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THERMOCOUPLE ELEMENT COMPOSITION

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This invention relates to thermocouples and, more particularly, to a combination of alloy compositions for the two components of a thermocouple which resist the deteriorative effect of various furnace atmospheres at high temperatures.

The electromotive force developed by any alloy at any given temperature is sensitive to changes in the nature and quantities of the metallic constituents present in the alloy. There are other constituents too, of a non-metallic nature, which are invariably present in all industrial alloys and which, if varied, have a marked effect in changing the electromotive force of a given alloy combination. These non-metallic constituents include oxygen, nitrogen and hydrogen which are adsorbed by the metallic constituents of the alloy, and they further include compounds such as oxides, nitrides, hydrides and sulfides which are soluble to a significant extent in the matrix of which the alloy is composed.

It is quite possible, industrially, to manufacture alloys of definite composition which will produce a definite electromotive force within specified limits at a given temperature. Both metallic and non-metallic constituents can be readily controlled, the former by metal additions and the latter by oxidizing or deoxidizing agents used in the melting operation. As a result, the thermocouple alloys reach the ultimate consumer with properties conforming to the electromotive force which is desired. However, the consumer uses these thermocouples for temperature control under conditions which frequently tend to alter the composition of the thermocouple alloys. For example, the atmospheres in industrial furnaces are in most cases either oxidizing or reducing. When these atmospheres produce changes in the composition of the thermocouple alloy, as they invariably do at high temperatures, a corresponding change will occur in the thermal electromotive force of the alloy and the couple will depart from its initial calibration. Further changes due to the formation of oxides, carbides, and sulfides can occur. These metallic compounds, initially formed on the surface of the alloys, can dissolve in the alloys and diffuse in from the surface inasmuch as they tend to precipitate on grain boundaries within the alloy during the cooling cycle and serve as regions for further attack by the heated furnace atmospheres during a subsequent heating cycle. Thus, in addition to changes in the electromotive force of the alloys, a general weakening of the structure results and the alloys develop brittle properties which destroy their usefulness.

Since both elements of any thermocouple contribute to the electromotive force of the combination, it is essential that both of them resist, to a high degree, the destructive changes which have been outlined hereinbefore. Nothing is gained when one element of the thermocouple is highly resistant to attack from furnace atmospheres if the other is easily destroyed. The utility of the thermocouple is strictly limited to the service which can be obtained from the weaker member of the alloy combination.

A thermocouple which has become popular because of its electromotive force characteristics comprises a combination in which the electropositive element is a nickel-chromium alloy containing approximately 8 to 10% of chromium with other metallic additions in minor amounts and the electronegative element is a nickel alloy with a manganese content of approximately 3% and aluminum and silicon in amounts usually not exceeding 2% each. The nickel-chromium alloy of 8 to 10% chromium was chosen for the positive leg of the thermocouple because it produced a greater electromotive force than would be produced if alloys of higher or lower chromium content were employed. But, I have found that alloys containing 18 to 22% chromium used with a nickel alloy containing not over 4% manganese, not over 3% aluminum, and silicon in amounts not exceeding 2% give a sufficiently high electromotive force to form satisfactory thermocouples, and are more stable in certain atmospheres than the thermocouple in which the positive leg is formed of the 8 to 10% chromium alloys heretofore used.

While the electropositive element may consist of 18 to 22% chromium and the balance substantially all nickel, except for incidental impurities normally associated with nickel and residual amounts of deoxidizers added to the melt, the alloy may contain up to 2% columbium, up to 2% iron, up to 2% manganese, from 0.5 to 2% silicon, and from 0.01 to 0.15% carbon. Presence of columbium and, to a lesser extent, silicon in these alloys is particularly desirous in those atmospheres in which chromium alloys are subject to "green rot" deterioration, such as furnace atmospheres that are alternately oxidizing and reducing in character. The electronegative leg, as stated, may contain from 2% to 4% manganese, approximately 1% to 3% aluminum, and silicon in amounts not more than 2%, less than 1% cobalt, balance essentially nickel. Its preferred proportions are carbon .02%, manganese 2.90%, silicon 1.10%, aluminum 1.75%, cobalt .50%, as little iron as possible, balance essentially nickel. An actual analysis of a sample of this alloy showed carbon .01%, manganese 2.98%, silicon .99%, aluminum 1.99%, balance essentially nickel.

