

UNITED STATES PATENT OFFICE

2,184,769

ZIRCONIUM MAGNETIC ALLOY

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No Drawing. Application March 16, 1937;
Serial No. 131,261

11 Claims. (Cl. 148—13.1)

This invention relates to magnetic alloys and more especially to alloys of zirconium and metals of the iron group suitable for use as permanent magnets together with a method of making the same.

It is well known in the art that the cohesive force of the metals of the iron group may be greatly increased by alloying these metals with carbon, chromium, tungsten or aluminum. Permanent magnets have also been made of combinations of the oxides of metals of the iron group which under certain conditions have characteristics rendering them suitable for such use. Some of these magnetic metals, however, are incapable of resisting the attacks of oxidizing atmospheres while others do not withstand the action of corrosive media. The more general object of the present invention is to bring about alloys, especially those of metals of the iron group, which not only have magnetic properties making them highly desirable for use as permanent magnets but which are capable of resisting the attacks of oxidizing atmospheres as well as withstanding the action of corrosive media.

Pure zirconium metal is one of the most corrosion-resistant metals available at the present time yet in pure state it is paramagnetic. Nickel has high permeability, is resistant to a certain degree to the corrosion-by-acid media, but does not have sufficient retentivity and cohesive force. Both of these metals when heated above certain temperatures form oxides which are paramagnetic. The combination of zirconium and nickel with the amount of zirconium decreasing from 95% to 35%, the balance being nickel, forms alloys which do not respond to the action of a magnetic field. When the amount of zirconium is decreased below 35%, the alloy responds to a magnetic field but is not suitable for use in the manufacture of permanent magnets.

In accordance with the present invention alloys of zirconium and metals of the iron group, for example nickel, are produced wherein the alloys respond readily to the magnetic field even where the amount of zirconium ranges from 35 to 95 percent. Moreover when the amount of zirconium is 40% or less the magnetic characteristics of the alloys, especially with respect to their permeability and retentivity is so markedly changed that the alloys form permanent magnets having characteristics comparable to if not exceeding those of any alloy previously known.

Primarily the invention depends on the discovery by me that powdered alloys of zirconium and nickel when subjected to a heat treatment, more fully described hereinafter, acquire magnetic properties which are radically different than those characterizing the alloys before such treatment.

The powdered alloys subjected to the heat

treatment may be produced in any preferred or suitable manner, for example, in accordance with the teaching of my copending application filed February 14, 1939, Serial No. 256,300. Thus a mixture of zirconium oxide and nickel oxide or zirconium oxide and powdered metallic nickel is mixed with powdered calcium hydride and heated in a closed retort until the reduction of the oxides is completed. The heating is continued for a few hours until the diffusion of particles of reduced zirconium and nickel into one another and the formation of particles of zirconium-nickel alloy is completed.

The series of binary alloys with zirconium decreasing from 95% to 35%, the balance being nickel, do not respond to the action of the magnetic field until they are heat treated.

This treatment consists in subjecting the powdered alloy to the temperature of about 345° C. As soon as any part of the charge reaches this temperature this part of the charge becomes incandescent and if placed in a dark place glows, indicating that an exothermic reaction is taking place.

The glowing spreads rapidly over the whole charge but in a few seconds diminishes in intensity and finally disappears. This reaction is accompanied by the evolution of hydrogen occluded in the alloy, which burns in contact with air.

The weighing of the samples before and after "glowing" showed practically no change in weight indicating that the chemical composition with the exception of the hydrogen content remained substantially unchanged. Yet the magnetic properties of the alloys are changed radically by this heat treatment. The alloys readily respond to the action of the magnetic field and have a high magnetic permeability and retentivity.

The powdered alloys with zirconium less than 33% respond to the action of the magnetic field even before the heat treatment. Yet when heated to about 345° C. they exhibit the same phenomenon of "glowing", after which their magnetic permeability and retentivity are greatly increased.

The calcination of these powdered alloys for a short time does not seem to have noticeable influence either on their magnetic properties or on their chemical composition. Yet prolonged calcination at the temperature of red heat results in the gradual oxidation of the alloy particles and the diminishing of the magnetic properties.

If the calcination is continued for one or two days, depending on the composition of the alloy, it is transformed entirely into a complex oxide with a complete loss of magnetic properties.

The above alloys, especially those with a high percentage of zirconium are sufficiently resistant to the attack by dilute acids, even in finely

powdered state. This fact is of especial importance since these alloys exhibit high magnetic properties when prepared by the above method which after reduction with calcium hydride involves leaching with dilute hydrochloric acid to remove the calcium oxide. The zirconium-nickel alloys in a cast condition especially with zirconium above 33% prepared by the usual fusion method do not possess any of the above described magnetic properties.

