Thermal Expansion Coefficient, Rigidity Modulus and Its Temperature Coefficient of the Alloys of Iron, Nickel, Cobalt and Chromium, and Relations of Super Invar to Stainless Invar and of Elinvar to Co-Elinvar

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Thermal Expansion Coefficient, Rigidity Modulus and Its Temperature Coefficient of the Alloys of Iron, Nickel, Cobalt and Chromium, and Relations of Super Invar to Stainless Invar and of Elinvar to Co-Elinvar*

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Synopsis

The influence of an addition of chromium on the thermal expansion, rigidity modulus and its temperature coefficient of the alloys of iron, nickel and cobalt has been determined. It has been found that, in the relations of the thermal expansion cofficient or the temperature coefficient of rigidity modulus to the concentration of the alloys of iron, nickel, cobalt and chromium, there are two ranges of the minimum values of the expansion coefficient or the maximum values of the positive temperature coefficient of the modulus, one of which originates at the composition of invar, that is, in the neighbourhood of the composition of super invar, or elinvar in the binary system of iron and nickel, and the other at those of stainless invar or co-elinvar in the ternary system of iron, cobalt and chromium; they come together at the section of 10 per cent of chromium of the quaternary system, showing that stainless invar or co-elinvar are closely connected respectively with invar (super invar) or elinvar, and also that the nickel and the cobalt contained in each alloy can be substituted almost linearly by each other.

I. Introduction

In 1934, one of the present authors(1) invented a new invar type alloy "Stainless Invar", deducing the rule on the small expansibility of invar which was previously proposed by him(2). Further, deducing the rule mentioned above, two of them(3) invented a new elinvar type alloy "Co-Elinvar" consisted of cobalt, iron and chromium. Since then, they(4) studied the influence of an addition of nickel on the properties of the ternary alloys, and it has been found that the cobalt content at the compositions showing the minimum coefficient of thermal expansion or the positive maximum value of the temperature coefficient of rigidity modulus shifts to the side of

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(1) H. Masumoto, Sci. Rep., Tôhoku Imp. Univ., **23** (1934), 265; Nippon Kinzoku Gakkai-Si, **2** (1938), 141.

(2) H. Masumoto, Sci. Rep., Tôhoku Imp. Univ., **20** (1931), 101; Kinzoku no Kenkyû, **8** (1931), 237.

(3) H. Masumoto and H. Saitô, Nippon Kinzoku Gakkai-Si, **6** (1942), 122; **8** (1944), 513; **16** (1952), 125; Sci. Pep. RITU, **A1** (1949), 17; **A4** (1952), 246.

(4) H. Masumoto, H. Saitô and T. Kôno, Nippon Kinzoku Gakkai-Si, **17** (1953), 255; Sci. Rep. RITU, **A6** (1954), 529; H. Masumoto, H. Saitô and Y. Sugai, Nippon Kinzoku Gakkai-Si, **18** (1954), 81; Sci. Rep. RITU, **A7** (1955), 533.

low cobalt content with an increase of nickel content, until it reaches zero at the composition of the minimum thermal expansion coefficient or the positive maximum temperature coefficient of the modulus in the binary system of iron and nickel, while the chromium content decreases after when the nickel content becomes more than about 15 per cent. And the concentration range having positive value of the temperature coefficient of the modulus becomes wider and also the change of the coefficient to the concentration becomes smaller with an addition of nickel. This facts show that there is a close connection between stainless invar or co-elinvar in the ternary system of cobalt, iron and chromium and invar or elinvar in the system of iron and nickel or super invar in the system of iron, nickel and cobalt. To make it clear, the present authors studied the properties of the quatenary alloys in the wide concentration range. In the followings, the results of measurement will be reported.

II. Specimens and method of measurement

The materials used in preparing the alloys were electrolytic cobalt, electrolytic iron, electrolytic nickel and metallic chromium. The chemical compositions of the metals used are shown in Table 1.

Table 1. Chemical composition of metals used.

Metal	Fe(%)	Co(%)	Ni(%)	C(%)	Mn(%)	Si(%)	Al(%)	P(%)	S(%)	Cu(%)
Electrolytic Co	0.16	—	0.31	0.03_1	0.00_3	0.00_6	Trace	0.00_1	Trace	—
Electrolytic Fe	—	—	—	0.14	0.00_5	0.02_1	0.02	0.00_2	None	—
Electrolytic Ni	0.01_7	0.28	—	0.01_4	Trace	0.00_6	—	Trace	0.00_1	None
Cr	0.29	—	—	0.03	0.03	0.51	0.17	0.00_0	0.00_3	—

The materials were melted in an induction furnace, 0.5 per cent of manganese and 0.1 per cent of aluminium were added to them for deoxidization. The melt was cast in a cylindrical iron mould, about 10 mm in diameter. Then the cast was forged into a rod, about 5 mm thick, and finally cold-drawn to wire, 3 mm and 0.5 mm in diameter. For the measurement of thermal expansion, a wire of a proper length was cut from the thick wire, and for the measurement of rigidity modulus and its temperature coefficient the thin wire was used.

All the specimens were heated at 1,000° for 1 hour in a vacuum furnace and then cooled down to room temperature in it.

The thermal expansion was measured with the vertical dilatometer made of super invar, which was previously designed by one of the present investigators and his collaborator(5), and the mean linear expansion coefficient in the temperature range from 10 to 50° was determined. The rigidity modulus at 20° and its mean temperature coefficient in the range from 20 to 50° were determined with an apparatus constructed by two of present investigators(3) basing on the tortion pendulum method.

