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PYROPHORIC ALLOYS OF LEAD AND ZIRCONIUM AND SPARKING DEVICES CONTAINING THE SAME

Robert J. Anicetti, Beverly, Mass., assignor to Metal Hydrides Incorporated, Beverly, Mass., a company of Massachusetts

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6 Claims. (Cl. 75—134)

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This invention relates to pyrophoric materials which are suitable for use as the pyrophoric material in industrial appliances where the pyrophoric properties are useful and especially to pyrophoric materials in which lead and zirconium are their essential components.

This application is a continuation-in-part of my application Serial No. 643,960, filed January 28, 1946, now abandoned.

It has been known in the art that cerium possesses marked pyrophoric properties but is too soft for industrial use. However, when alloyed with minor amounts of iron or certain other metals, it has been used extensively in industry as the pyrophoric material for cigarette lighters, etc. The properties of cerium and zirconium differ radically. For example, unlike cerium, zirconium is a very hard metal. It has found many uses in industry in the form of ferro-zirconium. Ferro-zirconium is not suitable for use in industry as a pyrophoric material. However, alloys of cerium and iron have been used extensively for this purpose. Although many other pyrophoric materials have been discovered, so far as I am aware, none of these other materials have possessed characteristics such that it has been able to replace, either wholly or in part, the expensive cerium alloys for use in industry as a pyrophoric material. Alloys of zirconium with various other metals have been produced but prior to my invention alloys of lead and zirconium have not been produced in proportions which exhibit pyrophoric properties.

I have discovered that pyrophoric materials suitable for industrial uses and having lead and zirconium as their essential components can be produced under certain conditions by heating a mixture of the components thereby causing the lead to diffuse into and alloy with the zirconium. If the zirconium used is in the form of large granules it is difficult to produce a satisfactory product. I have obtained best results using zirconium in the form of a powder in which the major portion of the particles are —200 mesh. Preferably, the average particle size of the zirconium should not exceed about 100 mesh. The proportions by weight should be between about 20 to 75 per cent lead and between about 25 to 80 per cent zirconium but my present preferred materials contain more than 30 per cent lead.

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It is extremely surprising and unexpected to discover that zirconium and lead form alloys in proportions which possess marked pyrophoric properties. Some prior highly skilled investigators had failed to produce satisfactory alloys of lead and zirconium in any proportions. Bulletin No. 186 of the Bureau of Mines (1921) states that all attempts to produce an alloy by smelting together zirconium and lead did not give satisfactory results. Hugh S. Cooper, at the meeting of the Electrochemical Society on May 5, 1923, referring to his work with various alloys of zirconium stated "Few alloys with lead were made and these seemed to disintegrate when exposed to air for some time." The United States patent to Petinot No. 1,335,982, dated April 6, 1920, describes the production of alloys of zirconium and lead by the reduction of calcium zirconate with carbon in the presence of molten lead.

While certain alloys of zirconium and lead possess marked pyrophoric properties, the binary alloys of titanium and lead in the same proportions do not possess these properties although zirconium and titanium are known to be substantial equivalents in many instances. Similarly, binary alloys of thorium and lead do not possess these properties.

However, I have discovered that the addition of titanium in an amount up to about 20 per cent by weight to zirconium and lead in the proportions stated provides a pyrophoric alloy having improved properties for many industrial uses. It also lowers the melting point of the zirconium-lead alloy. I have obtained good results using from about 10 to 20 per cent titanium having a particle size comparable with that of the zirconium used. My presently preferred materials contain between about 30 to 60 per cent lead with or without titanium and the balance zirconium. The titanium appears to impart hardness to the zirconium-lead alloy. It also appears to improve the friction characteristics of the alloy when zirconium and lead are present in certain proportions. For certain uses the presence of titanium in the pyrophoric material makes possible the use of a larger proportion of lead thereby reducing the cost of the pyrophoric material. Within certain limits a given amount of titanium may be used to replace a greater amount of zirconium, the difference in these

amounts being replaced by lead. The pyrophoric material of the invention may be diluted with substantial amounts of one or more additional compatible metals or alloys without detrimentally affecting its pyrophoric characteristics. For example, the pyrophoric material of the invention can be diluted with antimony, manganese, tin, etc., or with other known pyrophoric alloys such as alloys of antimony and manganese, which are compatible therewith. I believe I am the first to discover that a pyrophoric material suitable for industrial uses can be produced by combining lead and zirconium in the proportions of 20 to 75 parts by weight of lead and 25 to 80 parts by weight of zirconium with or without other metals and in which the combined amounts of lead and zirconium form the predominating portion of the pyrophoric material.

I have discovered that the pyrophoric material of the invention is compatible with and may be diluted with certain other previously known pyrophoric alloys. Thus, a good pyrophoric material may be produced in accordance with the invention which comprises two groups of metals, one of the groups consisting of lead and zirconium in the proportions hereinbefore specified and forming the predominating portion of the pyrophoric material. Preferably, the metals of the second group and their proportions are selected from those which when separately alloyed are known to produce a pyrophoric material. For example, it is known that (1) zirconium and tin or (2) manganese and antimony when separately alloyed in certain proportions produce pyrophoric materials. In the case of zirconium and tin, the proportion of tin is, preferably, between 20 and 40 parts by weight whereas manganese and antimony may be used in the proportions of 10 to 90 parts by weight of either. The hardness of the final product can be controlled as desired by suitably proportioning the relative amounts of manganese and antimony.

