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HIGH TEMPERATURE, OXIDATION RESISTANT NOBLE METAL-AL ALLOY THERMOCOUPLE

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Field of Search

References Cited

U.S. PATENT DOCUMENTS

Fink, Donald G. and Donald Christiansen, eds., Electronics Engineers Handbook, 1989, pp. 10-30-10-32.
Diefenderfer, A. James, Principles of Electronic Instrumentation, 1972, pp. 82-84.

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ABSTRACT

A thermocouple having an electropositive leg formed of a noble metal-Al alloy and an electronegative leg electrically joined at respective ends thereof to form a thermocouple junction. The thermocouple provides for accurate and reproducible measurement of high temperatures (600°-1300° C.) in inert, oxidizing, or reducing environments, gases or vacuum. Furthermore, the thermocouple circumvents the need for expensive, strategic precious metals such as rhodium as a constituent component. Selective oxidation of rhodium is also thereby precluded.

20 Claims, 2 Drawing Sheets
FIG. 1

FIG. 2
FIG. 3

\[ \text{emf (mv)} = 3.14 \times 10^{-5} (T^{1.5741}) \]
HIGH TEMPERATURE, OXIDATION RESISTANT NOBLE METAL-AL ALLOY THERMOCOUPLE

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the U.S. Government and may be manufactured and used by or for the Government, for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a thermocouple adapted for accurate and reproducible measurement of high temperatures in inert, oxidizing or reducing environments, gases, or vacuum, and more particularly to a thermocouple leg comprising a noble metal-Al alloy.

2. Description of the Prior Art

High melting, noble metal thermocouples made of e.g., platinum (Pt), rhodium (Rh), palladium (Pd), iridium (Ir), etc., and alloys thereof are known in the art. For example, the most widely used thermocouple for measurement of temperatures above 1000° C. is Pt-Pt13Rh, where one leg of the thermocouple is made of a wire or thin film of Pt and a second leg of the thermocouple is made of a wire or thin film of Pt13Rh (i.e., an alloy of platinum and rhodium containing 13 wt. % rhodium). The emf-temperature response of a Pt-Pt13Rh thermocouple, the basis of temperature measurement via thermocouples, is high (e.g., about 12.5 mv at 1200° C.), and its oxidation resistance is good. The Pt-Pt13Rh thermocouple can be used with minimal drift (i.e., a change in emf with time due to any cause such as composition change, oxidation or chemical attack) up to 1500° C. Other precious metal elements, e.g., Pd and Ir, or alloys thereof with Pt are also useful thermocouples. Such thermocouples are not widely used because they are more susceptible to oxidation than Pt, and degrade by drift caused by selective oxidation.

On the other hand, Pt-modified pack aluminide coatings and the oxidation properties of these coatings in Pt-Al bulk alloys are known in the art. However, none of this technology concerns coating of Pt wires, making Pt-Al alloy wires, or using Pt-Al wires as thermocouple devices. The essence of the Pt-modified aluminide coating is that a thin layer (less than about 0.025 mm) of Pt is plated or CVD coated onto a nickel-base superalloy to provide a thermocouple for accurate and reproducible measurement of high temperatures (600°-1300° C.) in inert (e.g., Ar, He), oxidizing (e.g., air, O2, CO2, H2O) gas atmospheres, contact with any silica-containing material, e.g., silica-based refractories and SiC or Si3N4 ceramics, can result in low melting Pt-Si compounds and destruction of the thermocouple.

The following patents relate to high temperature thermocouples, including Pt-Rh elements or analogous alloys which utilize rare and expensive metals or other metals.

U.S. Pat. No. 3,901,734 to Sibley et al relates to a thermocouple in which the positive element consists of an iron-nickel alloy and the negative element consists of a copper-nickel alloy. The compositions of these elements are such that inexpensive lead wires of copper, for example, may be used without any significant temperature error, where the thermocouple is used to monitor a temperature of about 1600° F. and the lead wire-thermocouple junction is at a temperature not exceeding about 400°-500° F. Particularly, the emf output of the Sibley et al thermocouple between 32° F. and about 500° F. is said to approach substantially zero when the compositions of the positive and negative thermoelements are properly selected.

U.S. Pat. No. 4,402,447 to Przybyszewski et al relates to a method for bonding a platinum base metal lead wire to a thin platinum alloy film (typically Pt or Pt10Rh) resting on a thin alumina insulating layer adhered to a metal substrate. Typically, the platinum alloy film forms an element of a thermocouple for measuring the surface temperature of a gas turbine airfoil.