(5) H. Masumoto and T. Kobayashi, Nippon Kinzoku Gakkai-Si, **12** (1948) No. 6, 1; Sci. Rep. RITU, **A2** (1950), 856.

III. Results of measurement

The results of measurement of the mean thermal expansion coefficient in the range of 10 to 50°, the rigidity modulus at 20° and its mean temperature coefficient in the range of 20 to 50° of the quaternary alloys of iron, nickel, cobalt and chromium are shown in Figs. 1~11. In the figures, the projection planes represent the section at 0, 5, 10 and 15 per cent of chromium respectively.

1. Linear expansion coefficient

According to the results of the measurement of thermal expansion coefficient of the ternary alloys of iron, nickel and cobalt, previously obtained by one of the present investigators(2), the composition of invar(6) at about 36 per cent of nickel in the binary system of iron dnd nickel shifts to the low nickel side, when cobalt is added to the binary alloy, and passing through the least value at the composition of about 32 per cent of nickel, about 5 per cent of cobalt and the rest of iron, that is, the composition of super invar(2), finally reaches the composition of about 50 per cent of cobalt and the rest of iron in the binary system of iron and cobalt, and the valley of the coefficient becomes shallower with an increase of cobalt content. In the followings, the influence of an addition of chromium on the expansibility of the ternary alloys of iron, nickel and cobalt will be shown.

(i) Alloys containing 5 per cent of chromium

As seen in Fig. 1, in the ternary side of iron, nickel and 5 per cent of chromium, the composition showing the minimum thermal expansion coefficient is at the composition of somewhat higher content of nickel, and the valley of the coefficient is wider and shallower in comparing with that in the binary system of iron and nickel. When cobalt is added to the alloys of iron, nickel and 5 per cent of chromium, the composition of the minimum thermal expansion coefficient mentioned above shifts to the side of low nickel and the valley of the coefficient becomes deeper at first and then shallower after passing through the least value at the composition of about 23 per cent of nickel, about 16 per cent of cobalt, 5 per cent of chromium and the rest of iron.

(ii) Alloys containing 10 per cent of chromium

As shown in Fig. 2, the relation between the linear thermal expansion coefficient and the concentration of the alloys of iron, nickel, cobalt and 10 per cent of chromium is qualitatively similar to that of the alloys containing 5 per cent of chromium shown in Fig. 1. The minimum value of the coefficient in the side of iron, nickel and 10 per cent of chromium is obtained at the composition of about 40 per cent of nickel and is somewhat larger than that in the 5 per cent chromium alloy. With an addition of cobalt to the ternary alloys of iron, nickel and 10 per cent of

(6) Ch.-Éd. Guillaume, C. R., **125** (1897), 235; J. de phys., **7** (1898), 262; P. Chevenard, Rev. de mét., mém., **11** (1914), 841; K. Honda and J. Ôkubo, Kinzoku no Kenkyû, **1** (1924), 537; Sci. Rep., Tôhoku Imp. Univ., **13** (1924), 101; A. Schulze, Phys. Z., **28** (1927), 669; C. Benedicks and P. Sederholm, Arkiv Mat. Astron. Fysik, **19-B** (1925), 1; H. Scott, Trans. Amer. Soc., Steel Treat., **13** (1928), 829; H. Masumoto, loc. cit.

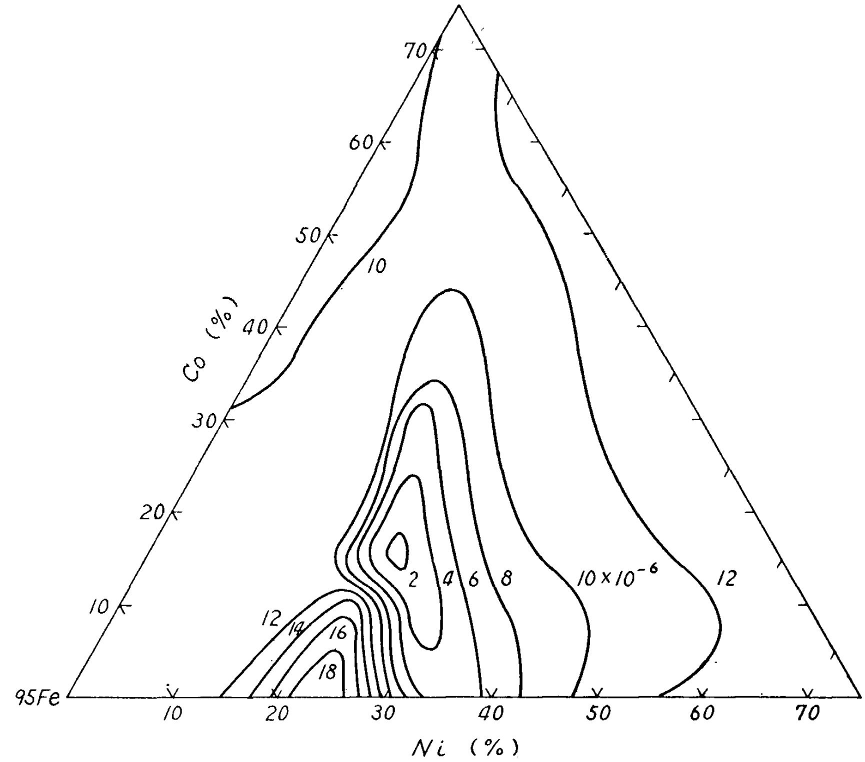

Fig. 1. Thermal expansion coefficient of Fe-Ni-Co-Cr alloys containing 5 per cent of chromium.

