

Aug. 16, 1966

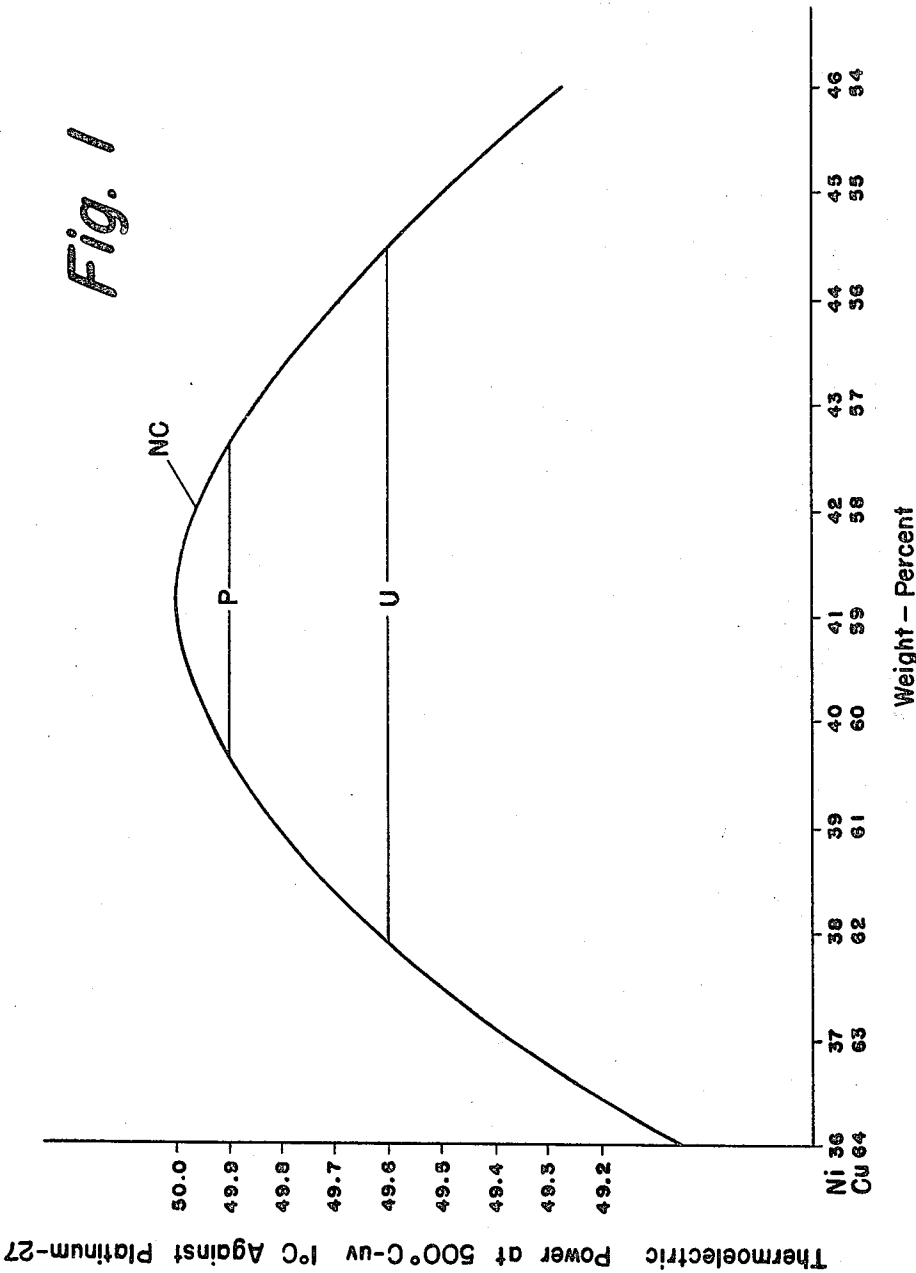
D. I. FINCH ETAL

3,266,891

COPPER-NICKEL THERMOCOUPLE ALLOYS

Original Filed May 4, 1959

3 Sheets-Sheet 1



