese and silicon were added just before pouring. Ingots 2 in. square were poured in cast iron molds and forged usually to $\frac{3}{8}$-in. round bars. These bars were rolled or swaged to $\frac{1}{4}$-in. dia. and were tested after annealing.

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[2] U. S. Patent 1680814.

[3] H. Scott: *Trans. Amer. Soc. Steel Treat.* (1928) 13, 829

EXPANSION CHARACTERISTICS

The significant expansion characteristics of the Fe-Ni-Co alloys are brought out clearly by a complete expansion curve of an alloy having insufficient nickel content to depress the gamma to alpha (Ar_3) transformation of iron, below atmospheric temperatures. Such a curve, taken through a complete cycle of heating from liquid-air temperature, about −180° C., to 780° C. and cooling again, is given in Fig. 1. It is evident that Ar_3 was consummated on the initial cooling to room temperature, after which the alloy has approximately the same expansivity (slope of curve) as ordinary steel. On the first heating Ac_3 starts at about 400° C. and progresses gradually to completion at 750° C. The alloy, now in the austenitic state, has a very high expansivity which it retains on cooling until it reaches inflection temperature (approximately 460° C.), below which its expansivity rapidly diminishes to a low value while the alloy is still in the austenitic state. At 100° C. Ar_3 starts and the reversible expansion range ends.

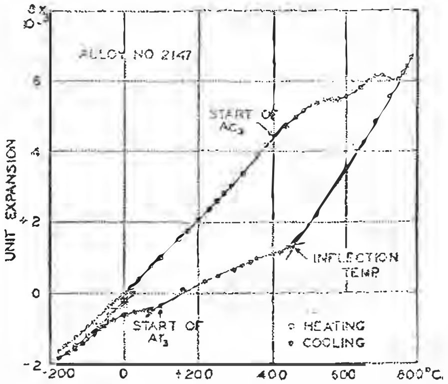

FIG. 1.—CONTINUOUS EXPANSION CURVE OF AN FE-NI-CO ALLOY ON HEATING FROM −180° C. TO 780° C. AND COOLING TO −180° C.

This curve shows both the low expansivity characteristic of these alloys and the A_3 transformations of iron.

It is important to recognize here that the expansion on cooling from 780° to 100° C. is reversible; *i. e.*, if cooling is stopped above 100° C. and the specimen is again heated, the expansion curve of cooling will be retraced. If, however, the cooling is stopped below 100° C., the expansion curve of cooling is not reproduced on heating again; in other words, the expansion is irreversible. Evidently, then, it is essential to depress Ar_3 below atmospheric temperature in order to enable practical utilization of the low and reversible expansivity available on cooling between the inflection temperature and Ar_3; 460° C. and 100° C. in this case.

The alloys of immediate concern were prepared by melting charges of 32 per cent. nickel and 1 per cent. manganese with different amounts of cobalt, the remainder of the charge being iron. Their compositions are given in Table 1, together with all the compositions considered. Only one of these alloys, No. 1782, showed Ar_3 on cooling to liquid-air temperature; then it started at −130° C. (Fig. 2). Consequently the expansion properties of this group can be investigated at normal temperatures with assurance of freedom from complications introduced by the irreversible transformation of iron.

Expansion curves of members of the group concerned are given in Figs. 3 and 4. These curves were all taken on heating. Some observations were taken on cooling also, but are not plotted. The observations on cooling usually fell close to those on heating, otherwise the curves on heating were not accepted as reliable. These curves are plotted from 0° C. to well above the inflection temperature, although in most cases the curves were taken from liquid-air temperatures. This was done to show the expansion range of chief interest on a scale sufficiently open to avoid confusion. Some curves below 0° C. will be introduced later.

TABLE 1.—*Composition of Alloys*

Alloy No.	Ni, Per Cent.	Co, Per Cent.	Mn, Per Cent.	C, Per Cent.	Fe,[a] Per Cent.
1655	28.4	9.8	0.86	0.03	60.8
1700	31.3		0.70	0.03	67.9
1708	26.6	9.9	2.30	0.05	61.2
1744	10.2		9.20	0.03	80.6
1782	31.8	6.0	0.84	0.02	61.3
1783	31.9	9.8	0.79	0.01	57.4
1784	31.9	14.2	0.85	0.01	53.1
1791	33.3		0.88	0.03	65.8
1987	31.7	16.0	0.65		51.6
1988	31.6	16.7	0.83		50.9
1989	31.6	18.6	0.78		49.0
2031	32.4	8.2	0.66		58.7
2034	32.7	11.0	0.62		55.6
2089	24.8	23.9	3.52		47.7
2090	30.5	19.0	0.81		49.6
2091	28.0	20.7	0.67	0.02	50.6
2092	26.4	23.3	0.74		49.5
2106	38.0	10.5	0.66		50.8
2113	27.4	22.1	0.69		49.8
2114	25.1	23.4	0.68	0.03	50.8
2115	24.3	24.4	0.63		50.6
2118	19.8	38.2	0.91	0.53	41.1
2119	15.2	42.6	0.93		41.2
2123	29.8	15.5	0.22		54.5
2125	28.0	17.4	0.64	0.02	54.0
2127	23.6	29.6	0.81		46.0
2146	23.4	25.4	0.35	0.14	50.7
2147			0.56	0.02	51.3
2148			0.52	0.11	51.3
2149	24.1	24.0	0.57	0.19	51.1
2150			0.61	0.33	51.0
2151	19.3	28.9	3.77		48.0

[a] By difference.

It is now of interest to compare the expansion properties of these alloys with those of appropriate cobalt-free alloys. This may be done by plotting as in Fig. 5, the expansion curves of selected alloys with and without cobalt having the same expansivity or temperature range

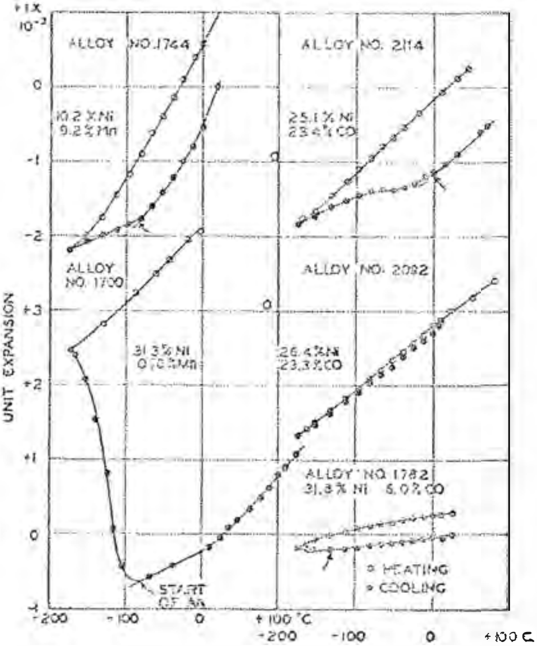

FIG. 2.—EXPANSION CURVES OF ALLOYS ON COOLING IN LIQUID AIR TO LOCATE COMMENCEMENT OF Ar_3 WHEN BELOW ATMOSPHERIC TEMPERATURE.

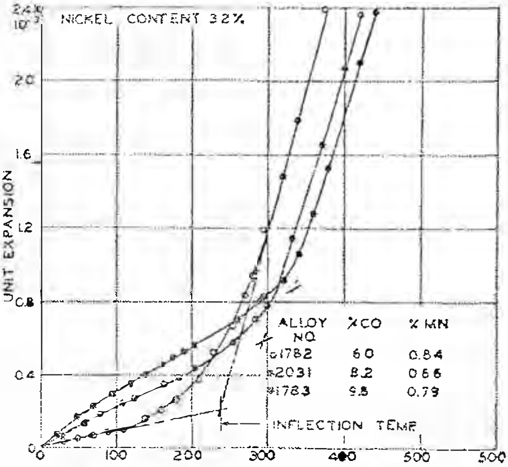

FIG. 3.—EXPANSION CURVES OF ALLOYS CONTAINING 32 PER CENT. NICKEL AND 6 TO 10 PER CENT. COBALT. Ar_3 HAS BEEN DEPRESSED BELOW ATMOSPHERIC TEMPERATURES.

of low expansivity. Of two alloys having nearly the same expansivity in the low range, Nos. 1794 and 1988, that having a substantial cobalt content, No. 1988, has a much longer range of low expansivity. In the same way, of two alloys having the same range of low expansivity, Nos. 1794 and 2034, the one having a high cobalt content, No. 2034, has much the lower expansivity over that temperature range.

The foregoing comparison is interesting but not quantitative; also, the results apply to only a single pair of alloys. To furnish a more general and useful basis for determining the effects of cobalt, it is necessary to evaluate the expansion characteristics numerically. The two properties of these alloys of chief interest are the inflection temperature and a value representative of the expansivity below the inflection temperature. The inflection temperature may be conveniently, though arbitrarily, evaluated by the temperature of intersection of two straight lines, one drawn tangent to the curve at the point of minimum slope and the other at the point where the slope of the curve first reaches a value of about 16 × 10^{-6} per deg. C. The slope of the line first mentioned evidently gives the value of the minimum expansivity, a significant and useful property of the alloy. For some purposes, however, a mean value of the expansivity is more useful. For this the slope of the straight line connecting the origin and the expansion value at the inflection temperature is taken and identified as the mean expansivity.

