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NICKEL-ALUMINUM ELECTRICAL RESISTANCE ELEMENTS

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U.S. Cl. 75—170 **10 Claims**

ABSTRACT OF THE DISCLOSURE

Wrought electrical resistance elements produced from nickel-aluminum alloy powders are compacted, sintered and extruded into rod form. The nickel-aluminum alloys contain from 25% to 35% aluminum and may also include small amounts of one or more rare earth metals.

The invention is directed to wrought electrical resistance elements composed of nickel-aluminum alloys produced by powder metallurgy techniques.

In resistance furnaces and other pieces of equipment in which temperatures in the range of 1250° C. to 1450° C. must be reached, various materials are used as heating elements but none is wholly satisfactory. The best iron-base alloys, for example, those containing about 20% chromium, about 5% aluminum and about 0.5% cobalt with the remainder iron, are limited to a maximum operating temperature of about 1350° C. Platinum and molybdenum are sometimes used but the former is expensive and the latter must be protected from oxidation by an atmosphere such as hydrogen. Ceramic materials, for example, silocon carbide, have poor resistance to mechanical shock and are prone to accidental damage.

Certain of the well-known nickel-base alloys, containing, for example, about 20% chromium, and about 3.5% aluminum with the remainder nickel, are not recommended for use at temperatures as high as 1250° C.

The intermetallic compound, NiAl, is known to have a high melting point and sufficient electrical resistivity to make it of substantial interest in the field of electrical resistance elements. However, this alloy has not been successfully utilized on a commercial scale as electrical resistance elements.

It has now been discovered that a special powder metal processing technique is capable of producing a stabilized fine grain size in nickel-aluminum resistance elements, which confers an extended work-life at operating temperatures of 1300° C. and higher.

It is an object of this invention to provide electrical resistance elements suitable for use at high temperatures and having an extended useful life.

Other advantages will become apparent from the following description.

In accordance with the invention, an alloy of suitable composition is melted and cast, and after solidification is comminuted to a relatively fine size, compacted, sintered at an elevated temperature and the sintered compact is consolidated by hot working. Preferably, this consolidation is effected by sealing the sintered compact in a container or can and, thereafter, extruding the canned compact to rod form at an elevated temperature.

The alloys employed in the electrical resistance elements of the invention are essentially binary alloys of nickel and aluminum based on the intermetallic compound NiAl and containing, by weight, from 25% to 35% aluminum, and advantageously, from 26% to 29% aluminum. The stoichiometric composition, 31.5% aluminum, has the advantage of possessing the highest melting point within the specified range, but the alloys become progressively more brittle, and therefore difficult to handle, as the aluminum content increases. The operating life of electrical resistance elements is still further improved if either cerium or lanthanum or both is included in the alloys, lanthanum being the more advantageous addition. These two elements may, of course, be added together in the form of mischmetal (about 50% cerium, about 45% lanthanum, balance other rare earth elements). Very small amounts of these elements (less than 0.1%) are effective, and no good purpose is served in adding more than 0.5% total of these elements. Advantageously, lanthanum is added in an amount not exceeding 0.25%.

It should be understood that the compound CoAl is similar in its properties to NiAl and is isomorphous with NiAl. Cobalt can therefore be substituted for up to one-half the weight of nickel present in the alloy of the invention.

The nickel-aluminum alloys are prepared in accordance with the process of the invention by melting a mixture of constituents under vacuum (normally approximately 10^{-3} mm. mercury) or under an inert atmosphere such as argon or helium, and thereafter casting the alloys under vacuum or under a suitable inert atmosphere to a convenient form such as bar. After cooling, the cast bars are crushed and comminuted to a predetermined fine particles size of no larger than minus 150 mesh, e.g., minus 325 mesh. The comminuted powder is compacted hydrostatically under a pressure of from about 20 to 50 ton f/square inch (long tons/square inch) and then the compacts are sintered at an elevated temperature of from 1000° C. to 1500° C. in a vacuum of 1 mm. or less of mercury for from 100 to ¼ hours, the time required being shorter the higher the temperature used. Thereafter the compacts are consolidated by first sheating the compacts in sealed cans formed of a suitable material, e.g., mild steel, and extruding at an elevated temperature of from 1100° C. to 1450° C. to rod or other desired form. The can or sheath is then removed by machining, pickling, or by other means, and the rods are straightened at a temperature of about 1000° C. The rods are then cut into desired lengths which may be ground preferably at elevated temperature, or alternatively, hot-drawn, to accurate diameter. Appropriate terminals may then be welded to the ends of the rod.