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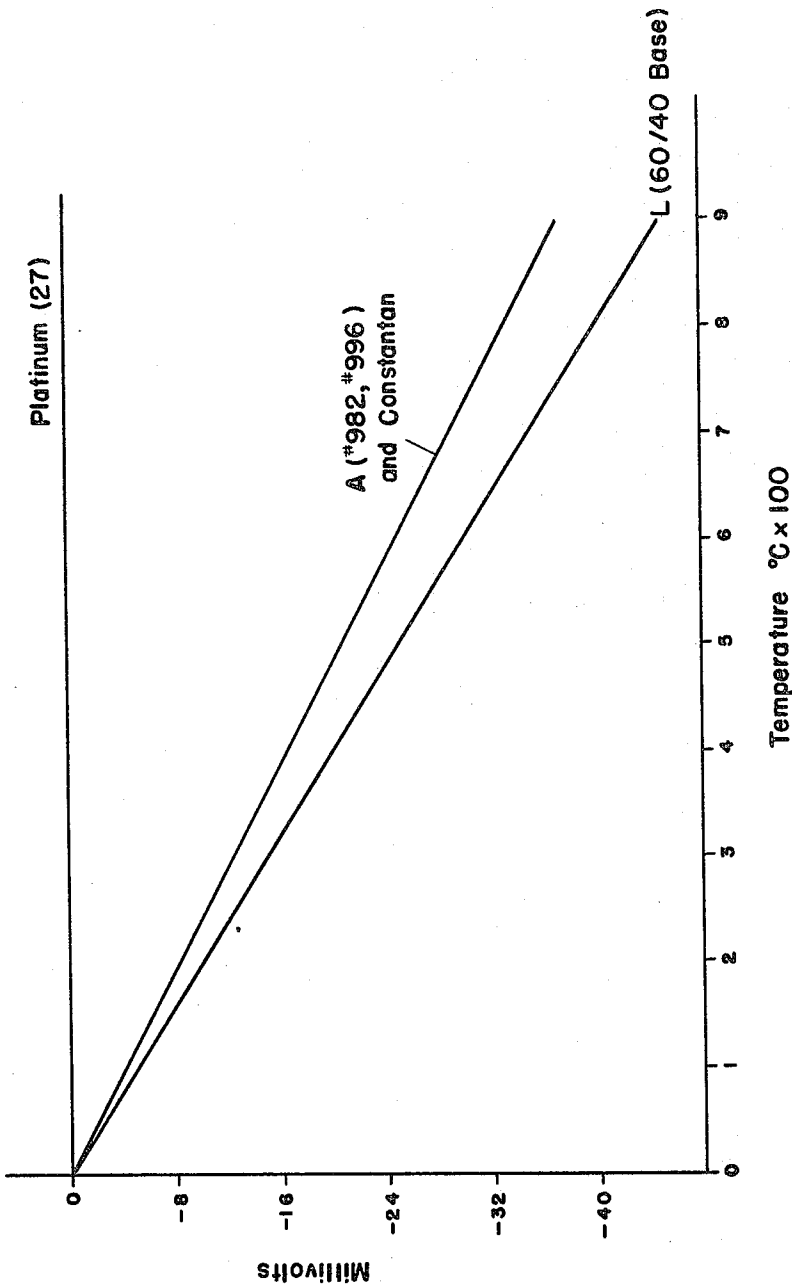
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COPPER-NICKEL THERMOCOUPLE ALLOYS