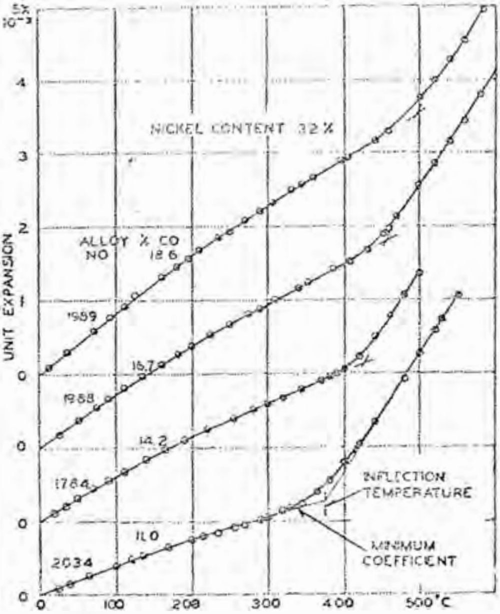

FIG. 4.—EXPANSION CURVES OF ALLOYS CONTAINING 32 PER CENT. NICKEL AND 11 TO 19 PER CENT. COBALT.

The properties just described of the alloys containing 32 per cent. nickel are given at the top of Table 2, following the same data on cobalt-free alloys taken from the previous report. We now have numerical values of the expansion characteristics of alloys with and without cobalt, which may be compared easily. From examination of the tabulated data, it is readily apparent that the inflection temperatures correspond closely in alloys having the same content of nickel plus cobalt whether the cobalt content is high or low. Accordingly, the expansion characteristics are plotted against nickel plus cobalt content in Fig. 6.

Referring to the inflection temperature first, plotting this property against nickel plus cobalt is fully justified because the observations for both cobalt-containing and cobalt-free alloys fall close to a smooth curve.

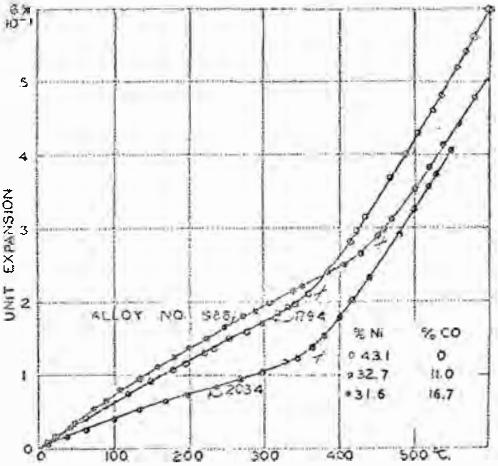

FIG. 5.—EXPANSION CURVES SHOWING EFFECT OF COBALT IN LOWERING EXPANSIVITY WHEN INFLECTION TEMPERATURE IS UNCHANGED AND IN RAISING INFLECTION TEMPERATURE FOR A GIVEN MINIMUM EXPANSIVITY.

This permits the statement of a general rule; namely, that cobalt has quantitatively the same effect on the inflection temperature as nickel. Accordingly, cobalt must be considered as a substitute for nickel rather than as an addition agent to the low-expansion nickel steels.

It may now be stated that comparison of alloys on the basis of nickel plus cobalt content is equivalent to comparison on the basis of equal temperature ranges of low expansion. That statement infers that the temperature range of low expansivity is the same for a given inflection temperature whether the cobalt content be low or high, which is supported by Fig. 5. This is the most satisfactory basis of comparison for, after all, the merit of the cobalt-containing alloys depends on the degree to which their expansivity is lower than that of cobalt-free alloys having the same temperature range of low expansivity. Consequently the difference between the curves of either minimum or mean expansivity of the cobalt-free and cobalt-containing steels is a direct measure of the improvement conferred by the substitution of cobalt for nickel.

The minimum and mean expansivities of the alloys considered are plotted against nickel plus cobalt content at the bottom of Fig. 6. In both cases the curves for the alloys containing cobalt are lower than those for the cobalt-free alloys, showing the improvement conferred by the substitution of cobalt for nickel. Moreover, the separation between

TABLE 2.—*Observed Expansion Properties of Alloys*

Alloy No.	Composition			ΣL″ %Fe	Inflection Temperature Deg. C.	Expansivity	
	Ni, Per Cent.	Co, Per Cent.	Mn, Per Cent.			Minimum	Mean
NICKEL VARIABLE							
1791	33.3	<1.0	0.88		125	1.2×10^{-6}	4.6×10^{-6}
1717	33.8	<1.0	0.88		150	1.1	3.8
1793	35.9	<1.0	0.87		210	1.1	3.0
1819	38.2	<1.0	1.00		250	1.5	3.0
1863	40.2	<1.0	0.80		310	2.2	3.4
1864	42.1	<1.0	1.54		325	3.7	4.8
1704	43.1	<1.0	0.92		370	5.0	6.2
1718	47.1	<1.0	0.82		430	7.0	7.8
10	50.2	<1.0	0.61		510	9.1	10.0
MANGANESE VARIABLE							
1912	45.2	<1.0	0.53		420	6.1	7.0
1913	45.4	<1.0	1.96		390	6.6	7.3
1914	45.4	<1.0	5.03		325	7.4	8.2
2123	28.8	15.5	0.22		415	3.3	4.3
2125	28.0	17.4	0.64		400	3.1	4.1
COBALT VARIABLE, NICKEL CONSTANT							
1782	31.8	6.0	0.84	0.56	240	0.9	2.4
2031	32.4	8.2	0.66	0.59	295	1.7	2.6
1783	31.9	9.8	0.79	0.59	335	2.4	3.0
2034	32.7	11.0	0.62	0.62	375	3.0	4.0
1784	31.9	14.2	0.85	0.64	425	4.3	5.4
1987	31.8	16.0	0.65	0.65	450	5.0	6.0
1988	31.6	16.7	0.83	0.67	450	5.4	6.3
1989	31.6	18.6	0.78	0.69	495	6.2	7.4
COBALT VARIABLE, NICKEL + COBALT CONSTANT							
1855	31.6	16.7	0.83	0.67	455	5.5	6.3
2091	28.0	20.7	0.67	0.59	460	4.7	5.8
2092	26.4	23.3	0.74	0.58	480	5.1	6.2
2114	25.1	23.4	0.68	0.54	465	4.2	5.5
2089	24.8	23.9	3.52	0.71	390	5.3	6.2
NICKEL + COBALT VARIABLE, MAXIMUM COBALT							
1782	31.8	6.0	0.84	0.56	240	0.9	2.4
2125	28.0	17.4	0.64	0.56	400	3.1	4.1
2091	28.0	20.7	0.67	0.59	460	4.7	5.8
2092	26.4	23.3	0.74	0.58	450	5.1	6.2
2127	23.6	29.6	0.81	0.57	500	6.6	7.7
2118	19.8	38.2	0.91	0.67	620	8.0	9.3
CARBON VARIABLE							
2114	25.1	23.4	0.68	0.54	465	4.2	5.5
2147	24.1	24.0	0.56	0.50	460[a]	3.9[a]	5.4[a]
2148	24.1	24.0	0.52	0.54	470	4.2	5.6
2149	24.1	24.0	0.57	0.57	470	4.3	5.8
2150	24.1	24.0	0.61	0.61	465	4.3	5.9

[a] Observations made during cooling.

the curves increases with the nickel plus cobalt content. It follows from this observation that the improvement is more or less in proportion to the amount of cobalt substituted for nickel, because the cobalt content increases in direct ratio to the nickel plus cobalt content in both series of alloys carrying cobalt.

Having found that the reduction in expansivity conferred by the substitution of cobalt for nickel increases with the amount of the substitution, it is evident that the limit of the improvement has not been reached in this group of alloys. All of the alloys except No. 1782 will permit a considerably higher substitution of cobalt without bringing Ar_3 in the vicinity of atmospheric temperatures. This introduces the question: what is the limiting amount of cobalt that can be substituted for nickel without bringing Ar_3 dangerously close to atmospheric temperature for all useful nickel plus cobalt contents? An answer to this question is necessary to establish optimum compositions of these alloys and is sought in the following section.

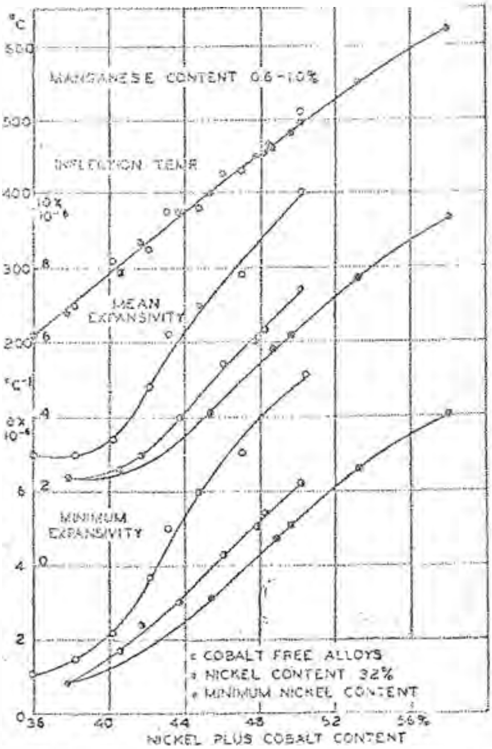

FIG. 6.—EFFECT OF NICKEL PLUS COBALT CONTENT ON INFLECTION TEMPERATURE AND EXPANSIVITY OF Fe-Ni-Co ALLOYS UNDER THREE DIFFERENT RELATIONS OF NICKEL TO COBALT CONTENT.