The electrical resistance elements made as described above are characterized by a fine grain size of from ASTM Grain Size No. 3.5 to ASTM Grain Size No. 7. This fine grain size is stabilized at operating temperatures by aluminum oxide particles at the grain boundaries. The aluminum oxide particles are formed during comminution of the alloy or during sintering, have a particle size of up to one micron, e.g., about 0.1 micron and constitute from about 0.025% to 0.5%, by volume, e.g., about 0.1%, by volume, of the alloy.

For the purpose of illustrating the advantages of the invention to those skilled in the art, the following example is given:

EXAMPLE

Nickel ("Mond" pellet), aluminum (99.99% pure) and either lanthanum or cerium in the desired proportions are melted under vacuum and cast under argon as bars one inch in diameter. These bars are first crushed in a jaw crusher and then milled for 24 hours in a ball mill with tungsten carbide balls to reduce them to powder of less than 44 microns size (minus 325 mesh). This powder is compacted under a pressure of 35 ton f/square inch, and the compacts are sintered at 1300° C. in a vacuum of approximately 10^{-3} mm. of mercury for 6 hours. The sintered compacts are sheathed in mild steel cans, sealed with nickel-chromium-cobalt base alloy (Nimonic 90 alloy) plugs, and extruded at 1300° C. to rod 0.25 inch in diameter. The sheathing is removed by partial oxidation of the sheath in air at approximately 1050° C. and pickling in dilute nitric acid. The rods are straightened at 1000° C., and then the rods are cut into lengths and centerless ground at 1000° C. to a diameter of 0.187 inch. The rods are then welded to nickel terminals 0.5 inch in diameter by the tungsten-arc (TIG) process using nickel as a filler.

The improved high-temperature life characterizing the alloys processed in accordance with the invention is shown by the results of tests in each of which four elements produced from a single compact were tested together, the electrical connections being such that the test stopped on the failure of the first element. In Table I below, the compositions of the alloys, the approximate operating temperature of the surface of each element, the number of hours before the first element failed and some comments on the performance of the resistance elements are given.

TABLE I

	Composition, weight percent	Element No.	Operating temperature, ° C.	Operating time, hours	Remarks
Alloys:					
1	26.8 Al 0.55 Ce Bal. Ni	1			After 1,000 hrs.[1]
		2	1,400	1,070	
		3			
		4			
2	27.3 Al 0.17 Ce Bal. Ni	1	1,360	904	No. 1 developed hot spot.[2]
		2	1,400		
		3	1,380		
		4	1,380		
3	26.9 Al 0.06 La Bal. Ni	1	1,300	1,200	(3)
		2	1,360		
		3	1,380		
		4	1,360		
4	27.6 Al 0. 08 La Bal. Ni	1	1,400	1,077	(4)
		2	1,420		
		3	1,420		
		4	1,420		
5	27.0 Al 0.25 La Bal. Ni	1	1,360	1,144	Current increased.[5]
		2	1,420		
		3	1,420		
		4	1,420		
6	26.9 Al Bal. Ni	1	1,400	627	Current switched off.[6]
		2	1,400	247	
		3	1,400	627	
		4	1,400	627	

[1] Current was increased to raise operating temperature to 1,500° C., elements 2,3,4 near to failure or failed at 1070 hrs.

[2] 1,540° C. after 815 hrs., and failed at 904 hrs.

[3] No failure of elements after 1,200 hrs; test discontinued.

[4] Element 1 failed when current increased after 1,077 hrs. to raise element temperatures.

[5] At 1,077 hrs. to raise element temperatures. However, hot spot (1,540° C.) developed on element 4, other element temperatures remaining at 1,400° C.

[6] At 247 hrs. to allow replacement of element No. 2, which cracked. Element No. 1 failed after further 380 hrs.

As will be observed from the results given in the above table, the operating life of the resistance elements of the invention is relatively long at operating temperatures of from 1300° C. to over 1400° C. The life of resistance elements ranges from well over 200 hours for the simple binary alloy, to from about 900 hours to 1200 hours for the alloys containing small amounts of the rare earth elements. It is clear that relatively small additions of lanthanum are more effective in increasing element life than relatively larger quantities of cerium. The resistance elements of the invention have a fine grain size stabilized by the presence of aluminum oxide formed during comminution and during sintering when the latter operation is carried out under relatively low vacuum (e.g., 10^{-2} to 1 mm. mercury).

In contrast to the remarkably long life achieved at high temperature with the resistance elements of the invention, are the results obtained with a commonly used ferrous alloy and a binary nickel-aluminum alloy in *cast* form. These results are set forth in the following Table II in which Alloy A is the ferrous alloy and Alloy B is a nickel-aluminum alloy produced in extruded form from a cast billet.