In preparing these zirconium magnetic alloys nickel may be replaced by other metals of the iron group. Zirconium-iron or zirconium-cobalt alloys exhibit similar magnetic properties to the zirconium-nickel alloys.

On the other hand when in preparing these binary alloys zirconium is replaced by other metals of the zirconium group, for instance, by titanium, the resulting titanium-nickel alloys do not exhibit the described magnetic properties.

In preparing my zirconium-nickel magnetic alloys no special effort is made to eliminate the last traces of other elements such as carbon, iron, manganese, tungsten or chromium. Also their presence is not necessary. The zirconium-nickel alloys prepared from chemically pure oxides exhibit all the described magnetic properties. Yet the addition of the third or fourth element to the binary alloys is not detrimental and in some particular cases is even advantageous.

The produced powdered alloys can be formed into bars or other desired forms by any methods well known to the art, such as pressing under a hydraulic press at room or elevated temperature, sintering in the furnace, etc.

The described heat treatment can also be carried out in the commercial vacuum of about 29 inches of mercury or in the stream of commercially pure hydrogen, carbon dioxide or other suitable gas. The temperature of treatment however, should be in these cases higher than when heat treatment is carried out in air in an open crucible.

The modifications of my process of preparing my magnetic alloys and their composition may occur to those skilled in the art but such as fall within the scope of my invention are contemplated by me as forming part of my invention.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. The herein described method of forming magnetic alloys of zirconium and a metal selected from a group consisting of nickel, iron and cobalt, which comprises producing a powdered alloy of the zirconium and selected metal and subjecting the powdered alloy to a temperature of not less than 345° C. and not more than 800° C.

2. The herein described method of forming a magnetic alloy of zirconium and a metal selected from a group consisting of nickel, iron and cobalt, which comprises producing a powdered alloy of the zirconium and selected metal and heating the powdered alloy in an atmosphere containing oxygen until the temperature of the alloy is above 345° C. but below 800° C. and thereafter discontinuing the application of heat.

3. The herein described method of forming a magnetic alloy of zirconium and a metal selected from a group consisting of nickel, iron and cobalt, which comprises producing a powdered alloy of the zirconium and metal and heating the

powdered alloys in a slightly oxidizing atmosphere until the temperature of the alloy is above 345° C. but below 800° C. and thereafter discontinuing the application of heat.

4. The method of making a magnetic alloy of zirconium and a metal selected from a group consisting of nickel, cobalt and iron, which comprises mixing the selected metal in powdered form with powdered zirconium oxide and powdered calcium hydride, heating the mixture until the reduction of the oxide by the calcium hydride is complete and the particles of reduced zirconium and the metal diffuse into one another and thereafter subjecting the powdered alloy to a temperature of at least 345° C. but not exceeding 800° C.

5. The method of making a magnetic alloy of zirconium and a metal selected from a group consisting of nickel, cobalt and iron, which comprises mixing the selected metal in powdered form with powdered zirconium oxide and powdered calcium hydride, heating the mixture until the reduction of the oxide by the calcium hydride is complete and the particles of reduced zirconium and the metal diffuse into one another and thereafter heating the powdered alloy in an atmosphere containing oxygen to a temperature of at least 345° C. but not exceeding 800° C.

6. The method of making a magnetic alloy of zirconium and a metal selected from a group consisting of nickel, cobalt and iron, which comprises mixing the selected metal in powdered form with powdered zirconium oxide and powdered calcium hydride, heating the mixture until the reduction of the oxide by the calcium hydride is complete and the particles of reduced zirconium and the metal diffuse into one another and thereafter heating the powdered alloy in a slightly oxidizing atmosphere to a temperature of at least 345° C. but not exceeding 800° C.

7. A permanent magnet formed of a powdered alloy consisting of zirconium and a metal selected from a group consisting of nickel, iron and cobalt, the zirconium content of the alloy being not less than 5% or more than 40% and said alloy being heat treated at a temperature of substantially 345° C.

8. A permanent magnet formed of a powdered alloy consisting of zirconium and a metal selected from a group consisting of nickel, iron and cobalt, the zirconium content of the alloy being not less than 5% or more than 40% and said alloy being heat treated at a temperature of not less than 345° C. and not more than 800° C.

9. A permanent magnet formed of a powdered alloy consisting of zirconium and any two metals selected from a group consisting of nickel, iron and cobalt, the zirconium content of the alloy being not less than 5% and not more than 40%, and said alloy being heat treated at a temperature of at least 345° C. but not more than 800° C.

10. A permanent magnet in accordance with claim 9 in which nickel in amounts not less than 5% or more than 40% is one of the selected metals, the balance being iron.

11. A permanent magnet in accordance with claim 9 in which cobalt in amounts not less than 5% or more than 30% is one of the selected metals.

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