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Fig. 2



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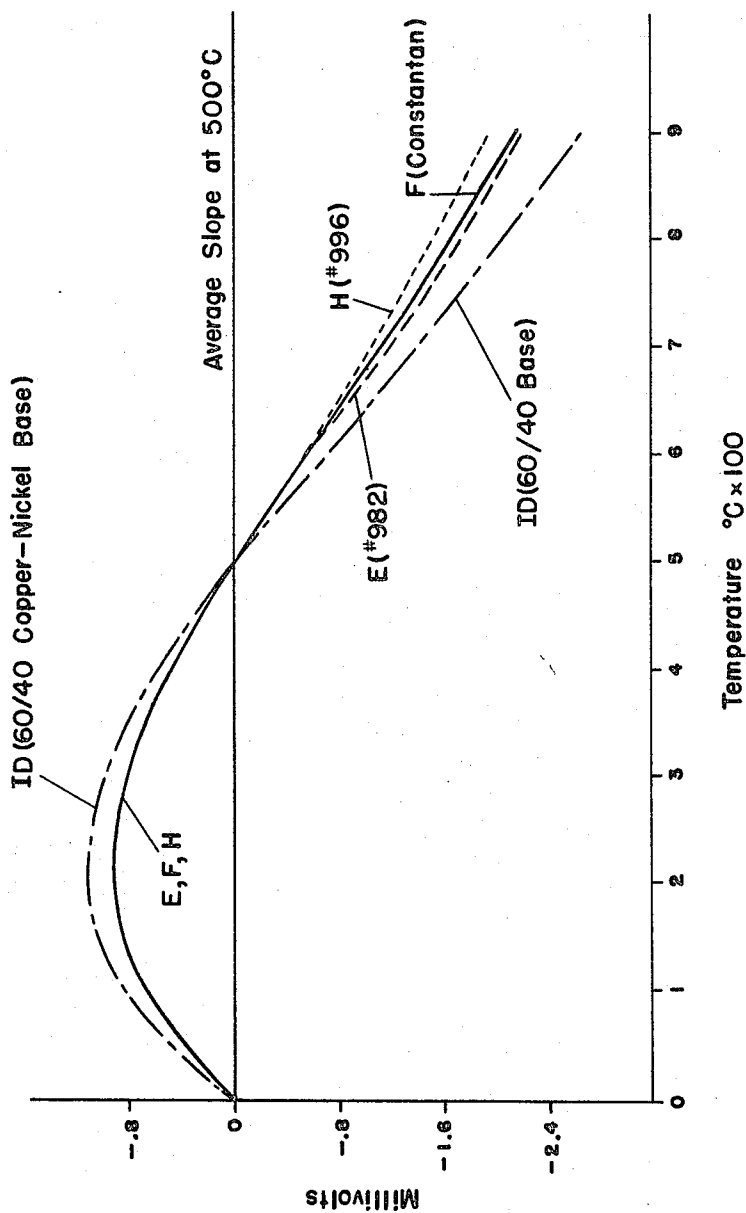
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COPPER-NICKEL THERMOCOUPLE ALLOYS

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Fig. 3



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COPPER-NICKEL THERMOCOUPLE ALLOYS

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Continuation of application Ser. No. 810,610, May 4, 1959. This application Oct. 21, 1963, Ser. No. 318,148

3 Claims. (Cl. 75-159)

This application is a continuation of pending application Serial No. 810,610, filed May 4, 1959, which is now abandoned, and which is a continuation-in-part of application Serial No. 666,652, filed June 19, 1957, now abandoned.

This invention relates to thermocouple elements composed of copper-nickel alloys.

For many years prior to the present invention, constantan elements have been coupled with such elements as iron, copper and Chromel elements to form thermocouples used for measurement of temperature. The few but widely used constantans were essentially alloys of copper and nickel with specified additions of manganese and iron whose percentage composition was that empirically found to afford, with certain appropriate thermoelements, a thermocouple whose voltage/temperature characteristic would acceptably match established thermoelectric curves or tables such as published by the U.S. Bureau of Standards in its NBS circular 561. Such thermocouples had the shortcomings that when used in corrosive atmospheres (both oxidizing and reducing, especially those containing sulphur), their life was shortened by structural failure of the constantan element and that the accuracy of the temperature measurements was progressively degraded because of changes in the voltage/temperature characteristic of the constantan elements. Prior attempts have been made to produce constantans of improved corrosion-resistance by additions of aluminum up to 10 percent. Such aluminum-containing constantans were not accepted by the art because of difficulties encountered in reproducing the alloys, because their voltage/temperature characteristics could not be controlled to match or to differ to predetermined extent from that of the previously used constantans, and because of previously unexplainable anomalies in, and instability of their voltage/temperature characteristics.