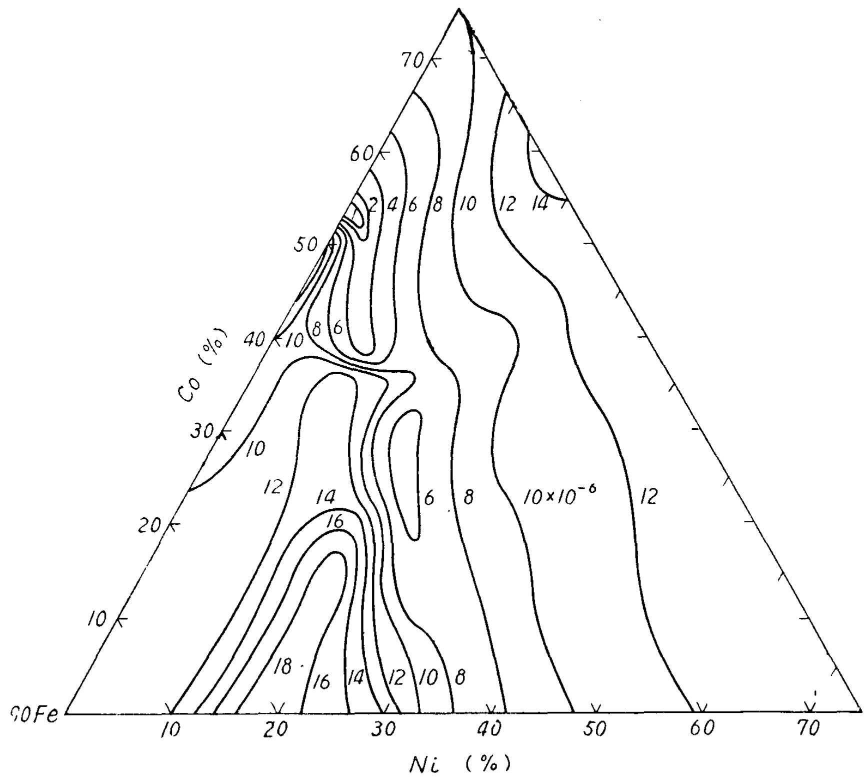

Fig. 2. Thermal expansion coefficient of Fe-Ni-Co-Cr alloys containing 10 per cent of chromium.

chromium, the composition of the minimum coefficient linearly shifts to the low nickel side and passes through the regoin of small coefficient at the composition of about 20 per cent of nickel, about 25 per cent of cobalt, 10 per cent of chromium and the rest of iron. In the side of iron, cobalt and 10 per cent of chromium, the coefficient shows a conspicuous least value smaller than 1×10^{-6} at the composition of stainless invar(1) containing about 53 per cent of cobalt, 10 per cent of chromium and the rest of iron. Thus, we can see that the two valleys of the thermal expansion coefficient in the section of 10 per cent of chromium of the quaternary system of iron, nickel, cobalt and chromium, which are originated from the compositions of invar and of stainless invar respectively, connect with each other forming a saddle at the composition of about 10 per cent of nickel, about 35 per cent of cobalt, 10 per cent of chromium and the rest of iron. From these results, it can be concluded that invar in the binary system of iron and nickel and super invar in the ternary system of iron, nickel and cobalt are in close connection with stainless invar in the ternary system of iron, cobalt and chromium, and the nickel and the cobalt content at the compositions of the quaternary alloys showing minimum thermal expansion coefficient can almost linearly be substituted by each other.

(iii) Alloys containing 15 per cent of chromium

In the case of the alloys containing 15 per cent of chromium, there are a valley of the thermal expansion coefficient which situates at the side of lower content of nickel and cobalt and is very shallower than in the case of the alloys containing

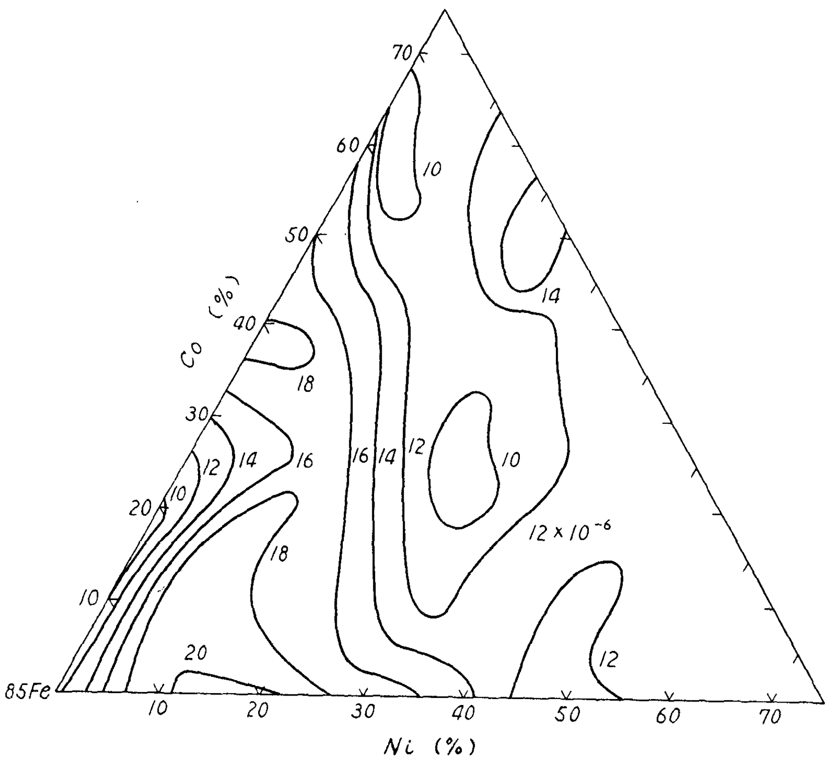

Fig 3. Thermrl expansion coefficient of Fe-Ni-Co-Cr alloys containing 15 per cent of chromium.

less chromium. The valley shows two indistinct minimum parts at the compositions of about 27 per cent of nickel, about 25 per cent of cobalt, 15 per cent of chromium and the rest of iron, and about 66 per cent of cobalt, 15 per cent of chromium and the rest of iron respectively.