U.S. Pat. No. 4,984,904 to Nakano et al relates to a platinum-platinum/rhodium alloy thermocouple housed in an immersion protection tube used to monitor the temperature of molten metal. The immersion protection tube formed of alumina-graphite is said to protect the thermocouple from high temperature exposure to a reducing atmosphere.

U.S. Pat. No. 5,043,023 to Bentley relates to a metal sheathed thermocouple cable comprising an oxidation-resistant nickel-based alloy. The thermocouple cable is said to have excellent thermoelectric and mechanical stability at high temperatures (beyond about 900° C.), and is said to avoid premature failure due to oxidation that occurs in "bare-wire" thermocouples.

The following technical publications relate to platinum modified aluminide diffusion coatings.


J. S. Smith et al., "Platinum Modified Aluminides- Present Status", presented at the Gas Turbine and Aeroengine Congress and Expedition-Brussels, Belgium (Jun. 11-14, 1990) provides an overview of the development of platinum modified aluminide diffusion coatings used to impart oxidation and hot corrosion resistance to nickel-base superalloys. This paper discusses various coating morphologies and application of a low pressure chemical vapor deposition (low pressure CVD) process for production of platinum modified aluminide gas phase coatings on gas turbine components.

SUMMARY OF THE INVENTION

Accordingly, a first object of this invention is to provide a thermocouple for accurate and reproducible measurement of high temperatures (600°-1300° C.) in inert (e.g., Ar, He), oxidizing (e.g., air, O2, CO2, H2O)
or reducing (e.g., H₂, CO, CH₄) environments, gases, or vacuum.

A second object of this invention is to provide a thermocouple which exhibits low emf drift (defined as the change in emf with time due to any cause such as composition change, oxidation or chemical attack) for measurement of high temperatures in the above described environments.

A third object of this invention is to provide a thermocouple element for high temperature measurement which circumvents the need for expensive, strategic precious metals such as rhodium (Rh) as a constituent component. In this manner, selective oxidation of Rh is prevented.

Other objects of this invention will become apparent in the following description and Example.

The present inventors have discovered that the above first and second objectives are achieved by a thermocouple comprising an electropositive leg and an electronegative leg, the electropositive leg and the electronegative leg being electrically joined at respective ends thereof to form a thermocouple junction, wherein the electropositive leg comprises a noble metal-Al alloy, while the electronegative leg comprises a noble metal-AI alloy. The electropositive and preferably the electronegative legs do not contain Rh.

Pt-AI alloys are known to form a protective AI₂O₃ scale when exposed to an oxidative atmosphere. It is also known to form oxidation resistant alloys with aluminum, in much the same way as Pt-Al alloys are oxidation resistant. Similarly, we also expect Rh, Pd, Ag and Au to form oxidation resistant alloys with aluminum, but with decreasing temperature capability. Thus, Ir-Al or Pt-Ir-Al or Pt-Al alloy thermocouple legs, for example, are within the scope of this invention.

What was not hitherto recognized is that a significant emf exists between joined wires of a noble metal and a noble metal-Al alloy to expose a high temperature differential, which allows these materials to advantageously be used as component parts of a novel type of thermocouple.

Also, we can envision a dilute Pt-Al alloy joined to a rich Pt-Al alloy that both form protective AI₂O₃ scales, and are more diffusionally stable than just a pure Pt leg coupled to a Pt-Al leg. That is, the chemical driving force for diffusion would be reduced.

Thus, a first advantage of the thermocouple of the present invention over prior art thermocouples is that the expensive, strategic precious metal rhodium is not needed as a constituent component. Other benefits are that protective AI₂O₃ scales form over the thermocouple leg, thereby lessen any oxidation and vaporization of constituent components. This is especially useful when the thermocouple leg is in the form of a thin film, where vaporization and reaction with the underlying substrate is critical and may be alleviated by the protective AI₂O₃ scales formed, for example, on Pt-Al alloys.

The present invention is not particularly limited, and it may comprise, for example, a thin wire or a thin film. A thermocouple wire in accordance with the present invention generally ranges from 0.25 to 2.0 mm in diameter, and Pt-Al coated wires in accordance with a preferred embodiment prepared, for example, by pack aluminizing or CVD (chemical vapor deposition) have a diameter of from 0.5 to 2.0 mm for optimum behavior. Thin film thermocouple elements in accordance with the present invention generally have a thickness in the range of from 0.02 to 0.20 mm. U.S. Pat. No. 4,402,447 to Przybyszewski et al describes the preparation of thin Pt/Rh alloy films and the joining of lead wires thereto for preparation of a high temperature thermocouple, and this is incorporated herein by reference.