It is the object of the present invention to provide copper-nickel thermocouple alloys containing aluminum which are reproducible, whose voltage/temperature characteristics are stable, and whose voltage/temperature characteristics may be preselected to match, or to differ to predetermined extent from that of the previously used constantans.

In accordance with the present invention, aluminum and one or more other elements hereinafter specified are added in solid solution and not in excess of limits of solid solubility to a copper-nickel base having a ratio closely approximating 60% copper, 40% nickel. The percentages of aluminum and other additives are preselected from tables compiled as the result of our extensive experimentation to predetermine the voltage/temperature characteristics of the resulting alloys. By such preselection, there may be reproducibly obtained many copper-nickel-aluminum alloys whose voltage/temperature characteristics closely match, or to predetermined extent differ from, the voltage/temperature characteristic of the previously used constantans.

For a more detailed understanding of the present invention, reference is made to the following description and to the accompanying drawings in which:

FIG. 1 is a curve representing the thermoelectric power of binary alloys of copper and nickel;

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FIG. 2 is illustrative of the voltage/temperature characteristics of specific alloys embodying the invention; and FIG. 3 is illustrative of the curvature deviations from the average slopes of the voltage/temperature characteristics of specified alloys embodying the invention.

As a result of many experiments, we have found that starting with a copper-nickel base having a copper-nickel ratio which approximates 60% copper, 40% nickel and adding small amounts of aluminum and other alloying elements, hereinafter specified, it is possible to produce and reproduce a substantial number of copper-nickel-aluminum alloys whose thermoelectric power may be preselected to match, or to predetermined extent, to differ from that of the previously used constantans, whose thermoelectric power is stable with time and temperature, and whose corrosion-resistance is equal to or greater than that of said previously used constantans.

Of the elements listed in column 1 of Table A below, those having the most effect upon improvement of the corrosion-resistance of the copper-nickel base were found to be aluminum, silicon and titanium, and those having a moderate improving effect upon corrosion-resistance were found to be cobalt, manganese and vanadium. The maximum to which aluminum and any other of the elements should be in the thermocouple element was found to be limited by the percentage which would be in solid solution in the alloy throughout the operating temperature range of the thermocouple. It was found that if such maximum amount was exceeded, the thermoelectric power of the alloy is not stable and cannot be reproduced. To a first approximation, the percentage limits of solid solubility of aluminum and other additive elements are given in column III of Table A below.

Table A

Control Element	Effect per percent of element in microvolts at 500° C. ¹	Percent Limit of Solid Solubility ¹
Aluminum (Al).....	2,700	4
Cobalt (Co).....	2,750	2
Iron (Fe).....	6,820	2
Manganese (Mn).....	1,900	15
Silicon (Si).....	5,530	4
Titanium (Ti).....	5,960	2
Vanadium (V).....	11,400	1

¹ First order approximation.

Limiting the amount of any element of Table A as added to a melt at alloying temperatures to a percentage less than the limit of its solid solubility does not inherently insure that essentially all of such additive will be in solid solution in the final thermocouple alloy. If, for example, any appreciable part of the added aluminum forms intergranular segregates in the alloy, its voltage/temperature characteristic will not be stable or reproducible, and the same is true for any of the other elements. To attain a preselected, stable and reproducible voltage/temperature characteristic, it is necessary that all of the aluminum and all of the other additive element or elements go into solution in the melt at alloying temperature and remain in solid solution in the alloy as fabricated into thermocouple elements. Such solid solubility can be attained by known melting techniques, including vacuum melting, protective atmospheres, deoxidation, and can be checked by known methods of analysis, such as X-ray or electron diffraction or metallographic, chemical or microchemical examination.