Limiting Compositions

If iron, nickel and cobalt were the only elements present in the alloys studied, the problem of finding the optimum compositions would be comparatively simple. It is necessary, however, to add manganese and silicon to these alloys when melted in an air atmosphere to render them easily forgeable. Carbon also is always present, being introduced with the charge or picked up from the furnace atmosphere during melting. Silicon is added in such small quantities that it has no considerable effect either on the expansion properties or on Ar_3 and consequently may be neglected. Carbon and manganese, however, have pronounced effects which require evaluation.

The presence of manganese or carbon in the Fe-Ni-Co system complicates the problem because it removes these alloys from the ternary class, which can be easily represented graphically, and into the quaternary class, which cannot be so represented. This complication, however, can be avoided provided that the content of secondary elements is small, as is true of the useful alloys. The expedient applicable for this purpose is to consider manganese and carbon multiplied by appropriate factors as equivalent to nickel as regards their effects on Ar_3. Thus these complex alloys are brought into the ternary class by taking the equivalent nickel content as one composition variable.

The effect of manganese in lowering Ar_3 may be evaluated from the fact that Ar_3 starts at −80° C. in both of two Fe-Ni-Mn alloys, which differ markedly in manganese content. Their expansion curves on cooling in liquid air are given in Fig. 2 and compositions in Table 1. As the ratio of their difference in nickel content to their manganese content is 2.5, it is evident that manganese is 2.5 times as effective as nickel in lowering Ar_3. Hence the equivalent nickel content can be expressed by:

$$\%\,L' = \%\,\mathrm{Ni} + 2.5\,(\%\,\mathrm{Mn})$$

in the absence of carbon. Lacking cobalt-free alloys in which carbon is variable, the determination of the relative effect of carbon is deferred. For the present only the relation of equivalent nickel content to Ar_3 in the practical absence of cobalt and carbon will be considered.

Plotting the data of Hanson and Hanson[4] and of the writer on the start of Ar_3 in Fe-Ni-Mn alloys against equivalent nickel content in Fig. 7, it may be seen that Ar_3 is depressed to −100° C. when the equivalent nickel content is 34 per cent. At that temperature Ar_3 is safely depressed so far as terrestrial temperatures are concerned, so this is a good value to aim at. In the series of Fe-Ni-Co alloys already considered, Ar_3 is depressed below −180° C., so higher cobalt contents can be

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[4] *Jnl.* Iron and Steel Inst. (1920) **102**, 39.

safely used. Consequently the cobalt contents with which Ar_3 is depressed to −100° C. is sought for all useful nickel plus cobalt contents.

Without any preëxisting information as to the location of Ar_3 in high-cobalt alloys, a preliminary survey of this field was made to avoid nonproductive expansion tests. The compositions with which Ar_3 is depressed below atmospheric temperature, about 25° C., can be determined by any test that distinguishes between the gamma state (Ar_3 below 25° C.) and the alpha state (Ar_3 above 25° C.) at ordinary temperatures. The quick Rockwell hardness test distinguishes between these states when the compositions compared are not greatly different. The use of a

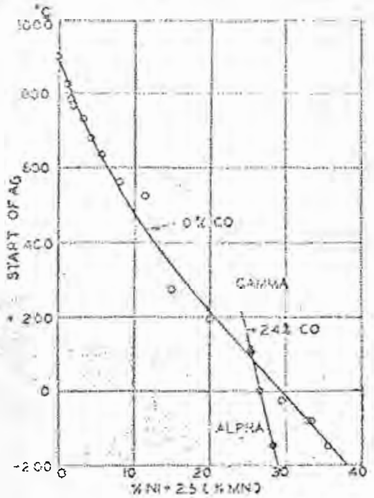

Fig. 7.—Temperature of start of Ar_3 in Fe-Ni-Co-Mn alloys plotted against equivalent nickel content.

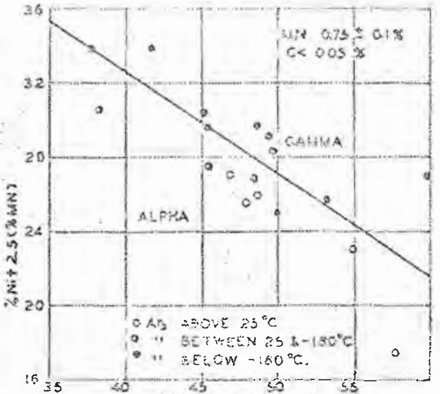

Fig. 8.—Variation of minimum permissible equivalent nickel content with nickel plus cobalt content as established by hardness tests.

supplemental reference temperature below atmospheric—that of liquid air—increased the definiteness and effectiveness of this test decidedly.

The results of hardness tests made to determine the constitution of the alloys containing cobalt are given in Table 3. The specimens were strips prepared by cold-rolling followed by annealing. The hardness of these strips was measured, then they were cooled to liquid-air temperature and held for 1 min. The hardness was again measured on return to 25° C. Higher hardness following cooling in liquid air shows that Ar_3 has progressed between +25 and −180° C. This observation and the relative hardness of the alloys permitted their classification according to the location of Ar_3 in three temperature ranges, as given in Table 3.

The minimum equivalent nickel content can now be approximately evaluated as a function of nickel plus cobalt content, for a given manganese content, by plotting the former variable against the latter and indicating the temperature range in which Ar_3 occurs, by the symbol plotted, as is done in Fig. 8. A curve may now be drawn to represent the compositions in which Ar_3 occurs between +25 and −180° C. Such a curve gives fair values of the minimum safe equivalent nickel content for

TABLE 3.—*Location of Ar_3 as Determined by Hardness Tests*

Alloy No.	Co, Per Cent.	L′, Per Cent.[b]	C, Per Cent.	Rockwell B Hardness		Temperature[c] of Ar_3
				Annealed	After Liquid-air Treatment	
			% Ni + Co = 45			
2123	15.5	30.3	0.02	83	82	●
2124[a]	18	27.5		92	102	◐
2125	17.4	29.6		83	94	●
2126	20	27		104	107	○
			% Ni + Co = 49			
2106	10.5	39.6	0.03	76	77	●
2113	22.1	29.1		76		●
2114	23.4	26.8		80	95	○
2115	24.4	25.9		85	101	○
2107[a]	25	25		106	107	○
			% Ni + Co = 53			
2127	29.6	25.7		83	84	●
2128[a]	32	23		101	104	○
			% Ni + Co = 58			
2116	0	60	0.53	76	75	●
2117	33	27		79	78	●
2118	38.2	22.1		89	89	●
2119	42.6	17.5		104	114	○
			% Ni + Co = 50			
2131[a]	35	15	0.3	112	112	○
2137[a]	30	20	0.4	117	117	○
2138[a]	30	20	0.5	115		○
2142[a]	28	22	0.2	112	112	○
2146	25.4	24.2	0.14	97	113	◐
			% Ni = 24.1			
2147	24.0	25.5	0.02	104	105	○
2148	24.0	25.4	0.11	96	111	◐
2149	24.0	25.5	0.19	97	105	●
2150	24.0	25.6	0.33	90	99	●

[a] Composition from charge.

[b] % L′ = % Ni + 2.5 (% Mn).

[c] ○ = Ar_3 above 25° C.

◐ = Ar_3 between 25° C. and −180° C.

● = Ar_3 below −180° C.

the major portion of the system when the manganese content is about 0.75 per cent.

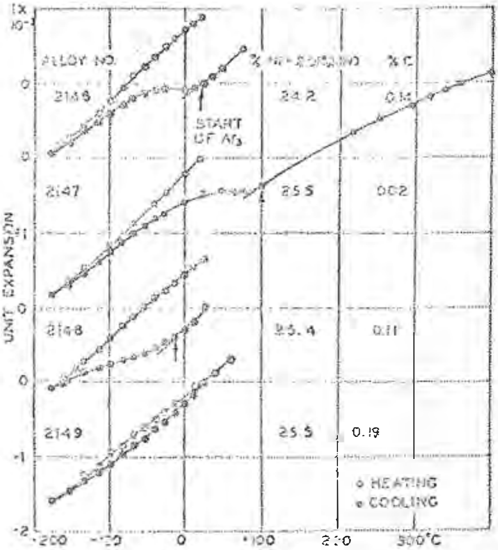

FIG. 9.—EXPANSION CURVES OF ALLOYS ON COOLING IN LIQUID AIR, SHOWING EFFECT OF CARBON CONTENT ON Ar_3.

The type of observations just described furnished the initial data required, but does not permit the exact evaluation of the effect of composition variables on the maximum feasible cobalt content. For this purpose the exact location of Ar_3 is required and was determined from expansion curves taken during cooling in liquid air and heating thereafter. The significant curves obtained are plotted in Figs. 2 and 9 and reduced data from these and other curves are given in Table 4. The beginning of Ar_3 is identified by an arrow on the curves. This identification takes cognizance of the expansion-curve loop between heating and cooling on immersion in liquid air. The magnitude of this effect can be noted on the curves of alloys 2149 and 2092, which show no Ar_3 and consequently would be identical on heating and cooling were there no temperature lag between the specimen and thermocouple.