2. Rigidity modulus

The results of the measurement of rigidity modulus at 20° of the alloys of iron, nickel and cobalt and those of the quaternary alloys of iron, nickel, cobalt and 5 to 15 per cent of chromium are shown in Figs. 4 to 6.

(i) The ternary alloys of iron, nickel and cobalt

As seen in Fig. 4, in the ternary system of iron, nickel and cobalt, there is a valley of the rigidity modulus, which starts at the composition of about 42 per cent of nickel and the rest of iron and ends at that of about 75 per cent of cobalt and

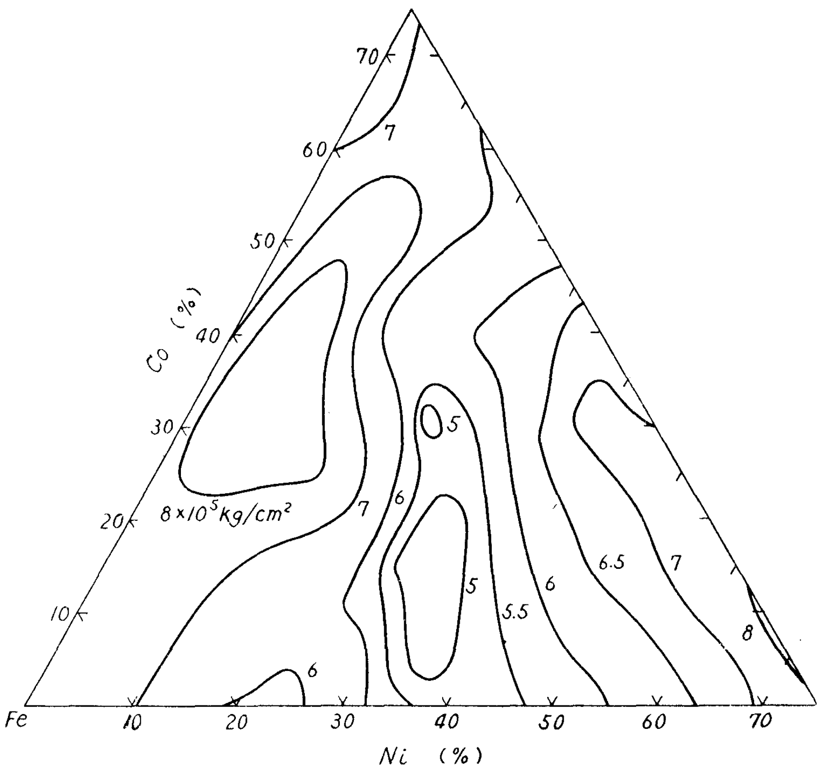

Fig. 4. Rigidity modulus of Fe-Ni-Co alloys.

the rest of iron passing through the least value at the composition of about 32 per cent of nickel, about 14 per cent of cobalt and the rest of iron and a shallow minimum part of about 24 per cent of nickel, about 30 per cent of cobalt and the rest of iron, resulting each one maximum in both sides of the valley. And the maximum in the side of low nickel content of the valley is steeper than that in the side of high nickel content.

(ii) Alloys containing 5 per cent of chromium

In the section of 5 per cent of chromium of the quaternary system of iron, nickel, cobalt and chromium shown in Fig. 5, there exists also a valley, which is similar in figure to that in the ternary system of iron, nickel and cobalt shown in Fig. 4. The valley situates in the range containing higher nickel and is generally shallower and narrower than that in the case of the ternary alloy. The least value