As appears from column II of Table A, the addition of aluminum modifies to a predetermined extent the voltage/temperature characteristic of the copper-nickel base and the same is true of each of the other above specified corrosion-resisting elements. When aluminum and any one

or more of the other corrosion-resisting elements are added to the base alloy, their individual effects upon the voltage/temperature characteristic are cumulative. Thus, up to the limits of composite solid solubility, aluminum plus any one or more of the other corrosion-resisting elements may be added in percentages preselected to attain any one of many voltage/temperature characteristics which to predetermined extent differs from that of the copper-nickel base.

The element iron included in Table A does not appreciably affect the corrosion-resistance of the base alloy but has been found to have a stable and reproducible effect upon the voltage/temperature characteristic formed by addition of aluminum plus any one or more of the other corrosion-resisting elements to the copper-nickel base. Iron is usually present as a residual in commercial copper-nickel alloys so that, whether so included or added, its presence should be taken into consideration in the preselection of the percentages of aluminum and other corrosion-resisting additive for attainment of a predetermined voltage/temperature characteristic. When iron is used as an additive, the amount present in the final alloy must be essentially wholly in solid solution: any appreciable excess will affect the stability and reproducibility of the voltage/temperature characteristic of the alloy.

To permit the maximum permissible addition of aluminum plus other corrosion-resisting elements, with or without iron, for control of the corrosion-resistance and voltage/temperature characteristic with freedom from the significant effects of small but critical changes in the ratio of copper to nickel, the copper-nickel ratio must be held close to 60% copper, 40% nickel. As shown by curve NC of FIG. 1, this ratio is close to the one affording the maximum negative thermoelectric force against platinum (Platinum 27, herein designated as platinum is an accepted reference established by the National Bureau of Standards as a basis for comparing the thermoelectric forces of thermocouple elements) for a binary alloy of copper and nickel. Preferably, the copper-nickel ratio in the base alloy should closely approximate 60% copper, 40% nickel, i.e., it should be within the narrow range P of FIG. 1—from 60.5% copper/39.5% nickel to 57.5% copper/42.5% nickel. For the wider range U of FIG. 1, i.e., from 62% copper/38% nickel to 56% copper/44% nickel, it is possible reproducibly to make thermocouple alloys having preselected voltage/temperature characteristics but the copper/nickel ratio must be rigidly held to a fixed value in this range. For ratios higher or lower than range U, it is practically impossible to reproduce an alloy having a preselected voltage/temperature characteristic.

As shown by curve L of FIG. 2, the average slope, as defined by a straight line through the 0° C. and 500° C. points, of the voltage/temperature curve of a thermocouple having the 60/40 copper-nickel base as one element and platinum as the other element is very close to -50 microvolts per degree centigrade. (The precise value is -49.9 microvolts per degree C.) The effect of addition of aluminum and any of the other corrosion-resisting elements is to make the average slope of the voltage/temperature characteristic less negative or more positive with respect to platinum. The magnitude of the shift of slope with respect to that of the base alloy can be closely predetermined from inspection of column II of Table A: for example, if the additives present in the final alloy are 0.25% aluminum, 0.25% titanium, 0.20% silicon, 0.25% cobalt, the slope of the voltage/temperature curve of the alloy against platinum becomes very close to -42 microvolts per degree centigrade.

It is to be noted, and as appears from Table A, that the different corrosion-resisting elements have different magnitudes of effect upon the slope of the voltage/temperature characteristic for equal small additions but since they have different limits of solubility in the copper-nickel base, an element having a small percent effect may,

because of its higher limit of solubility, be utilized in larger amounts for enhancement of corrosion-resistance and for greater modification of the voltage/temperature characteristic of the base alloy. It is also to be noted that for a small addition of any of the elements well within its limit of solid solubility, its effect upon the voltage/temperature characteristic is substantially linear but for larger additions approaching its limit of solid solubility, its effect on average slope decreases. In other words, the effect per percent addition of an element is not strictly linear throughout the entire range of its solid solubility.

By recourse to the information compiled in Table A, there may be preselected the percentages of aluminum plus one or more of the other corrosion-resisting elements which as added to the base alloy will reproducibly provide thermocouple alloys whose respective voltage/temperature characteristics are stable and are of preselected slope to predetermined extent different from that of curve L (FIG. 2) for the base alloy. Such new thermocouple alloys include alloys, examples of which are later herein given whose voltage/temperature characteristics have the same slope as curve A (FIG. 2), the voltage/temperature characteristic of the few previously used constantans.