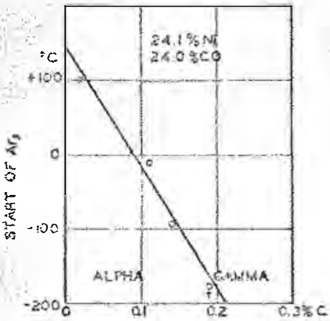

FIG. 10.—TEMPERATURE OF START OF Ar_3 AS A FUNCTION OF CARBON CONTENT; NICKEL, COBALT AND MANGANESE CONTENTS CONSTANT.

Sufficient data are now available to show the position of Ar_3 at low temperatures in the presence of 24 per cent. Co as a function of nickel content (Fig. 7) and of carbon content (Fig. 10). As the cobalt content is practically the same in both groups of alloys, the effect of carbon relative to nickel may be evaluated. The ratio of the slope of the curve for nickel variable to that for carbon variable gives the value desired, which is 18. Hence the equivalent nickel content is completely defined by:

$$\% L'' = \% \text{Ni} + 2.5(\% \text{Mn}) + 18(\% \text{C})$$

This expression, however, is significant only with low carbon contents because dissolved carbon alone lowers Ar_3. Free carbon, either as carbide or graphite, obviously has no effect on the position of Ar_3.

TABLE 4.—*Location of Ar_3 as Determined by Expansion Tests*

Alloy No.	Co, Per Cent.	L″, Per Cent.[a]	$\frac{\% L''}{\% Fe}$	Start of Ar_3	
				Temperature Deg. C.	Symbol[b]
1700	0	33.6	0.49	− 80	◐
1744	0	33.7	(9.2% Mn)	− 80	◐
1791	0	36.0	0.55	−175	●
1655	9.8	31.1	0.51	+ 25	◐
1782	6.1	34.3	0.56	−130	◐
1783	9.8	34.1	0.59	−175	●
1784	14.2	34.2	0.64	−175	●
1988	16.7	33.9	0.67	−175	●
2091	20.7	29.9	0.59	−175	●
2113	22.1	29.3	0.59	−175	●
2092	23.3	28.5	0.58	−175	●
2114	23.4	27.3	0.54	0	◐
2147	24.0	25.9	0.50	+100	○
2148	24.0	27.4	0.54	− 10	◐
2149	24.0	28.9	0.57	−175	●
2140	25.4	26.7	0.53	+ 25	◐
2146	24.0	28.0	0.55	− 90	◐

[a] $\% L'' = \% \text{Ni} + 2.5 (\% \text{Mn}) + 18 (\% \text{C})$.

[b] ○ = Ar_3 above 25° C.
◐ = Ar_3 between 25° C. and −180° C.
● = Ar_3 below −180° C.

The solid solubility of carbon in the high-cobalt alloys was estimated from chemical determinations of total and graphitic carbon. Two alloys containing 0.53 and 0.33 per cent. total carbon gave 0.19 and 0.01 per cent. graphitic carbon respectively. Accordingly, the solid solubility of carbon in these alloys is about 0.50 per cent. A greater content may be kept in solid solution with higher total contents, provided that the metal be cooled rapidly from a high temperature and not reheated beyond 400° C. thereafter. This is shown by the expansion curve of the 0.53 per cent. carbon alloy given in Fig. 11. On the first heating of this alloy after rapid cooling from the annealing temperature, an irreversible contraction starts at 460° C. and continues to 640° C. Evidently this contraction is due to the precipitation of carbon as graphite from solid solution.

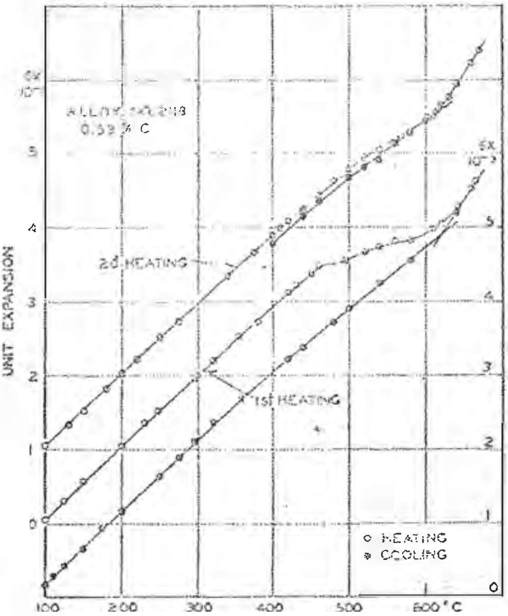

FIG. 11.—EXPANSION CURVES OF HIGH-CARBON ALLOY, SHOWING CONTRACTION CAUSED BY PRECIPITATION OF CARBON.

With the foregoing information, it is possible to give the maximum permissible cobalt content for these alloys. This might be done graphically as in Fig. 8, which applies for a manganese content of 0.75 per cent., carbon nil, but a different curve would be required for each manganese and carbon content. Fortunately such a cumbersome representation is not necessary. Certain fundamental considerations revealed a simple means for accomplishing the same thing developed in the following digression.

According to the curves for the carbon-free alloys, it appears that cobalt has a decided effect in lowering Ar_3. This is clearly shown by the equivalent nickel contents required to depress Ar_3 to −100° C. in the absence and in the presence of cobalt. The content is 34 per cent. in the absence of cobalt and 28 per cent. in the presence of 24 per cent. Co. This effect is apparently anomalous because cobalt is known to have the reverse effect in Fe-Co alloys. Analysis of the problem, however, shows that the anomaly results from improper representation of the data.

If a hypothetical element which has no effect on Ar_3 should be introduced into an Fe-Ni alloy, without change in the ratio of nickel to iron, Ar_3 should remain at the same temperature. The nickel content, in that event, as normally expressed in percentage of the total weight, will be lower than without the inert addition. Consequently the nickel content should be given in terms of the iron content, to retain the characteristic effects of nickel in the presence of the inert element. If the added element is not inert, its characteristic effect on iron in the presence of nickel is revealed.

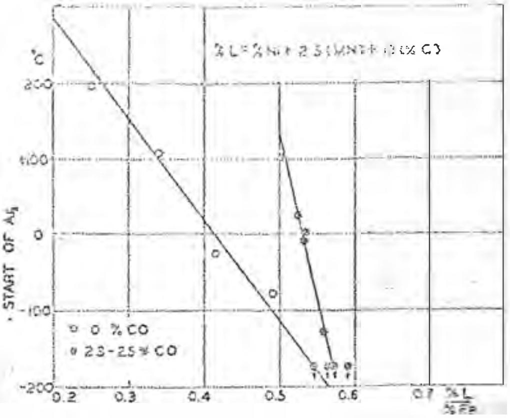

FIG. 12.—TEMPERATURE OF START OF Ar_3 AS FUNCTION OF RATIO OF EQUIVALENT NICKEL CONTENT TO IRON CONTENT OF FE-NI-CO-MN-C ALLOYS.

Applying the foregoing proposition to the present case, where cobalt takes the place of the inert element, Fig. 12 was prepared. Here Ar_3 is plotted against the ratio of the equivalent nickel content to the iron content for alloys containing 0 and 24 per cent. Co. So represented, Ar_3 is higher in the presence of cobalt than in its absence with high nickel contents just as in the absence of nickel. It therefore appears that the characteristic effect of one component of a ternary solid-solution alloy on the base metal is not obscured by the third component when the content of the first component is expressed in terms of the weight of base metal.

Further information of the validity of this principle is supplied by comparing the effect of cobalt in the presence and absence of nickel.

From Table 4 the following values were estimated for a constant ratio of effective nickel content to iron content of 0.55:

Co Content in Per Cent. of Fe Content	Start of Ar_3	
	In Fe-Co Alloys,[a] Deg. C.	In Fe-Ni-Co Alloys, Deg. C.
0	880	−150
16	920	−120
47	960	−90

[a] Data from Ruer and Kaneko: *Ferrum* (1913) 2, 34.

Thus Ar_3 is raised by cobalt to the same degree in the presence of a high nickel content as in its absence when the cobalt content is expressed in percentage of the iron content. Such a treatment should also simplify the analysis of changes in physical properties of other complex iron-base alloys with composition when the relations are not linear.

One may take advantage of this principle to express the maximum permissible cobalt content of the quinternary alloys in a simple manner. From Fig. 12 a value of the ratio of equivalent nickel content to iron content may be picked with which Ar_3 will fall safely below atmospheric temperatures. Thus for a value of the ratio of 0.55, Ar_3 will occur between about −80° and −180° C. for a range of useful compositions. That is to say, Ar_3 is safely depressed when:

$$\frac{\%\,\mathrm{Ni} + 2.5(\%\,\mathrm{Mn}) + 18(\%\,\mathrm{C})}{\%\,\mathrm{Fe}} = 0.55 \qquad [1]$$

Substituting for the iron content, 100 minus the content of the other components and transposing:

$$\%\,\mathrm{Co} = 100 - 2.82(\%\,\mathrm{Ni}) - 5.5(\%\,\mathrm{Mn}) - 34(\%\,\mathrm{C}) \qquad [2]$$

This relation gives a fair value of the maximum feasible cobalt content in terms of components, which normally would be determined analytically.