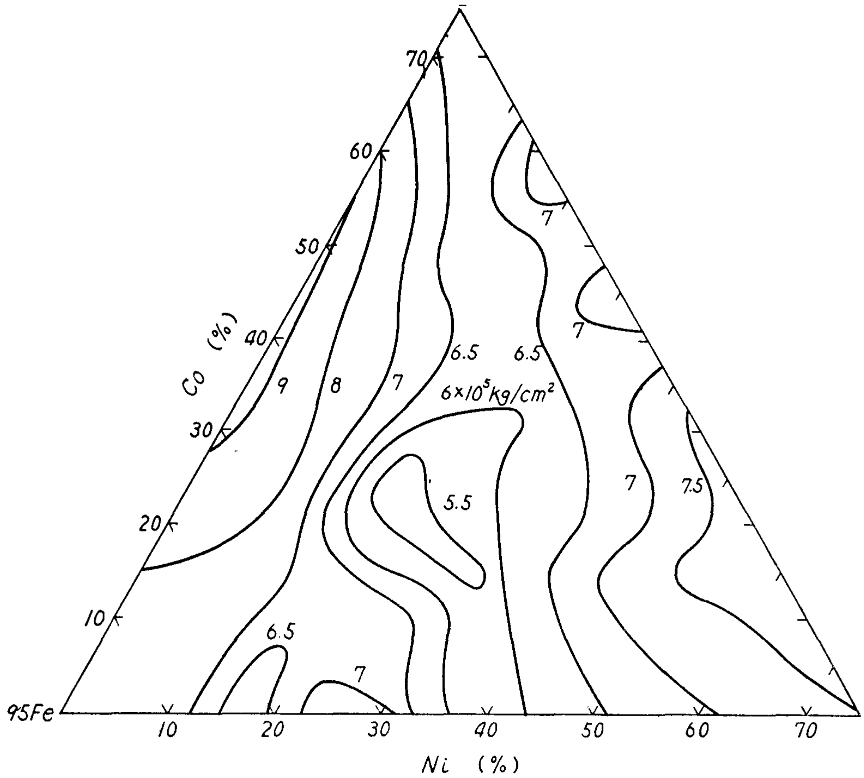

Fig. 5. Rigidity modulus of Fe-Ni-Co-Cr alloys containing 5 per cent of chromium.

of the modulus is obtained at the composition containing about 20 per cent of nickel, about 25 per cent of cobalt, 5 per cent of chromium and the rest of iron. And, the inclination of the modulus to the concentration in the side of low nickel content of the valley becomes larger with a decrease of nickel content as same as in the case shown in Fig. 4.

(iii) Alloys containing 10 per cent of chromium

As shown in Fig. 6, in the quaternary system of iron, nickel, cobalt and 10 per cent of chromium, a valley similar in figure to that in the ternary system mentioned above runs from the composition of about 40 per cent of nickel, 10 per cent of chromium and the rest of iron to that of about 66 per cent of cobalt, 10 per cent of chromium and the rest of iron, at which the least value of the modulus was obtained. And the valley is shallower and wider than that in the section of 5 per cent of chromium. The inclination of the modulus to the concentration in the side of low nickel content of the valley is steeper than that in the high nickel side, but its height is not so high as that in the case shown in Fig. 5.

(iv) Alloys containing 15 per cent of chromium

In the section of 15 per cent of chromium in the quaternary system of iron, nickel, cobalt and chromium, as seen in Fig. 7, a valley of rigidity modulus runs

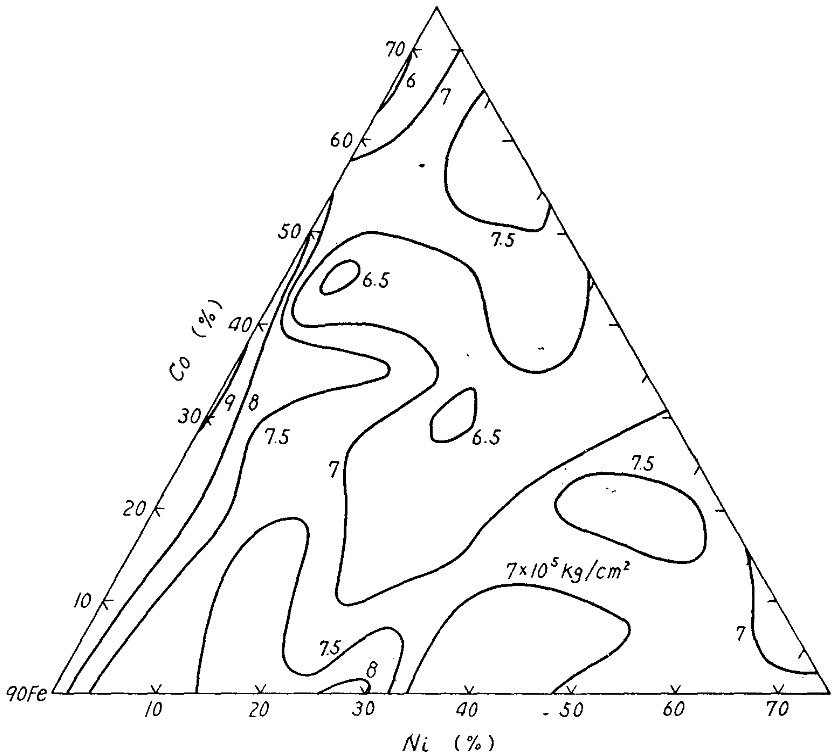

Fig. 6. Rigidity modulus of Fe-Ni-Co-Cr alloys containing 10 per cent of chromium.