The noble metal for use in the present invention is selected from Pt, Ir, Rh, Pd, Ag, Au and combinations thereof. Pt and Ir are preferred. Pt is most preferred.

When the thermocouple leg of the present invention does not contain Rh, the noble metal is selected from Pt, Ir, Pd, Ag, Au and combinations thereof. The noble metal may take the form of a simple mixture, solid solution or intermetallic compound (e.g., a Pt₅Al₃ compound), or combinations thereof. The minimum Al content of the noble metal-Al alloy is about 5 atom %, and preferably about 10 atom % for totally protective oxide formation, whereas the maximum Al content of the noble metal-Al alloy is about 67 atom % due to increasing brittleness with an increase in Al content. The Al content is preferably from 10 to 50 atom %.

As discussed above, the electropositive leg comprises a noble metal-Al alloy. The electronegative leg can comprise, for example, a noble metal or a noble metal-Al alloy, as long as the Al contents of the first and second legs are sufficiently different to produce an acceptable emf. In a preferred embodiment, both legs comprise a noble metal-Al alloy to thereby benefit from the oxidation resistance provided by the protective AI₂O₃ scale. A preferred combination is 15-67 atom % Al and more preferably 40-60 atom % Al for the noble metal-Al alloy of the electropositive leg and 5-10 atom % Al for the noble metal-Al alloy of the electronegative leg. Particularly, this preferred combination allows a useful emf to be generated because of the substantial difference in Al contents, but still allows some formation of a protective AI₂O₃ scale on the electronegative leg, while minimizing the potential for interdiffusion and emf drift.

The form of the thermocouple leg of the present invention is not particularly limited, and may comprise, for example, a thin wire or a thin film. A thermocouple wire in accordance with the present invention generally ranges from 0.25 to 2.0 mm in diameter, and Pt-Al coated wires in accordance with a preferred embodiment prepared, for example, by pack aluminizing or CVD (chemical vapor deposition) have a diameter of from 0.5 to 2.0 mm for optimum behavior. Thin film thermocouple elements in accordance with the present invention generally have a thickness in the range of from 0.02 to 0.20 mm. U.S. Pat. No. 4,402,447 to Przybyszewski et al describes the preparation of thin Pt/Rh alloy films and the joining of lead wires thereto for preparation of a high temperature thermocouple, and this is incorporated herein by reference.

The noble metal for use in the present invention is selected from Pt, Ir, Rh, Pd, Ag, Au and combinations thereof. Pt and Ir are preferred. Pt is most preferred. When the thermocouple leg of the present invention does not contain Rh, the noble metal is selected from Pt, Ir, Pd, Ag, Au and combinations thereof. The noble metal may take the form of a simple mixture, solid solution or intermetallic compound (e.g., a Pt₅Al₃ compound), or combinations thereof. The minimum Al content of the noble metal-Al alloy is about 5 atom %, and preferably about 10 atom % for totally protective oxide formation, whereas the maximum Al content of the noble metal-Al alloy is about 67 atom % due to increasing brittleness with an increase in Al content. The Al content is preferably from 10 to 50 atom %.
The thermocouple legs comprising noble metal-Al alloys can be prepared, for example, by pack aluminizing, CVD coating, sputtering under a vacuum, or by pre-alloying in the master melt form of the wire or thin film production process. For example, pack aluminizing is readily accomplished by placing a noble metal wire in a bed of inert Al₂O₃ sand containing about 2 wt. % Al powder and about 2 wt. % NH₄Cl activator at a temperature of about 1,000° C. The amount of aluminum incorporated into a coating of the noble metal wire increases with the pack aluminizing time. Pack aluminizing times of 1 to 4 hours are typical.

On the other hand, low pressure chemical vapor deposition may be employed to prepare a noble metal modified aluminate gas phase Al coating on a suitable substrate such as a Pt wire (or one of the other noble metals as defined above) followed by a post coating diffusion treatment (annealing) to form a noble metal-Al alloy. In the CVD coating process, HCl or HF is typically passed over a source of aluminum to generate an aluminate gas. Advantageously, annealing can be conducted as part of the CVD cycle. Alternatively, sputter coating of noble metal-Al alloys under vacuum is well adapted for preparing thin film alloy thermocouple elements for use in this invention. The thin film alloy thermocouple element might be deposited, for example, on a substrate such as a turbine airfoil test component as described by Przybylszewski et al, supra. In this case, the substrate does not participate in forming the noble metal-Al alloy.