Since all of the accepted thermocouple voltage/temperature curves deviate slightly from linearity, it is necessary that such deviations be considered in producing from Table A a new thermoelement which as a replacement of the previously used constantans will match the established tables.

Though appearing so as curve L of FIG. 2, the voltage/temperature characteristic of the copper-nickel base is not precisely linear. The curvature or the deviation from exact linearity is shown as curve ID of FIG. 3 in which the voltage scale is greatly expanded and in which the average slope is represented by the horizontal line so designated.

Such deviation from linearity of the voltage/temperature characteristic of the base alloy is affected by addition of any of the elements of Table A. The sense and magnitude of the effect of addition of each of those elements is shown in Table B below. In explanation of the legends of Table B, the percentage change in deviation of the copper-nickel base is used as a measure of the effect of any one element upon the curvature; positive (+) curvature correction is defined as that effect which tends to minimize the deviations from linearity of the average slope; and negative (-) curvature correction is defined as the accentuation of the deviations from linearity of the average slope. The effect of the individual elements upon curvature varies both with the amount of the alloying element present in the copper-nickel base and with the operating temperature to which the thermocouple element is subjected. In Table B, the approximate effects upon curvature of a given amount (0.3% wt.) of each alloying element in the copper-nickel base are given for the operating temperature range of 0° C. to 900° C.

Table B.—Approximate curvature effects of 0.3% (wt.) of alloying elements in the 60/40 copper-nickel base over the temperature range of 0° C. to 900° C.

Element:	Effect, percent
Aluminum (Al) -----	+0.2.
Cobalt (Co) -----	-3 below 400° C. -10 above 600° C.
Iron (Fe) -----	+10.
Manganese (Mn) -----	+3.
Silicon (Si) -----	+8.
Titanium (Ti) -----	+16.
Vanadium (V) -----	+26.

It will be noted from Table B that aluminum, which has good corrosion protection properties, has negligible curvature-correction power so that positive curvature correction is effected by titanium, silicon, iron and/or

manganese and negative curvature-correction is effected by cobalt.

As examples of specific copper-nickel thermocouple alloys whose different percentage compositions and components have been selected from Tables A and B to obtain voltage/temperature characteristics which both as to slope and curvature very closely match (i.e., within $\pm 1/2\%$) prior established thermoelectric curves and tables, reference is made to Table C below, to curve A of FIG. 2, and to curves E, F and H of FIG. 3. In many instances, matching within $\pm 1\%$ is acceptable.

Table C

Element	Alloys	
	#982	#996
Copper (Cu).....	59.46	59.43
Nickel (Ni).....	39.51	39.39
Aluminum (Al).....	.23	.27
Cobalt (Co).....	.23	.25
Iron (Fe).....	.03	.02
Manganese (Mn).....	nil	.46
Silicon (Si).....	.21	nil
Titanium (Ti).....	.27	nil
Vanadium (V).....	nil	.18

As shown in Table C, the alloys #982 and #996 are of different compositions but their voltage/temperature characteristics as shown by curve A of FIG. 2 are essentially identical to each other and very closely match the prior established constantan vs. platinum table (see National Bureau of Standards RP2415, Table 2, column A-1). In FIG. 3, the departures from exact linearity have been plotted on a greatly expanded voltage scale. As shown by curves E and H, the voltage/temperature curves of alloys #982 and #996 very closely match that of the previously used constantans (curve F) up to 600° C. Very small deviations of the voltages of these alloys occur at temperatures above 600° C.

Either of the above alloys may be used interchangeably for each other or in replacement of the previously used constantans without need for recalibration of the scales of the associated temperature-measuring instruments. The corrosion-resistance of alloy #982 is nearly twice (1.8) that of the previously used constantans; the corrosion-resistance of alloy #996 is at least equal to that of the previous constantans. Notwithstanding the inclusion of aluminum in both of these alloys, they are easily reproducible to obtain a stable voltage/temperature characteristic which closely matches that of previously used constantans. As above stated, previously attempted copper-nickel-aluminum alloys were unsuited for thermocouple elements because they were not reproducible, because of instability of their voltage/temperature characteristics, and because their voltage/temperature characteristics did not match the established tables.