A much more useful expression can be obtained by substituting inflection temperature for nickel content, because usually the maximum cobalt content permissible with a given temperature range of low expansivity is desired. To obtain this expression it is necessary to determine the relation between inflection temperature and composition. From Fig. 6 it is evident that the inflection temperature varies linearly with the nickel plus cobalt content when the manganese content is 0.75 per cent. and carbon content nil. In this case the inflection temperature θ in degrees Centigrade may be expressed by:

$$\theta = 19.5(\%\,\mathrm{Ni} + \%\,\mathrm{Co}) - 450 \qquad [3]$$

Manganese and carbon may also affect the inflection temperature. The inflection temperature is plotted against manganese content for 45 per cent. Ni and against carbon content for 24 per cent. Ni and 24 per cent. Co in Fig. 13 to show their effects. Carbon has a negligible influence on the inflection temperature, but that of manganese is important. The slope of the curve for manganese variable shows the inflection temperature to be lowered 22° C. for each per cent. of increase in manganese content. Assuming that manganese has the same effect

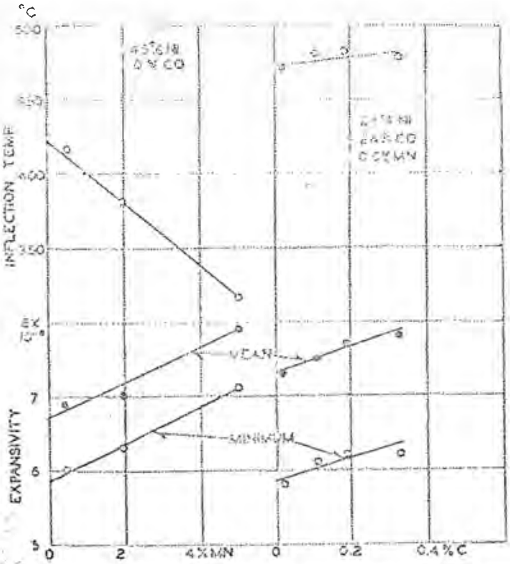

FIG. 13.—EFFECTS OF MANGANESE AND CARBON CONTENT ON EXPANSIVITY AND INFLECTION TEMPERATURE.

in the presence of cobalt, the inflection temperature may be completely expressed by:

$$\theta = 19.5(\%\ \mathrm{Ni} + \%\ \mathrm{Co}) - 22(\%\ \mathrm{Mn}) - 465 \qquad [4]$$

for the range of composition having low expansivity. Combining this relation with the preceding one to eliminate nickel gives:

$$\%\ \mathrm{Co} = 0.0795\theta + 4.8(\%\ \mathrm{Mn}) + 19(\%\ \mathrm{C}) - 18.1 \qquad [5]$$

which is the relation desired. The corresponding nickel content may be found in the same way to be:

$$\%\ \mathrm{Ni} = 41.9 - 0.0282\theta - 37(\%\ \mathrm{Mn}) - 19(\%\ \mathrm{C}) \qquad [6]$$

The equations just derived define completely the best compositions for any inflection temperature between 200° and 600° C. and for any assigned value of manganese and carbon content. To use them it is evidently necessary first to choose a value of the inflection temperature from a consideration of the particular application problem at hand. Values of the manganese and carbon contents may then be chosen on the basis of metallurgical requirements. The nickel and cobalt contents required to give the best expansivity under these limitations with Ar_3 safely depressed are then given by equations 5 and 6.

The equations just discussed indicate that the cobalt content must be increased with the manganese and carbon contents in order to keep the inflection temperature constant. It might be inferred that addition of manganese or carbon, or both, will permit improvement of the expansion properties by virtue of the larger additions of cobalt then feasible. This is true, however, only if the addition of either manganese or carbon raises the expansivity less than the corresponding increment of cobalt lowers it, assuming that the inflection temperature is maintained constant. The determination of whether or not advantage is to be gained by increasing manganese or carbon requires, therefore, an evaluation of their effects on the expansion properties. The quantitative determination of the effects of composition on expansivity will be considered in the following section.

ESTIMATION OF OPTIMUM EXPANSIVITY

The estimation of the best expansion properties available in the Fe-Ni-Co-Mn-C system for any particular application requiring low expansivity has been stated to be the chief objective of this investigation. This objective could be accomplished by graphical methods alone, but would entail excessive experimental effort because a large number of tests of alloys melted precisely to intended compositions would be required. Consequently an attempt was made to determine the laws of variation of the expansion properties with composition in the hope that they would lead to simple and general mathematical expressions for these relations from which the best properties could be estimated.

One step in the direction indicated was made in the last section and consisted of putting the relation between inflection temperature and composition in the form of equation 4. The existence of this and other simple relations, however, is contingent on the effects of each of the several composition variables being additive; *i. e.*, independent of the quantity of other components present. The additive principle just stated usually applies for moderate composition changes in solid-solution alloys and Fig. 6 indicates that it governs the inflection temperature so far as cobalt is concerned. It is probable that this principle applies to the expansivity, therefore the effects of the several composition variables were investigated with the object of testing its validity.

The effects of manganese on the expansion properties were evaluated from the data on cobalt-free 45 per cent. nickel alloys given in a previous paper[5] and are plotted in Fig. 13. The effect of carbon was determined from a group of high-cobalt alloys in which carbon alone was varied. Expansion curves of this group are given in Fig. 14. Serious irregularities in the quantities of components other than carbon were avoided by casting several small ingots from the same melt following successive additions of carbon. The expansion properties are plotted against carbon content in Fig. 13.

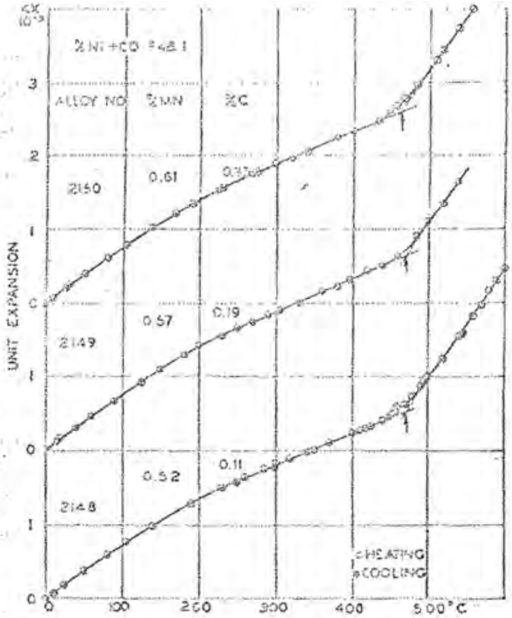

FIG. 14.—EXPANSION CURVES OF ALLOYS DIFFERING ONLY IN CARBON CONTENT.

Having determined the effects of the most troublesome variables, the precise evaluation of the effect of cobalt becomes possible. It is desirable, however, to have more information on the expansion properties of high-cobalt alloys than is obtainable with the 32 per cent. nickel series. Consequently several new groups of alloys were prepared. The expansion curves of one group in which cobalt is the variable and the nickel plus cobalt content constant are given in Fig. 15. Curves of a group having nearly the same minimum equivalent nickel content with cobalt variable are given in Fig. 16 and of a group having widely different manganese contents in Fig. 17. They supply comprehensive data which have been reduced to give Table 2 with which to work out the laws governing the variation of properties with composition.

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[5] H. Scott: *Op. cit.*

The relation of the expansion properties to the cobalt content may now be examined without interference from the secondary variables, manganese and carbon, by adjusting the observed property values to zero content of those elements on the basis of Fig. 13, as given in Table 5. In some cases the values are unattainable in fact because the nickel content is so low that Ar_3 would occur above atmospheric temperature in

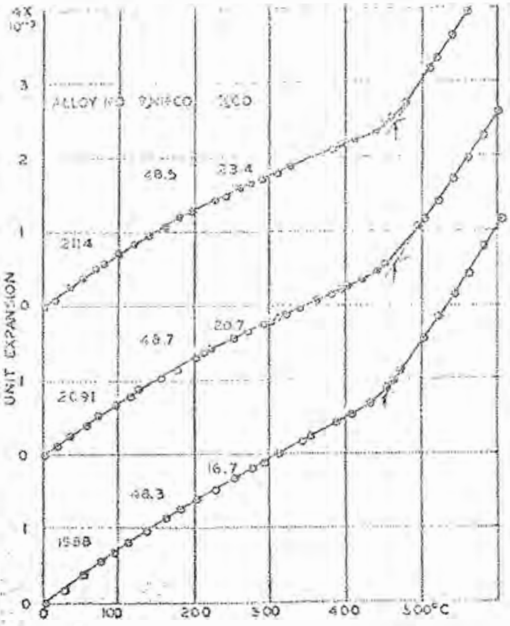

FIG. 15.—EXPANSION CURVES OF ALLOYS HAVING DIFFERENT COBALT CONTENTS BUT SAME CONTENT OF NICKEL PLUS COBALT.