J. S. Smith et al, and M. R. Jackson et al, supra, describe pack aluminizing and CVD coating; Przybylszewski et al, supra, describe sputtering under vacuum; and S. M. Sze, VLSI Technology, McGraw-Hill Book Company, pages 347-361 (1983) describes various techniques for Al metallization including physical vapor deposition, resistance heated evaporation, E-beam evaporation, inductive heating, sputtering and CVD. A post coating diffusion (annealing) treatment following Al metallization is typically carried out at a temperature of from 1000° to 1200° C. for a time of from 1 to 20 hrs. in argon or vacuum (i.e., non-oxidizing). All of the above techniques are readily adapted by one of ordinary skill in the art for preparing the noble metal-Al alloy for use in this invention.

The term "coating" is used herein to describe a noble-metal-Al alloy formed in the outer portion of a substrate by pack aluminizing, as well as a noble metal-Al alloy formed, e.g., by Al deposition onto a substrate followed by post coating diffusion treatment. Inhomogeneity of a CVD coated or pack aluminized wire may cause diffusion instability. This could result in emf drift of the thermocouple, and is preferably minimized. We have found that annealing of the CVD coated or packed aluminized thermocouple element at about 1400° C. for about two hours in an inert atmosphere such as argon provides for homogenization of the outer aluminate coating, and effectively minimizes diffusional instability.

When Pt is supplied as a coating, we found successful operation of a Pt-Al thermocouple leg (following diffusion heat treatment) in the Pt₃Al₂ to Pt₅Al₃ range. Thick PtAl₂ coatings (0.18-0.25 mm) can cause cracking of a 1.0 mm diameter Pt wire if bent. We expect thin PtAl₂ coatings of about 0.02-0.10 mm to be most useful. The amount of Pt consumed is generally on the order of 1/3 of the coating thickness. We expect noble metal-Al alloy coatings having a thickness of from 0.02 to 0.20 mm to be useful in this invention.

The preferred phases of the Pt-Al alloy are Pt₃Al₂ or Pt₅Al₃ when the thermocouple is formed as a coating. However, as a bulk wire, the alloy may have to be PtAl or even less Al, and thus less emf, in order to maintain sufficient bulk ductility. Coated Pt wires thus offer a dual advantage of a ductile, low Al, core material combined with a thin high Al, high emf, Pt aluminide coating. For purposes of the aluminized wire, we optimized the thickness of the Pt₃Al₂ phase based on good emf response and suitable ductility. This was accomplished by aluminizing at 1,000° C. for 1.4 and 16 hrs. as discussed in the Example below. We found that the 4 hr. treatment provided the best overall results.

In accordance with a preferred embodiment of this invention, the electropositive and electronegative legs comprising a Pt-Al alloy do not contain Rh. In this manner, selective oxidation and the expense of Rh is thereby precluded.

The electropositive leg and electronegative leg of the thermocouple of the present invention may be electrically joined at respective ends thereof to form a thermocouple junction, for example, by welding or by mechanical joining such as compression bonding. U.S. Pat. No. 4,415,758 to Lacoste et al describes a process for making a thermocouple junction between two small size thermocouple leg wires and is incorporated herein by reference. When used in the form of a thin film, the electropositive leg comprising a noble metal-Al alloy film and the electropositive leg comprising, for example, a Pt film may overlap to form a thermocouple junction as described by Przybylszewski et al., supra.

A thermocouple circuit in accordance with the present invention comprises an electropositive leg and an electronegative leg electrically joined together at one end (sensing junction) and terminated at their other end in such manner that the terminals (reference junction) are both at the same and known temperature (reference temperature). Connecting leads from the reference junction to a load resistance (e.g., an indicating meter such as a galvanometer or voltmeter, or the input impedance of other readout or signal-conditioning equipment) complete the thermocouple circuit. The connecting leads may be of copper alloy or some other metal different from the metals joined at the sensing junction. U.S. Pat. No. 3,372,062 to Zysk describes base metal leads for a noble metal thermocouple and is incorporated herein by reference. A current is caused to flow through the circuit whenever the sensing junction and the reference junction are at different temperatures. The reference junction may be held at a known constant temperature, or may be electrically compensated for variations from a preselected temperature.