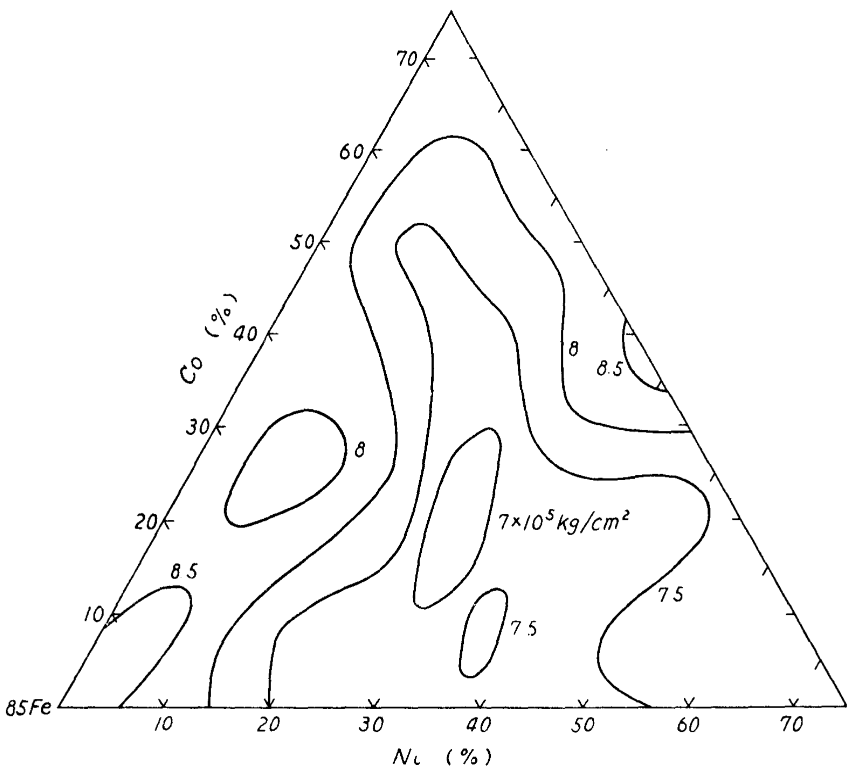

Fig. 7. Rigidity modulus of Fe-Ni-Co-Cr alloys containing 15 per cent of chromium.

from the composition of about 40 per cent of nickel, about 15 per cent of chromium and the rest of iron to that of about 65 per cent of cobalt, 15 per cent of chromium and the rest of iron, passing through the least value at the composition of about 29 per cent of nickel, about 20 per cent of cobalt, 15 per cent of chromium and the rest of iron. The valley is very wide and shallow in comparing with those in the section of low chromium.

3. Temperature coefficient of rigidity modulus

The temperature coefficients of rigidity modulus in the range of 20 to 50° of the alloys of iron, nickel, cobalt and 0 to 15 per cent of chromium are shown in Figs. 8 to 11 in the relation to the concentration of the alloys.

(i) The ternary alloys of iron, nickel and cobalt

As shown in Fig. 8, the temperature coefficient of rigidity modulus of the ternary alloys of iron, nickel and cobalt are generally negative and of the order larger than -20×10^{-5}, while in the binary side of iron and nickel, it shows a positive maximum value in the neighbourhood of the composition of about 34 per cent of nickel and the rest of iron, that is, the composition showing the minimum value of the thermal expansion coefficient. The existence of this positive maximum value of the temperature coefficient of rigidity modulus is the cause for the appearance of elinvar[7]. When cobalt is added to the binary alloys of iron and nickel,

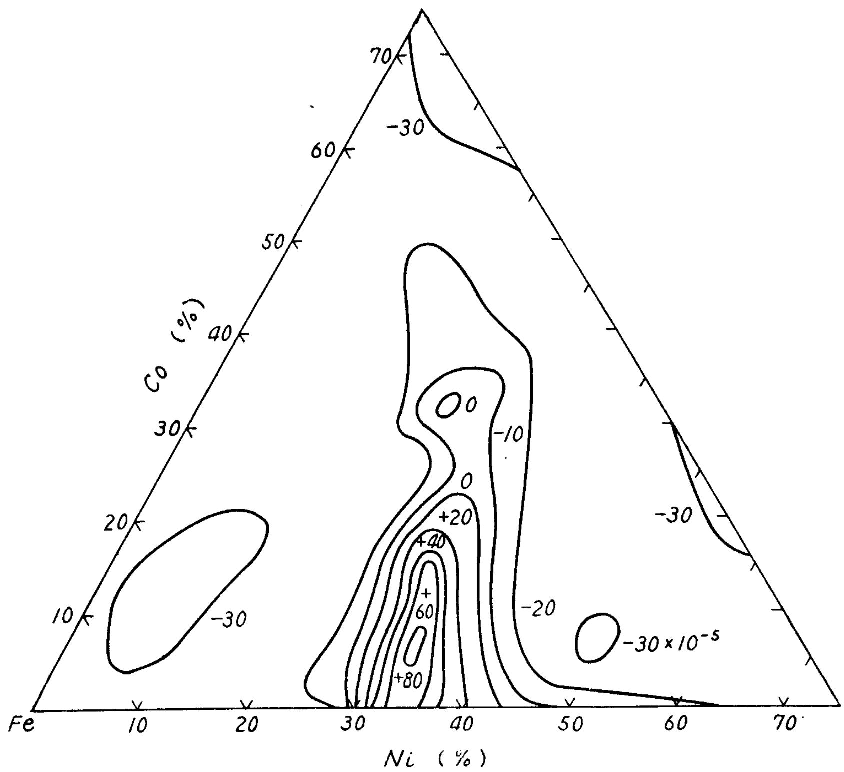

Fig. 8. Temperature coefficient of rigidity modulus of Fe-Ni-Co alloys.

(7) P. Chevenard, C. R., **170** (1920), 1499 ; Trav. et mém. Bur. int. des poids et mês., **17** (1927), 144 ; Ch.-Éd. Guillaume, Arch. Sci. phys. et nat., **5-2** (1920), 413 ; Rev. de mêt., mêm, **25** (1928), 35 ; O. Engler, Ann. der Phys., **5-31** (1938), 145 ; H. Masumoto and H. Saitô, loc. cit.

the composition showing the positive maximum coefficient shifts to the side of low nickel content and the positive value becomes larger till reaches its largest value at the composition of about 33 per cent of nickel, about 6 per cent of cobalt and the rest of iron, that is, in the neighbourhood of the composition of stainless-invar(1). With a further increase of cobalt content, the positive maximum value of the coefficient becomes smaller and reaches zero in the nighbourhood of the composition of about 28 per cent of nickel, about 23 per cent of cobalt and the rest of iron. Thereafter the coefficient changes its sign and the composition showing the minimum value of the negative coefficient shifts to the side of low content of nickel passing through a small positive maximum at the composition of about 23 per cent of nickel, about 32 per cent of cobalt and the rest of iron.