In accordance with the invention, a mixture of small pieces of lead, preferably a powder, and zirconium or zirconium hydride with or without titanium or titanium hydride or other materials is loaded into a crucible and the latter placed in a high frequency electric induction furnace. After adjusting the cover, the furnace is connected with a vacuum system and the air and moisture is evacuated, preferably, while raising the temperature to assure removal of gases. Then an inert gas, such as argon or helium, is admitted and the charge is heated gradually until the charge becomes molten. Preferably, a temperature between 1350° C. and 1600° C. is used but a temperature as low as 1000° C. may be used in some cases depending upon the composition of the charge. After the charge is liquified, heating is stopped and the liquid mass either frozen in the crucible or a detachable plug is removed from the bottom of the crucible and the liquid mass allowed to escape by bottom pouring into molds in the lower part of the furnace and frozen in the molds while maintained in an inert environment.

I have obtained best results using zirconium metal of which 70 per cent was —325 mesh and 30 per cent —100 +325 mesh or zirconium hydride of which 85 per cent was —325 mesh and 15 per cent was —100 +325 mesh. When titanium is a component, I prefer to employ titanium metal or titanium hydride of comparable particle sizes. The zirconium metal and zirconium hydride which I have used was prepared by reducing zirconium oxide by heating with either calcium hydride or magnesium and thereby converting the calcium hydride and magnesium to metal oxides, the latter being removed by leaching. The titanium and titanium hydride was prepared by similarly reducing titanium oxide by heating with calcium hydride. These materials had the following approximate analysis in which the amounts are per cent by weight:

Zr	98.5	96.5	97.0	97.0	----	----
H₂	0.10	0.3	1.9	1.9	3.3	0.2
C	0.10	0.10	0.1	0.05	0.1	0.2
N	0.80	0.06	0.8	0.05	0.8	0.8
Ca	0.30	0.05	0.4	0.05	0.3	0.5
Mg	-----	0.3	0.05	0.3	----	----
Si	-----	----	----	0.30	----	----
Ti	-----	----	----	----	94.5	96.0

Example I

Lead ingots measuring about 1" x 1" x 1½" and having an aggregate weight of 1.1 pounds were placed in a clay-graphite crucible having a detachable plug in its bottom. Zirconium metal powder weighing 0.67 pound and titanium powder weighing 0.23 pound were placed in the crucible and permitted to fall in the spaces between the lead ingots. The particle size of the zirconium powder was about 70 per cent —325 mesh and 30 per cent —100 +325 mesh. The particle size of the titanium powder was comparable to that of the zirconium. The crucible then was placed in a high frequency electric induction furnace and, after adjusting the cover, the furnace was evacuated to remove air and moisture. Argon was then admitted and the charge heated to 1400° C. which required about 30 minutes. The charge was held at that temperature for about 5 minutes and the source of heat was then shut off. Then the plug in the bottom of the crucible was pushed out with a long graphite rod causing the liquid mass in the crucible to flow into a split gang mold positioned in the cooler bottom portion of the furnace. The mold was permitted to cool substantially to normal room temperature and then was removed from the furnace. The solid rods had an analysis of 33.5 per cent zirconium, 11.5 per cent titanium and 55 per cent lead and possessed good sparking characteristics.

The same method of producing the alloy is applicable when the hydrides of the metals are used except that the evolved hydrogen (between about 600° C. and 1200° C.) is removed through a pet cock and is burned as it escapes. It is desirable to maintain a pressure within the furnace slightly above atmospheric pressure and, to assure this, additional inert gas, such as argon or helium, may be admitted if necessary.

Example II

Zr	Ti	Pb	Sb	Mn	Sn
25	15	60	------	------	----
33.5	11.5	55	------	------	----
50	--------	50	------	------	----
30	20	50	------	------	----
60	--------	40	------	------	----
50	10	40	------	------	----
40	20	40	------	------	----
30	--------	70	------	------	----
80	--------	20	------	------	----
40	10	50	------	------	----
45	--------	45	1	9	----
40	--------	40	2	18	----
35	--------	35	3	27	----
30	--------	30	4	36	----
50	--------	20	------	------	30
45	--------	45	------	10	----
49	--------	49	2	------	----

In my copending application, Serial No. 67,089, filed December 23, 1948, now abandoned, I have

claimed a pyrophoric material consisting essentially of zirconium and lead in the proportions described herein and also containing titanium in an amount up to 40 per cent by weight.

I claim:

1. An air stable pyrophoric material in solid massive form which is suitable for industrial appliances, such as cigarette lighters, consisting essentially of lead and zirconium in the proportions of 20 to 75 per cent by weight of lead and 25 to 80 per cent by weight of zirconium and in which the combined amounts of zirconium and lead are at least 60 per cent by weight of said material.

2. An air stable pyrophoric material in solid massive form which is suitable for industrial appliances, such as cigarette lighters, consisting essentially of lead and zirconium in the proportions of 30 to 60 per cent by weight of lead and 25 to 65 per cent by weight of zirconium and in which the combined amounts of zirconium and lead are at least 60 per cent by weight of said material.

3. A pyrophoric material as described by claim 1 in which the lead and zirconium are present in substantially equal amounts.

4. In a sparking device having a sparking element of pyrophoric material, the improvement wherein the sparking element consists essentially of lead and zirconium in the proportions of 20 to 75 per cent of lead and 25 to 80 per cent by weight of zirconium and in which the combined amounts of zirconium and lead are at least 60 per cent by weight of said element.

5. In a sparking device having a sparking element of pyrophoric material, the improvement

wherein the sparking element consists essentially of lead and zirconium in the proportions of 30 to 60 per cent of lead and 25 to 65 per cent by weight of zirconium and in which the combined amounts of zirconium and lead are at least 60 per cent by weight of said element.

6. In a sparking device having a sparking element of pyrophoric material, the improvement wherein the sparking element consists essentially of lead and zirconium in substantially equal amounts and in which the combined amounts of zirconium and lead are at least 60 per cent by weight of said element.

ROBERT J. ANICETTI.

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