TABLE II

	Composition, weight percent	Element No.	Operating temperature, ° C.	Operating time, hours	Remarks
Alloys:					
A[1]	20 Cr 5 Al 0.5 Co Bal. Fe	1	1,3 0		Elements 2,3,4.[2]
		2	1,400	103	
		3	1,400		
		4	1,380		
B	28.5 Al Bal. Ni	1	1,400	99	(3)
		2	1,400		
		3	1,400		
		4	1,350		

[1] 0.3 inch diameter rod.

[2] Severely melted—thin adherent scale on each element.

[3] All elements developed large cavities, and melted droplets exuded from cracks in the thick oxide scale.

From the above table it is seen that the ferrous alloy (Alloy A) resistance elements failed at just over 100 hours under test conditions substantially similar to those used for the resistance elements of the invention.

It should be further observed from Table II that when the cast nickel-aluminum alloy (Alloy B) is employed as a resistance element, and operated at temperatures in the range from 1350° C. to 1450° C., e.g., 1400° C., the operating life achieved is similar to that obtained with the commonly used ferrous alloys, and is substantially lower than the life obtained with the resistance elements made in accordance with the invention. An oxide scale forms on the cast nickel-aluminum alloy resistance elements at these operating temperatures and tends to spall off, resulting in additional oxidation of the metal, loss of aluminum and localized melting and failure.

The alloys of the invention may contain the usual impurities in small amounts, in a total amount of up to 1%. These impurities may comprise up to 1% iron, up to 0.5% silicon and up to 0.1% carbon. Additionally, residual deoxidants (e.g., lithium, magnesium, zirconium.

titanium or calcium can be present in amounts up to 0.2% total).

It is found that the alloys of the invention can readily be welded to pure nickel and other metals, including nickel-aluminum alloys containing up to about 14% aluminum. This is a considerable advantage, since it means that rods of the alloys according to the invention can be welded to terminals of a relatively ductile material, such as nickel-aluminum alloys of lower aluminum content than the resistance elements or to nickel itself or to nickel or iron base alloys. The alloys of the invention are brittle at ambient-temperatures, and autogenous welding presents great difficulty if crack-free joints are required.

High temperature nickel-aluminum alloy electrical resistance elements have thus been shown to be capable of preparation by means of a relatively simple process, yielding elements which have an extended operating life at temperatures in excess of 1300° C.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A wrought high temperature electrical resistance element formed from a sintered nickel-aluminum alloy including by weight, from 25% to 35% aluminum, balance essentially nickel, the alloy element having a fine grain size of from ASTM No. 3.5 to ASTM No. 7 and the fine grain size being stabilized at operating temperatures by aluminum oxide particles at the grain boundaries, the aluminum oxide constituting from 0.025% to 0.5%, by volume, of the alloy in particles up to one micron in size.

2. The electrical resistance element of claim **1** wherein the alloy includes at least one rare earth element selected from the group consisting of lanthanum and cerium in a total amount of up to 0.5%.

3. The electrical resistance element of claim **2** wherein cobalt is substituted for up to one-half the amount of nickel present.

4. The electrical resistance element of claim **1** wherein the alloy includes lanthanum in an amount not exceeding 0.25%.

5. The electrical resistance element of claim **1** in which the alloy contains from 26% to 29% aluminum.

6. The electrical resistance element of claim **5** wherein cobalt is substituted for up to one-half the nickel present and the alloy includes at least one rare earth element selected from the group consisting of lanthanum and cerium in a total amount of up to 0.5%.

7. The electrical resistance element of claim **6** wherein the alloy includes lanthanum in an amount not exceeding 0.25%.

8. A process for the production of wrought high temperature electrical resistance elements which comprises melting and casting the constituents of an alloy containing, by weight, from 25% to 35% aluminum, up to 0.5% of at least one rare earth element selected from the group consisting of lanthanum and cerium and the balance nickel, or nickel and cobalt with at least one-half of the said balance constituting nickel, comminuting the alloy to a fine particle size, forming the comminuted alloy into compacts, sintering the compacts at a temperature of from about 1000° C. to 1500° C. for from 100 to ¼ hours in a vacuum of from 10^{-2} to 1 mm. of mercury to permit limited oxidation of the alloy, and thereafter hot working the sintered compacts to effect consolidation.

9. A process according to claim **8** wherein the comminuted powder is compacted at a pressure of about 20 tons per square inch to about 50 tons per square inch to form compacts.

10. A process according to claim **9** wherein the sintered compact is sealed in a container or can and thereafter hot extruded at a temperature of about 1100° C. to about 1450° C.

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RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

148—32; 75—213, 214, 225; 29—182.5, 420.5

PO-1050
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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,554,740 **Dated** January 12, 1971

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Table I, under heading "Composition, weight percent" Alloy 1, for "0.55 Ce" read --0.055 Ce--

Column 4, Table II, under heading "Operating temperature, °C." for the first temperature set forth thereunder "1,3 0" read--

Signed and sealed this 26th day of October 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patent