(ii) Alloys containing 5 per cent of chromium

As seen in Fig. 9, in the ternary side of iron, nickel and 5 per cent of chromium, the composition showing the positive maximum value of the temperature coefficient of rigidity modulus is at the composition of somewhat higher content of nickel in comparing with that in the case containing no chromium (Fig. 8). When cobalt is added to the ternary alloys, the range showing positive value of the temperature coefficient of rigidity modulus becomes wider shifting as a whole to the side of low nickel content and shows a positive largest value at the composition of about 32 per cent of nickel, about 17 per cent of cobalt, 5 per cent of chromium and the rest of iron.

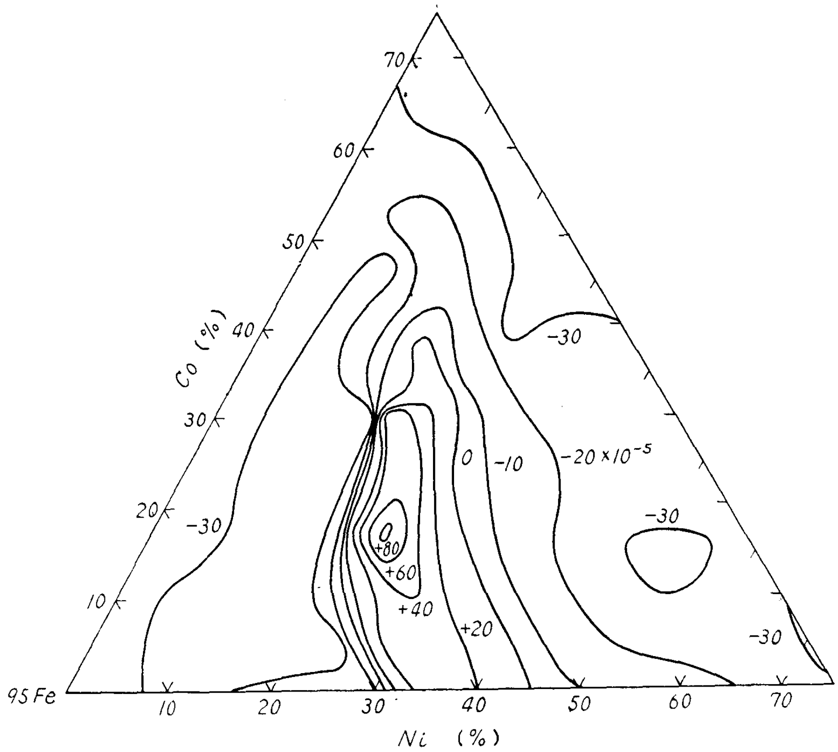

Fig. 9. Temperature coefficient of rigidity modulus of Fe-Ni-Co-Cr alloys containing 5 per cent of chromium.

(iii) Alloys containing 10 per cent of chromium

The relation of the temperature coefficient of rigidity modulus to the concentration of the quaternary alloys of iron, nickel, cobalt and 10 per cent of chromium, as shown in Fig. 10, is almost similar to those mentioned above with the exception of the existence of another positive maximum which relates to co-elinvar(2). In the side near the ternary system of iron, nickel and 10 per cent of chromium, the positive maximum value of the coefficient is obtained at the composition containing higher cobalt than in the alloys containing less chromium, that is, about 17 per cent of nickel, about 26 per cent of cobalt, 10 per cent of chromium and the rest of iron.

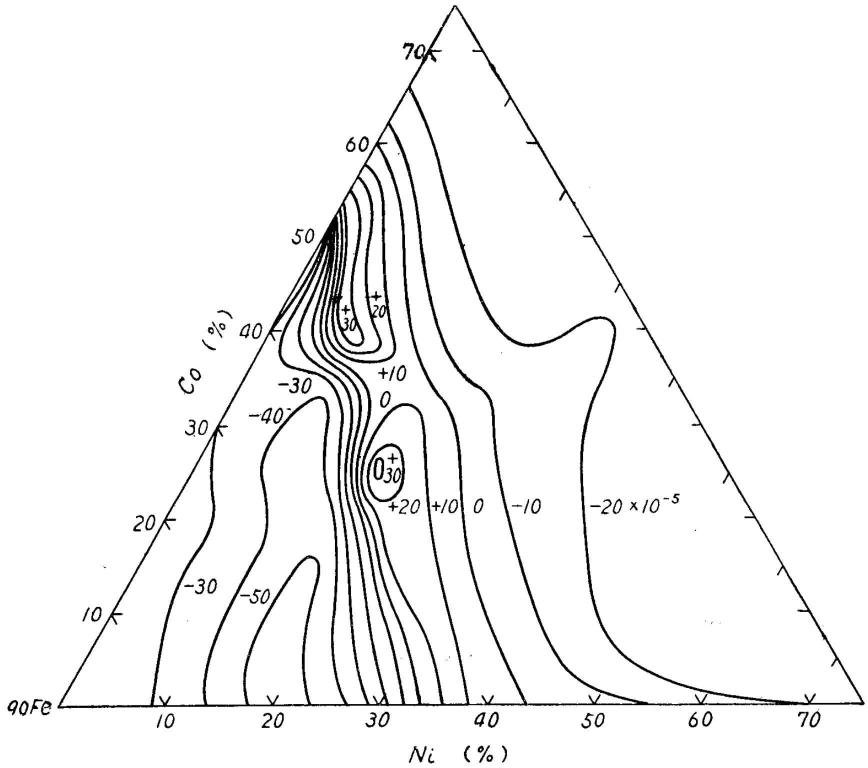

Fig. 10. Temperature coefficient of rigidity modulus of Fe-Ni-Co-Cr alloys containing 10 per cent of chromium.