In general, these and other aluminum-containing alloys of compositions preselected from Tables A and B to replace commercial constantan and which have equal or enhanced corrosion-resistance additionally include two or more other elements of the table, the total percentage of the additives usually being less than 2% and in no case exceeding 5 percent. In all cases, the total amount of additives should not be in excess of that insuring solid solubility of all of it in the thermocouple alloy throughout the operating temperature range and the relative amounts of the additives, including the aluminum, should be such that the algebraic sum of their effects upon the thermoelectric power of the copper-nickel base alloy is substantially equal to the difference between the thermoelectric power of the base alloy and that desired after addition of aluminum plus other elements selected from Tables A and B.

What is claimed is:

1. A thermocouple element consisting of an alloy essentially comprising a copper-nickel base whose copper-nickel ratio is within the range 62% copper/38% nickel to 56% copper/44% nickel, having a stable voltage/temperature characteristic over the temperature range of from 0° C. to 900° C. which differs from that of the copper-nickel base to an extent predetermined by inclusion in the alloy of the additional elements including aluminum up to 4% and having an effect per percent of 2700 microvolts at 500° C., for enhancement of corrosion-resistance and change of slope of the voltage/temperature characteristic without substantial alteration of curvature of that characteristic of the copper-nickel base, and including cobalt up to 2% and having an effect per percent of 2750 microvolts at 500° C. to change the slope and to provide negative correction of the curvature below 400° C. and above 600° C. of the voltage/temperature characteristic of the copper-nickel base and at least one element from the group consisting of iron, manganese, silicon, titanium and vanadium to change the slope and to provide positive correction of the curvature of the voltage/temperature characteristic of the copper-nickel base, said additional elements being present entirely in solid solution and not in excess of limits of solid solubility to the substantial exclusion of the formation of any of said additional elements into intergranular segregates, and having the below-specified effect per percent of element in microvolts at 500° C., said aluminum being present in an amount sufficiently effective to increase the corrosion-resistance of said alloy and said cobalt and said at least one other element being present in amount sufficiently effective to make the voltage/temperature characteristic of said thermocouple element with respect to platinum less negative to a predetermined extent from that of the copper-nickel base:

Element	Effect per percent of element ¹ in microvolts at 500° C.	Percent Limit of Solid Solubility
Iron.....	6820	2
Manganese.....	1900	15
Silicon.....	5530	4
Titanium.....	5960	2
Vanadium.....	11,400	1

¹ First order approximation.

2. A thermocouple element whose voltage/temperature characteristic against platinum has the predetermined average slope of -41.4 microvolts per degree centigrade within a tolerance of $\pm 1\%$ composed of the following elements substantially in the following proportions:

	Percent by weight
Aluminum	0.23
Silicon	0.21
Cobalt	0.23
Titanium	0.27
Iron	0.03

and the balance a base of copper-nickel having a ratio of copper to nickel in the range of 60.5% copper/39.5% nickel to 57.5% copper/42.5% nickel and incidental impurities, all of said elements being present entirely in solid solution to the substantial exclusion of intergranular segregates.

3. A thermocouple element whose voltage/temperature characteristic against platinum has the predetermined average slope of -41.5 microvolts per degree centigrade

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within a tolerance of $\pm 1\%$ composed of the following elements substantially in the following proportions:

	Percent by weight
Aluminum -----	0.27
Vanadium -----	0.18
Cobalt -----	0.25
Manganese -----	0.46
Iron -----	0.02

and the balance a base of copper-nickel having a ratio of copper to nickel in the range of 60.5% copper/39.5% nickel to 57.5% copper/42.5% nickel and incidental impurities, all of said elements being present entirely in solid solution to the substantial exclusion of intergranular segregates.

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