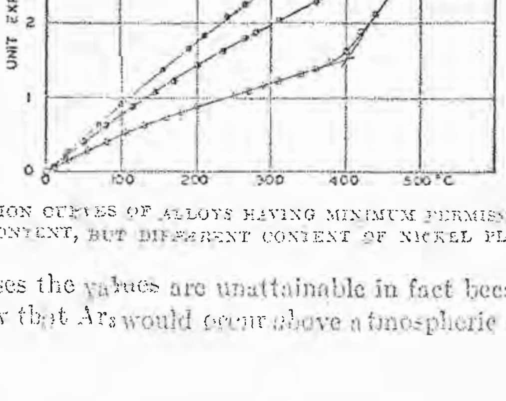

FIG. 16.—EXPANSION CURVES OF ALLOYS HAVING MINIMUM PERMISSIBLE EQUIVALENT NICKEL CONTENT, BUT DIFFERENT CONTENT OF NICKEL PLUS COBALT.

the absence of manganese and carbon, but this situation does not detract from their utility in their intended application, which is the establishment of basic relations.

TABLE 5.—*Effect of Composition Variables on Expansion Properties*
Expansion Data Are Adjusted for Deviation of Actual Composition from Those Given

Alloy No.	Per Cent Variable	Inflection Temperature, Deg. C.	Expansivity		Merit Index	
			Min.	Mean	Min.	Mean
	MANGANESE VARIABLE; 0% Co, 0% C					
1912	45.0 Ni, 0.53 Mn	417	6.0×10^{-6}	6.9×10^{-6}	245	220
1913	45.0 Ni, 1.96 Mn	381	6.3	7.0	201	181
1914	45.0 Ni, 5.03 Mn	316	7.1	7.9	113	90
1791	43.1 Ni, 0.92 Mn	370	5.0	6.2	227	193
1864	42.1 Ni, 1.54 Mn	325	3.7	4.8	219	188
	NICKEL VARIABLE; 0% Co, 0% Mn, 0% C					
1863	40.2 Ni	327	2.0	3.2	270	236
1864	42.1 Ni	357	3.3	4.4	263	231
1791	43.1 Ni	389	4.8	6.0	252	218
1912	45.2 Ni	431	6.0	6.9	259	234
1718	47.1 Ni	447	6.8	7.6	253	230
10	50.2 Ni	523	9.0	9.9	266	240
	COBALT VARIABLE; 0% Mn, 0% C					
1783	9.8 Co, 31.9 Ni	352	2.2	2.8	289	272
2034	11.0 Co, 32.7 Ni	358	2.9	3.9	305	277
1784	14.2 Co, 31.9 Ni	443	4.1	5.2	326	294
1987	16.0 Co, 31.8 Ni	464	4.8	5.8	327	298
1988	16.7 Co, 31.6 Ni	467	5.2	6.1	318	293
1989	18.6 Co, 31.6 Ni	511	6.0	7.2	340	305
	Ni + Co VARIABLE; MAXIMUM Co, 0% Mn					
2123	29.8 Ni, 15.5 Co	420	3.3	4.3	326	297
2125	28.6 Ni, 17.4 Co	413	3.0	4.0	327	299
2114	25.1 Ni, 23.4 Co	480	4.0	5.3	365	328
2091	28.0 Ni, 20.7 Co	474	4.5	5.6	345	314
2092	26.4 Ni, 23.3 Co	496	4.9	6.[illegible]	356	324
2127	23.6 Ni, 29.6 Co	567	6.4	7.5	384	353
2118	19.8 Ni, 38.2 Co	640	7.8	9.1	417	380
2089	24.8 Ni, 23.9 Co	464	4.5	5.4	335	310
	CARBON VARIABLE; 0% Mn, 24.0% Co					
2114	0.03 C, 25.1 Ni	492	4.3	5.6	369	332
2147	0.02 C, 24.1 Ni	472^a	3.8^a	5.3^a	363	320
2148	0.11 C, 24.1 Ni	481	4.1	5.5	364	324
2149	0.19 C, 24.1 Ni	482	4.2	5.7	362	319
2150	0.33 C, 24.1 Ni	478	4.2	5.8	358	312
2114	0.03 C, 24.1 Ni	472	3.6	4.9	369	332
	MANGANESE VARIABLE; 0% Co, 0% C					
2123	0.22 Mn				259	230
2125	0.64 Mn				242	213
2114	0.68 Mn				251	214
1988	0.88 Mn				231	208
2089	3.32 Mn				143	117

[a] Observations taken during rapid cooling.

Both the expansivity and inflection temperature vary in the same manner with the nickel content, or with the nickel plus cobalt content

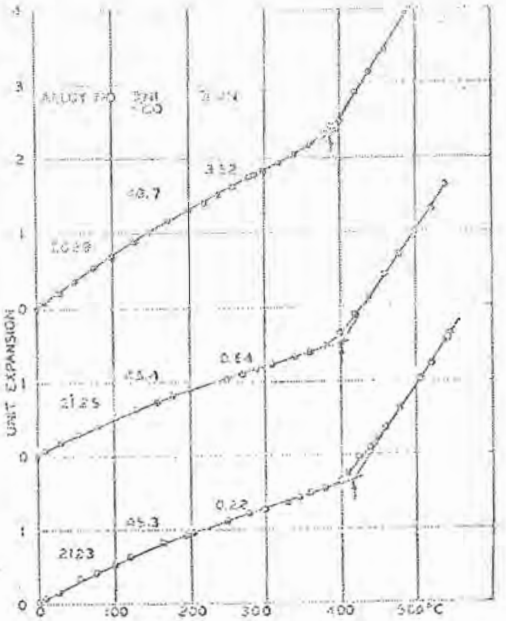

FIG. 17.—EXPANSION CURVES OF ALLOYS DIFFERING CONSIDERABLY IN MANGANESE CONTENT.

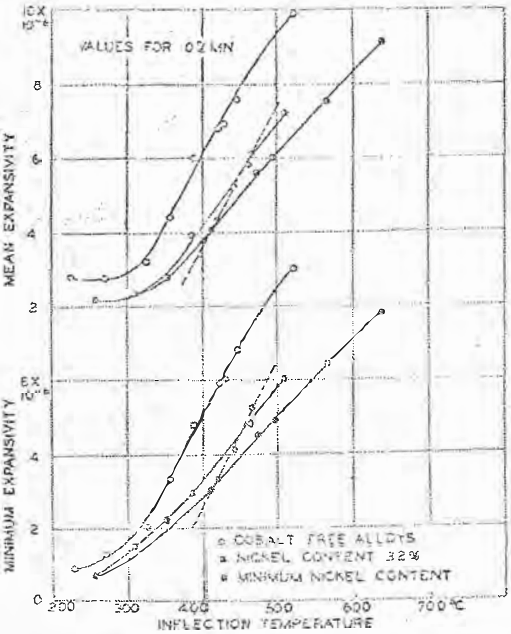

FIG. 18.—VARIATION OF MINIMUM AND MEAN EXPANSIVITY WITH INFLECTION TEMPERATURE.

For three relations between cobalt and nickel contents as estimated for zero manganese content. Broken lines apply for alloys containing constant cobalt content of 16 to 17 per cent.

when the cobalt content is a linear function of it, and this suggests plotting one property against the other, as in Fig. 18, to eliminate nickel as a variable. It is now apparent that the expansivity varies linearly with the inflection temperature over a useful range of compositions under the conditions specified. The inflection temperature varies linearly with nickel plus cobalt content, hence the expansivity must do likewise. Furthermore, from the relation of cobalt content to nickel plus cobalt content, it may be concluded that the change of the expansion properties with cobalt content is linear. Consequently the relations of these properties to composition can be expressed for a limited range of compositions by mathematical equations of the simplest form.

The curves of Fig. 18 are expressed by the equation:

$$\alpha = A(\theta - B) \qquad [7]$$

where α is the expansivity, θ the inflection temperature, and A and B are constants when the inflection temperature comes between 350° and 500° to 600° C. For the simplest case, cobalt zero, the constant A may be evaluated from the slope of the curves. Accordingly:

$$A = A_1 = A_2 = 0.035 \times 10^{-6}$$

where A_1 is the value for the minimum expansivity α_1 and A_2 the value for the mean expansivity α_2. The corresponding values of B are given by the value of the inflection temperature at which the linear portions of the curves for zero cobalt alloys extended have zero expansivity, whence: $B_1 = 262°$ C. and $B_2 = 232°$ C.

Having obtained and evaluated an equation for expansivity in terms of inflection temperature of Fe-Ni alloys, the next step is to introduce terms to express the effects of other components of the complex alloys. It has already been shown that the effect of cobalt also can be easily expressed and this may be verified by connecting the plotted values for two alloys having the same cobalt content, 16 to 17 per cent., but different nickel contents by a straight line, the broken line of Fig. 18. This line has practically the same slope as the curve for the alloy of zero cobalt content, consequently the intercept of the linear portion of the curve, which determines the value of the constant B, is in this case changed by the addition of 16 to 17 per cent. Co, but the slope, which determines the value of the constant A, is not altered. It is assumed, therefore, that the effects of manganese and carbon also are reflected in the value of B only.