In testing alloys of the prior art for use in thermocouples in an atmosphere containing appreciable amounts of carbon monoxide, carbon dioxide and hydrogen, and a lesser amount of methane, I have found that the alloy comprising the positive leg shows great deviation in E. M. F. during operation. These tests were carried out in the reducing atmosphere for a period of 171 hours at a temperature of 1750° F. The changes in E. M. F. in several alloys tested were as follows:

The prior art thermocouple consisting of a positive leg of 8 to 10% chromium, balance essentially nickel, and a negative leg of substantially 3% manganese, not over 2% silicon, not over 3% of aluminum, balance essentially nickel; —7.92 mv.

A thermocouple having a positive leg of 18 to 22% chromium, balance essentially nickel, and the negative leg described in the preceding statement, hereinafter referred to as thermocouple, No. I; +0.11 mv. (As stated above, the positive leg of this thermocouple may and does contain minor amounts of other metals. Thus, the alloy actually used in the tests consisted of C .05%, Mn 0.5%, Si 1.2%, C, 19.5%, balance essentially Ni).

Where the atmosphere contains gases in which chromium alloys are susceptible to "green rot" deterioration, up to 2% of columbium may be added to the alloy of the positive leg. A thermocouple consisting of a positive leg of such an alloy and the negative leg heretofore described, and hereinafter referred to as thermocouple No. II, the deviation was +0.11 mv. (Except for the columbium, the positive leg of the thermocouple was essentially that described in the previous statement. It actually consisted of C .06%, Mn .06%, Si .86%, Cr 19.04%, Cb 1.12%, and balance essentially nickel.)

These two thermocouples, which are characterized by high resistance to deterioration at high temperatures in conventional furnace atmospheres, develop electromotive forces of sufficient amount to make them useful as thermocouples. The relation between temperature and electromotive force is given in the table.

Table

Temperature, °F.	No. I, mv.	No. II, mv.
32	0.00	0.00
100	0.93	1.00
200	2.30	2.43
300	3.75	3.96
400	5.15	5.41
500	6.55	6.89
600	8.03	8.42
700	9.55	9.98
800	11.10	11.56
900	12.70	13.26
1,000	14.40	15.04
1,100	16.20	16.93
1,200	18.09	18.85
1,300	19.98	20.80
1,400	21.95	22.82
1,500	23.92	24.85
1,600	25.92	26.90
1,700	27.97	28.99
1,800	30.00	31.09
1,900	32.07	33.27
2,000	34.17	35.42
2,100	36.30	37.58
2,200	38.40	39.75
2,300	40.56	41.90

The much greater stability of thermocouples I and II, when compared to the prior art thermocouple, in reducing and oxidizing furnace atmospheres, makes such thermocouples desirous and useful in many situations in which thermocouples are used.

I claim:

1. A thermocouple comprising an electropositive element composed of an alloy of from 18 to 22% chromium and the balance essentially nickel, and an electronegative element composed of an alloy containing approximately 2% to 4% manganese, approximately 1% to 3% aluminum, approximately 1% silicon, and the balance essentially nickel.

2. A thermocouple comprising an electropositive element composed of an alloy of from 18 to 22% chromium, up to 2% columbium, and the balance essentially nickel, and an electronegative element composed of an alloy containing approximately 2% to 4% manganese, approximately 1% to 3% aluminum, approximately 1% silicon, and the balance essentially nickel.

3. A thermocouple comprising an electropositive element composed of an alloy of from 18 to 22% chromium, up to 2% columbium, up to 2% manganese, 0.5 to 2% silicon, 0.01 to 0.15% carbon, and the balance essentially nickel, and an electronegative element composed of an alloy containing approximately 2% to 4% manganese, approximately 1% to 3% aluminum, approximately 1% silicon, and the balance essentially nickel.

4. A thermocouple comprising an electropositive element consisting of substantially 19.5% chromium, substantially 0.05% carbon, substantially 1.2% silicon, substantially 0.5% manganese, and the balance essentially nickel, and an electronegative element containing approximately 2% to 4% manganese, approximately 1% silicon, approximately 1% to 3% aluminum, and the balance essentially nickel.

5. A thermocouple comprising an electropositive element consisting of substantially 19.5% chromium, substantially 0.06% carbon, substantially 0.8% silicon, substantially 0.06% manganese, substantially 1.1% columbium, and the balance essentially nickel, and an electronegative element containing approximately 2% to 4% manganese, approximately 1% silicon, approximately 1% to 3% aluminum, and the balance essentially nickel.

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