The two maxima mentioned above connect with each other at the composition of about 14 per cent of nickel, about 35 per cent of cobalt, 10 per cent of chromium and the rest of iron, resulting a wide range of the positive value of the temperature coefficient of rigidity modulus extending from ternary side of iron, nickel and 10 per cent of chromium to the side of iron, cobalt and 10 per cent of chromium. From this result, we can see that elinvar in the binary system of iron and nickel is in close connection with co-elinvar in the ternary system of cobalt, iron and chromium and also the nickel and the cobalt content at the compositions of the quaternary alloys showing positive maximum value of the temperature coefficient of rigidity modulus can almost linearly be substituted by each other.

(iv) Alloys containing 15 per cent of chromium

In the whole section of 15 per cent of chromium in the quaternary system of iron, nickel, cobalt and chromium, as seen in Fig. 11, the temperature coefficient of rigidity modulus is negative. The range of the minimum value of the coefficient runs from the composition of about 44 per cent of nickel, 15 per cent of chromium and the rest of iron to that of about 60 per cent of cobalt, 15 per cent of chromium and the rest of iron, and its value is almost constat in whole minimum range of the coefficient.

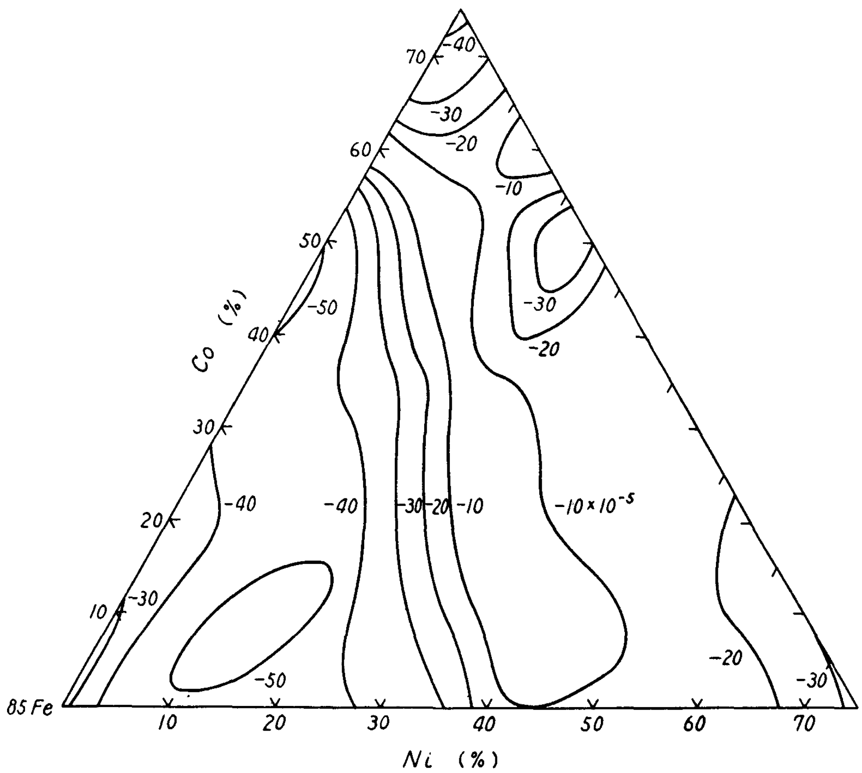

Fig. 11. Temperature coefficient of rigidity modulus of Fe-Ni-Co-Cr alloys containing 15 per cent of chromium.

Summary

The effect of an addition of chromium on the thermal expansion, rigidity modulus and its temperature coefficient of the ternary alloys of iron, nickel and cobalt was studied and the following results were obtained.

(1) The valley of the thermal expansion coefficient at the composition of invar or super invar shifts to the side of low nickel content with an addition of chromium less than about 10 per cent, while the valley of the coefficient at the composition of stainless invar shifts to the side of low cobalt and low chromium content with an addition of nickel. Thus, two valleys connect with each other.

(2) In the ternary system of iron, nickel and cobalt, the rigidity modulus shows a valley running from the composition of about 42 per cent of nickel and the rest of iron to that of about 75 per cent of cobalt and the rest of iron. When chromium is added to the ternary system, the valley becomes wider and shallower.

(3) The composition of the positive maximum of the temperature coefficient of

rigidity modulus in the binary system of iron and nickel which is the cause for the appearance of elinvar shifts to the side of low nickel content with an addition of cobalt and chromium less than 10 per cent.

In the section of 10 per cent of chromium in the quaternary system of iron, nickel, cobalt and chromium, there is another positive maximum of the temperature coefficient of rigidity modulus which makes the cause for the appearance of co-elinvar, and the composition of this maximum shifts to the side of low cobalt with an addition of nickel and connects with the maximum originated from the binary system of iron and nickel mentioned above.

(4) From the results mentioned above, it can be concluded that invar or super invar in close connection with stainless invar, and also elinvar with co-elinvar, and the nickel and the cobalt content at the compositions showing the minimum value of thermal expansion coefficient or the positive maximum of the temperature coefficient of rigidity modulus can almost linearly be substituted by each other.

In conclusion, the present authors wish to express their thanks to Mr. S. Tetsuka and Mr. M. Shinozaki for their kind assistance in making observation. Part of the expense for the present investigation was paid from the grant in aid for fundamental scientiffic research of the Ministry of Education.