The foregoing assumption affords a useful basis for expressing the merit of an alloy from its expansion characteristics alone. Transposing equation 7:

$$B = \theta - \frac{\alpha}{A} = \theta - \frac{\alpha \times 10^{+6}}{0.035} \qquad [8]$$

it is evident that the value of B will decrease as the expansivity increases or the inflection temperature decreases. Consequently the value of B

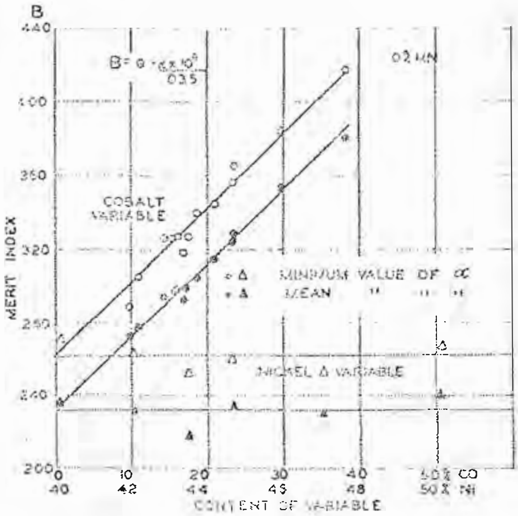

FIG. 19.—VARIATION OF MERIT INDEX WITH NICKEL AND COBALT CONTENT, OTHER ELEMENTS CONSTANT.

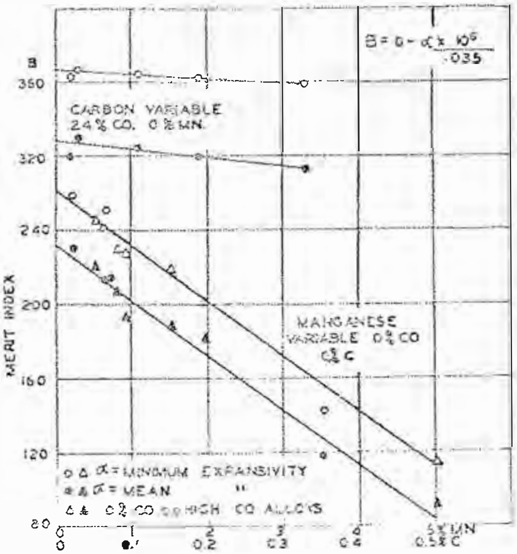

FIG. 20.—VARIATION OF MERIT INDEX WITH MANGANESE AND CARBON CONTENT, OTHER ELEMENTS CONSTANT.

is a direct measure of the merit of an alloy as long as the inflection temperature comes within the limits previously mentioned. As this single characteristic value for an alloy finds considerable use as a quantitative measure of the effects of alloying additions to Fe-Ni alloys, it is designated "merit index" to facilitate further discussion.

The merit indices of all the alloys studied, as obtained by equation 8, are given in Table 5. Plotting the values of this property against the several composition variables gives Figs. 19 and 20. Here the value for nickel variable is constant, as required by equation 7. Cobalt has a decided beneficial effect, manganese is harmful and the effect of carbon is slight. To show the effect of manganese in the high-cobalt alloys, their merit index values are adjusted to 0 per cent. Co on the basis of the curve for cobalt variable. The fact that the values thus obtained fall on the same curve as do those for alloys actually free from cobalt verifies the previous conclusion that the effect of cobalt is additive. The same is true of manganese also, otherwise there would be considerable scatter of the points for cobalt variable, because they represent alloys of which the manganese contents differ considerably. Whether or not the additive principle holds for carbon is immaterial because the effect of this element in allowable percentages is very small.

These simple relations between merit index and composition enable the formulation of convenient mathematical expression for expansion properties as a function of composition. These relations take the forms:

$$\alpha_1 = A(\theta - B_1 + C_1Y + D_1Z + E_1W) \qquad [9a]$$

$$\alpha_2 = A(\theta - B_2 + C_2Y + D_2Z + E_2W) \qquad [9b]$$

where C, D and E are constants and Y, Z, and W are the cobalt, manganese and carbon contents respectively in percentages of total weight of alloy. Putting Y, Z, and W equal to zero, B_1 and B_2 have the values already given for pure Fe-Ni alloys. Considering the other constants one at a time, it is evident that their values are given by the slopes of the corresponding curves of Figs. 19 and 20. Evaluating these slopes:

$$C_1 = C_2 = -4.00$$

$$D_1 = D_2 = +\ 30$$

$$E_1 = E_2 = +\ 40$$

and substituting in equations 9*a* and 9*b*:

$$\alpha_1 \times 10^6 = 0.035\theta - 0.140Y + 1.05Z + 1.4W - 9.17 \qquad [10a]$$

$$\alpha_2 \times 10^6 = 0.035\theta - 0.140Y + 1.05Z + 1.4W - 8.12 \qquad [10b]$$

These equations apply to any composition with which θ falls between 350° and 500° to 600° C. and Ar_3 below atmospheric temperature.

Before accepting these equations, it is desirable to justify the remaining unconfirmed assumption on which they are based; namely, that the constant A of equation 7 is not changed by variation in composition. This may be done by substituting A for 0.035 in equations 10*a* and 10*b*, transposing and calculating its value from the observed expansion property values of Table 2. The values obtained are given in Table 6. They come very close to the mean value 0.035 except for very low or high inflection temperatures, for which the equations do not apply. Such agreement would not exist if the value of A changed appreciably with the cobalt or manganese content. The effects of allowable carbon contents is insignificant, hence the original assumption is fully justified. The concordance of the calculated values of A also establishes the accuracy of the values used for this constant and for the other constants defining the effects of the composition variables.

TABLE 6.—*Values of Constants A_1 and A_2 Calculated from Observed Expansion Properties of Individual Alloys*

Alloy No.	θ° C.	A_1	A_2
1863	310	0.0349	0.0346
1864	325	345	347
1794	370	356	360
1912	420	350	346
1718	430	356	350
10	510	345	342
		Mean 0.0350	0.0349
1782	240	(0.0417)	(0.0435)
2031	295	383	378
1783	335	361	348
2034	375	347	346
1784	425	342	344
1987	450	347	348
1988	450	356	352
1989	495	346	349
		Mean 0.0355	0.0352
2125	400	0.0350	0.0349
2123	415	347	345
2091	460	349	350
2114	465	342	346
2092	480	348	350
2127	550	346	347
2118	620	340	345
		Mean 0.0346	0.0347

$$A_1 = \frac{\alpha_1 \times 10^6 + 0.14Y - 1.05Z - 1.4W + 9.17}{\theta}$$

$$A_2 = \frac{\alpha_2 \times 10^6 + 0.14Y - 1.05Z - 1.4W + 8.12}{\theta}$$

The equations thus established are useful in their present form, but the major object of this investigation is to find the optimum compositions. The attainment of this objective requires the determination of whether or not manganese or carbon can be added to advantage, a possibility previously suggested. For this purpose it is necessary to introduce the composition limitation as to maximum permissible cobalt content expressed by equation 5. Introducing this restriction by elimination of the cobalt variable from equations 10*a* and 10*b* gives:

$$\alpha_1 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 6.65 \qquad [11a]$$
$$\alpha_2 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 5.60 \qquad [11b]$$

which are the equations desired. They hold when Ar_3 is depressed to approximately −100° C.; *i. e.*, for nickel and cobalt contents given by equations 5 and 6.

In order to apply the foregoing equations it is necessary to assign values to the inflection temperature and the manganese and carbon contents from consideration of the conditions of the particular problem at hand. For example, to find the expansion properties of alloys containing conventional contents of secondary elements and the maximum feasible cobalt content, substitute % Mn = 0.7 and % C = 0.1, in equations 11*a* and 11*b*, whence:

$$\alpha_1 \times 10^6 = 0.024\theta - 6.50$$
$$\alpha_2 \times 10^6 = 0.024\theta - 5.45$$
$$\%\ \text{Ni} = 37.4 - 0.0282\theta$$
$$\%\ \text{Co} = 0.0795\theta - 12.8$$

It remains only to introduce an appropriate value of the inflection temperature, θ, to find the expansivities obtainable therewith and the nickel and cobalt contents necessary to give these properties. The values obtained from these equations also furnish a check on the accuracy of the equations for they should give very closely the expansion properties of alloys 2091, 2092, 2125 and 2127, and in fact do so.

Looking at the final equations, 11*a* and 11*b*, from the viewpoint of the best attainable compositions, it may be seen from the signs of the respective terms that manganese is detrimental and carbon beneficial when the maximum feasible cobalt content is maintained. The benefit conferred by carbon is indirect because it lowers the merit index slightly when other elements are constant. The meritorious effect of carbon is due to the fact that it is extremely active in lowering Ar_3 and this permits correspondingly large additions of cobalt. The maximum advantage attainable with reversible expansivity, however, is small, about 0.4×10^{-6} per deg. C., because the maximum carbon content is restricted to about 0.3 per cent. The optimum expansivity is, therefore, obtained with 0.3 per cent. C and 0 per cent. Mn when the cobalt content has its maximum feasible value. Actually 0.2 per cent. Mn does little harm to the expansion properties although its metallurgical effect is such as to greatly facilitate commercial manufacture of these alloys. Consequently one may obtain the composition and expansivity of the best practicable alloys by substituting % Mn = 0.2 and % C = 0.3 in equations 11*a* and 11*b*, from which:

$$\alpha_1 \times 10^6 = 0.021\theta - 6.9$$
$$\alpha_2 \times 10^6 = 0.021\theta - 5.9$$
$$\%\ \mathrm{Ni} = 35.6 - 0.282\theta$$
$$\%\ \mathrm{Co} = 0.0795\theta - 11.5$$

These equations have the same significance as the preceding, in which θ is the only independent variable.