The thermocouple of the present invention may also take the form of a thermopile comprising a plurality of sensing junctions of the same material pairs in close proximity to each other and connected in series so as to multiply the emf output obtainable from a single sensing junction. The isothermal reference junctions are usually also in close proximity to each other to assure an equal temperature for each reference junction. For details regarding thermocouple circuits, reference may be made to Electronics Engineers' Handbook, 3rd Ed. McGraw-Hill Book Company, pages 10-30 to 10-32 (1989); Vassos et al, Analog and Digital Electronics for Scientists, pages 252-254, John Wiley & Sons, Inc. (1972); and A. J. Diefenderfer, Principles of Electronic
Three (3) Pt-AI wires were prepared by aluminizing three (3) Pt wires for 1, 4 or 16 hrs. Aluminizing was accomplished by standard pack aluminizing at 1,000°C in a bed of inert Al2O3 sand containing 2 wt. % Al powder and 2 wt. % NH4Cl activator. The aluminum pickup was monitored by Pt sheet specimens in the same packs, gaining 1.3 and 4.7 mg/cm2 for the 1 and 4 hr. treatments, respectively. The 16 hr. sheet sample showed aspects of this invention, which Example is not intended to limit the scope or applicability of this invention.

EXAMPLE

The excellent fit of the first equation to the data is shown in FIG. 3. A similar fit was obtained with the second equation:

\[ emf = 3.14E-5(T^{1.5741}) \]

or

\[ emf = 4.50E-11T^3 + 1.01E-6T^2 + 7.226E-4T - 4.448E-2 \]

The thermocouple of claim 1, wherein the noble metal is selected from the group consisting of Pt, Ir, Rh, Pd, Ag and Au.

The thermocouple of claim 1, wherein the noble metal is selected from the group consisting of Pt and Ir.

The thermocouple of claim 1, wherein the noble metal is Pt.

The thermocouple of claim 1, wherein the electronegative leg comprises a noble metal-Al alloy.

The thermocouple of claim 1, wherein the electronegative leg comprises a wire having a diameter of from 0.25 to 2.0 mm.

The thermocouple of claim 1, wherein the electronegative leg comprises a wire having a thickness of from 0.02 to 0.20 mm, which films overlap at respective ends thereof to form a thermocouple junction.

The thermocouple of claim 1, wherein the metal-Al alloy has an Al content of from 5 to 67 atom %.

The thermocouple of claim 1, wherein the metal-Al alloy has an Al content of from 5 to 10 atom % and the noble metal-Al alloy of the thermocouple leg has an Al content of from 5 to 67 atom %.

The thermocouple of claim 1, wherein the metal-Al alloy has an Al content of from 5 to 67 atom % and the metal-Al alloy of the thermocouple leg has an Al content of from 5 to 67 atom %.

The thermocouple of claim 1, wherein the metal-Al alloy coating has a thickness of from 0.02 to 0.20 mm.

The thermocouple of claim 1, wherein the metal-Al alloy coating has a thickness of from 0.25 to 2.0 mm.

The thermocouple of claim 1, wherein the substrate is Pt, the noble metal of the noble metal-Al alloy coating is Pt, and the noble metal-Al alloy has an Al content of from 5 to 67 atom %.

The thermocouple comprising an electronegative leg and an electronegative leg, said electronegative leg and said electronegative leg being electrically joined at respective ends thereof to form a thermocouple junction, wherein the thermocouple leg comprises a Pt wire having a Pt-Al alloy coating and the electronegative leg comprises a Pt wire or a Pt wire having a Pt-Al alloy coating.

The thermocouple of claim 14, wherein the Pt-Al alloy coating of the electropositive leg has an Al content of from 5 to 67 atom % and the electronegative leg comprises a Pt wire.

The thermocouple of claim 14, wherein the Pt-Al alloy coating of the electropositive leg has an Al content of from 5 to 67 atom % and the electronegative leg comprises a Pt wire having a Pt-Al alloy coating having an Al content of from 5 to 10 atom %.

The thermocouple of claim 14, wherein the Pt-Al alloy coating of the electropositive leg has an Al content of from 5 to 67 atom % and the electronegative leg comprises a Pt wire having a Pt-Al alloy coating having an Al content of from 5 to 10 atom %.

The thermocouple of claim 16, wherein the metal-Al alloy leg has a diameter of from 0.25 to 2.0 mm and the electronegative leg wire has a diameter of from 0.25 to 2.0 mm.

The thermocouple of claim 14, wherein both the electropositive and electronegative legs do not contain Rh.

A thermocouple comprising an electronegative leg and an electronegative leg, said electronegative leg and said electronegative leg being electrically joined at respective ends thereof to form a thermocouple junction, wherein the thermocouple leg comprises a noble metal-Al alloy.

The excellent fit of the first equation to the data is shown in FIG. 3. A similar fit was obtained with the second equation:

\[ emf = 3.14E-5(T^{1.5741}) \]

or

\[ emf = 4.50E-11T^3 + 1.01E-6T^2 + 7.226E-4T - 4.448E-2 \]

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