The preceding discussion shows the desirability of keeping the manganese content down. It is not as important so far as expansivity is concerned in the alloys of maximum feasible cobalt content as in cobalt-free alloys. Comparison of the manganese terms of equations 10 and 11 shows that the harmful effect of manganese in alloys of maximum feasible cobalt content is less than 0.4 of that in cobalt-free alloys. There is another factor, however, which makes manganese highly undesirable in the high-cobalt alloys also; namely, the high cost of cobalt. Equation 5 shows that a cobalt increment nearly five times the manganese increment is necessary to maintain the desired composition property relations. Economy as well as expansivity requires, therefore, the minimum practicable manganese content in these alloys.

The equations given for expansivity apply only to alloys whose inflection temperatures are above 350° C. Alloys of lower expansivity, such as invar, are of considerable importance also, so it is of some interest to consider the improvements possible with them by the substitution of cobalt for nickel. Here the equations 1 to 6, which do not contain an expansivity term, hold also, though probably not so closely as for alloys having higher inflection temperature. Hence one may estimate the best compositions in this range also. A fair idea of the improvement in expansivity over that obtainable in the absence of cobalt may also be obtained by taking the difference between equations 10 with $Y = 0$ and equations 11. Denoting the difference in expansivity by $\Delta\alpha$:

$$\Delta\alpha \times 10^6 = 0.011\theta + 0.67Z + 2.6W - 2.52 \qquad [12]$$

for both minimum and mean expansivity. From this equation the improvement due to increasing the cobalt content to the maximum permissible point becomes greater as the manganese and carbon contents increase. On the basis of conventional values—0.5 per cent. Mn. and 0.1 per cent. C.—the improvement is given by:

$$\Delta\alpha \times 10^6 = 0.011\theta - 1.92$$

Taking the case of invar, $\theta = 225°$ C. and the expansivity is lowered by 0.5×10^{-6} per deg. C. This is a substantial improvement over invar, which has a minimum expansivity of about 1.0×10^{-6} per deg. C. By taking advantage of this, a higher degree of dimensional stability in the cold-worked condition may be attainable in the proposed alloy than is possible with invar.

Summary

Mr. Brace's discovery that the addition of cobalt lowers the expansivity of low-expansion nickel-iron alloys suggested detailed investigation of the iron-nickel-cobalt system with the object of determining optimum compositions and their associated expansion properties. The results of such an investigation are described here.

Early in this work it was recognized that the improvement of the expansion properties attainable by the addition of cobalt is strictly limited by the gamma-alpha (Ar$_3$) transformation of iron. Consequently an initial series of alloys was prepared with cobalt variable and the nickel content constant and sufficiently high to depress Ar$_3$ below atmospheric temperatures. The expansion curves of these alloys show the same characteristics as do those of nickel steels; namely, a region of low expansivity followed by a sharp rise in expansivity with increasing temperature. In order to make possible numerical expression of the expansion characteristics of the various alloys, three values were taken from each curve and identified as "inflection temperature," "mean expansivity" and "minimum expansivity" respectively. The inflection temperature gives the upper limit to the temperature range of low expansivity, the mean expansivity gives expansion per unit length from 0° C. to the inflection temperature divided by that temperature, while the minimum expansivity gives the lowest value of the slope of the expansion curve.

Graphical coordination of the data on the preliminary series of alloys showed that:

1. The inflection temperature is unchanged by the substitution of cobalt for nickel.

2. The minimum, or mean, expansivity is lowered substantially in proportion to the amount of cobalt substituted for nickel.

Comparison of these alloys on the basis of equal inflection temperature led to the conclusion that the best expansion properties are to be obtained with the maximum substitution of cobalt for nickel, with which Ar$_3$ remains safely depressed below atmospheric temperatures. Ar$_3$ is considered to be safely depressed when at −100° C. So low a temperature is taken because small variations in manganese and carbon content from an intended composition have a large effect on Ar$_3$. Aiming at −100° C., variations of the magnitude normally encountered in commercial alloy preparation are not likely to bring Ar$_3$ within the range of atmospheric temperatures to which these alloys may be exposed in industrial applications such as thermostatic devices.

In accordance with the foregoing conclusion, it was sought to determine the range of composition of the Fe-Ni-Co alloys (containing nominal amounts of manganese and carbon) within which Ar_3 is safely depressed. Both hardness and expansion tests were used to determine whether or not Ar_3 had occurred between atmospheric and liquid-air temperatures. These tests showed that Ar_3 is depressed to about −100° C. when the ratio of the equivalent nickel content to the iron content of an alloy has the value of 0.55 irrespective of its cobalt content up to 50 per cent. at least. The equivalent nickel content is defined by:

$$\% L = \% \text{ Ni} + 2.5(\% \text{ Mn}) + 18(\% \text{ C})$$

when the manganese content is below approximately 5 per cent. and the carbon content less than 0.3 per cent. This condition allows the maximum permissible cobalt content to be expressed in terms of the other components normally determined analytically, thus:

$$\% \text{ Co} = 1.55(\% \text{ Ni} + \% \text{ Co}) + 3.05(\% \text{ Mn}) + 18.5(\% \text{ C}) - 55 \qquad [2]$$

This simple relation was established after it was discovered that the lowering of Ar_3 by a given increase in the ratio of the nickel to the iron content is substantially the same in the presence of cobalt as in its absence.

In the light of the foregoing information alloys of intermediate and maximum permissible cobalt contents were prepared and tested. Graphical representation of the data obtained permitted the conclusion that the merit of an alloy may be expressed by a single value obtained by subtracting the expansivity divided by 0.035×10^{-6} from the inflection temperature. This "merit index" was found to vary linearly with the weight percentage of the individual components in such a way as to justify the conclusion that the effects of cobalt and manganese on the expansion properties are additive and that that of carbon is negligible.

These observations suggested the possibility of expressing the test results in the compact form of equations and furnished the values of the necessary constants. Writing θ for inflection temperature, X for the nickel content, Y for the cobalt content, Z for the manganese content and W for carbon content, the inflection temperature of any alloy of the group studied is given by:

$$\theta = 19.5(X + Y) - 22Z - 0W - 165 \qquad [4]$$

Introducing the restriction as to Ar_3, equation 2, the cobalt and nickel contents with which Ar_3 remains depressed to about −100° C. are given by:

$$Y = 0.0795\theta + 4.8Z + 19W - 18.1 \qquad [5]$$
$$X = 41.9 - 0.0282\theta - 3.7Z - 19W \qquad [6]$$

when the inflection temperature comes between 200° and 600° C. The expansivities obtainable with these compositions are given by:

$$\alpha_1 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 6.65 \qquad [11a]$$
$$\alpha_2 \times 10^6 = 0.024\theta + 0.38Z - 1.2W - 5.6 \qquad [11b]$$

where α_1 is the minimum expansivity and α_2 is the mean expansivity when θ comes between 350° and 600° C.

The equations for expansivity show that manganese is detrimental in the low-expansion alloys containing the maximum permissible cobalt contents and that carbon is beneficial. Consequently the optimum compositions are those required by equations 5 and 6 when the manganese content is zero and the carbon content has its highest permissible value, about 0.3 per cent. The favorable effect of carbon is indirect, for the reason that its effect upon Ar_3 is such as to permit the use of higher cobalt contents than would otherwise be allowable with regard to the restrictions already set up. Manganese, on the other hand, is not only directly harmful, but is also undesirable from an economic standpoint because its presence requires a compensating addition of cobalt approximately five times as great.

The expansivity equations do not hold for low inflection temperatures such as are required for minimum expansivity at atmospheric temperature. The beneficial effect of the substitution of cobalt for nickel may nevertheless be estimated approximately. In the case of invar, the expansivity in the ordinary temperature range can be reduced by about 0.5×10^5 per deg. C. This improvement in the expansivity of invar may make it possible to secure better dimensional stability than has been available hitherto.

ACKNOWLEDGMENTS

The writer expresses his appreciation of the liberal policy of the management of the Westinghouse Electric & Manufacturing Co. and of Mr. S. M. Kintner, Director of Research, which enabled the preparation and publication of this paper. Grateful acknowledgment is also made of the assistance of Messrs. J. R. Gier, Jr., who prepared the alloys, and R. H. Wynne, who was responsible for the difficult analytical work involved in the determination of nickel and cobalt in iron.

DISCUSSION

C. G. FINK, New York, N. Y. (written discussion).—The low-expansion Fe-Ni-Co alloys undoubtedly will be of increasing scientific and commercial value, and the data submitted by Mr. Scott are most valuable for further research in the field. We have for a number of years studied the expansion properties of the Fe-Ni and the Fe-Ni-Cu series. The copper-clad leading-in wire is a direct result of this study. This wire has a low-expansion Ni-Fe core with a copper sheath around it. Mr. Scott may be interested in the curve published on page 271 of volume 56 of the *Transactions* of the American Electrochemical Society, showing the coefficient of expansion of Fe-Ni alloys between 25° and 400° C., the coefficient of platinum being taken as 100.° It will be noted that invar has a coefficient of expansion almost as high as platinum within that temperature range.

H. SCOTT.—Professor Fink's remarks inspire a desire to hear further from him on the subject of copper-clad wire for sealing into glass, a subject which has received no attention in the literature commensurate with its industrial importance.