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R. A. DIFFENBACH ET AL
METHOD FOR PRODUCING ALUMINUM ALLOY SHAPED PARTICLES AND
ACTIVE RANEY CATALYSTS THEREFROM

3,719,732

Filed Dec. 17, 1970

2 Sheets-Sheet 1

FIG. 1

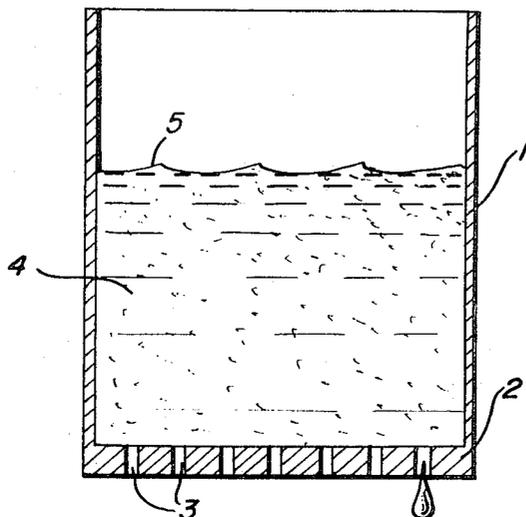
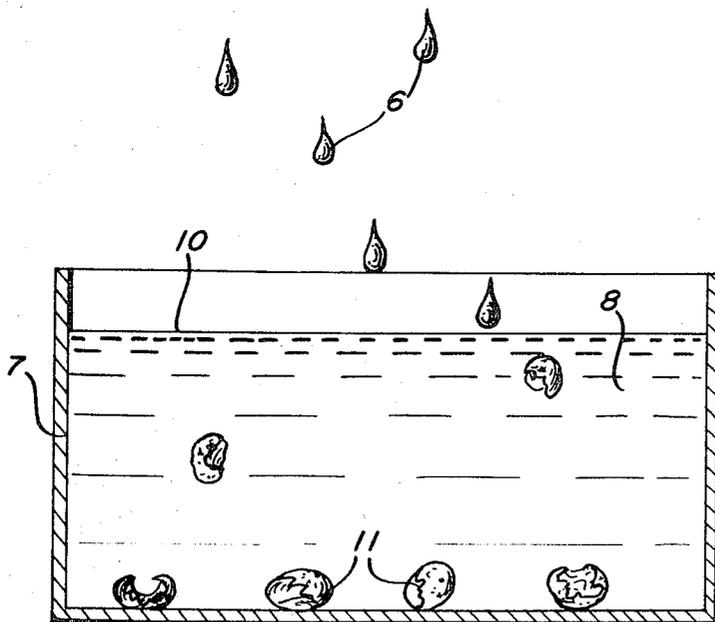
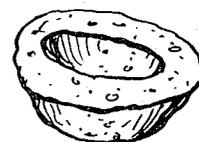


FIG. 4



FIG. 5



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FIG. 2

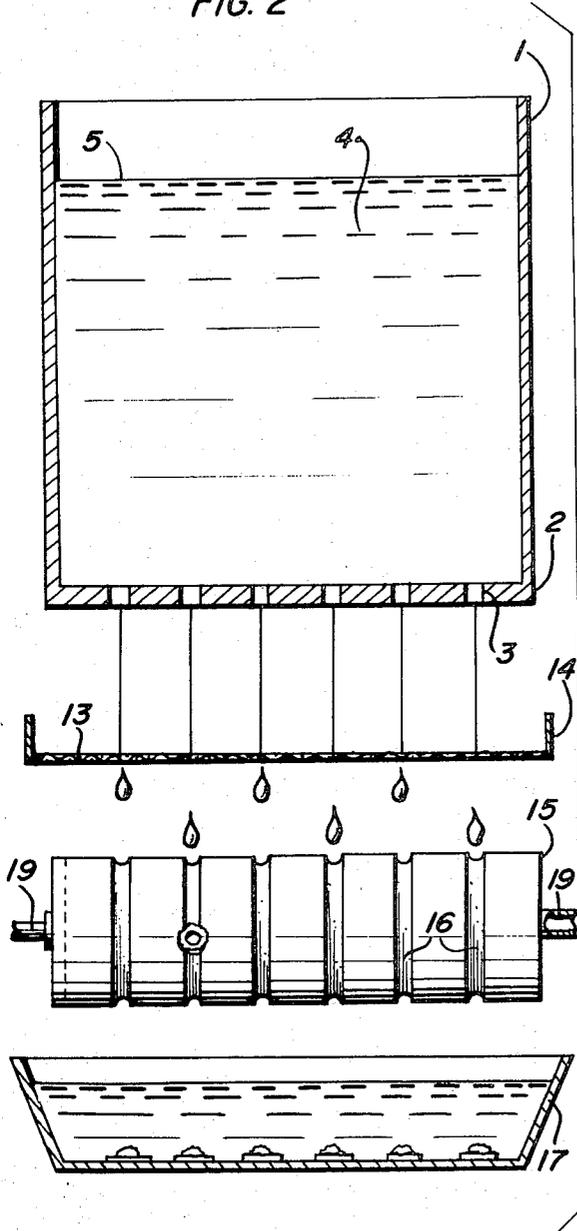
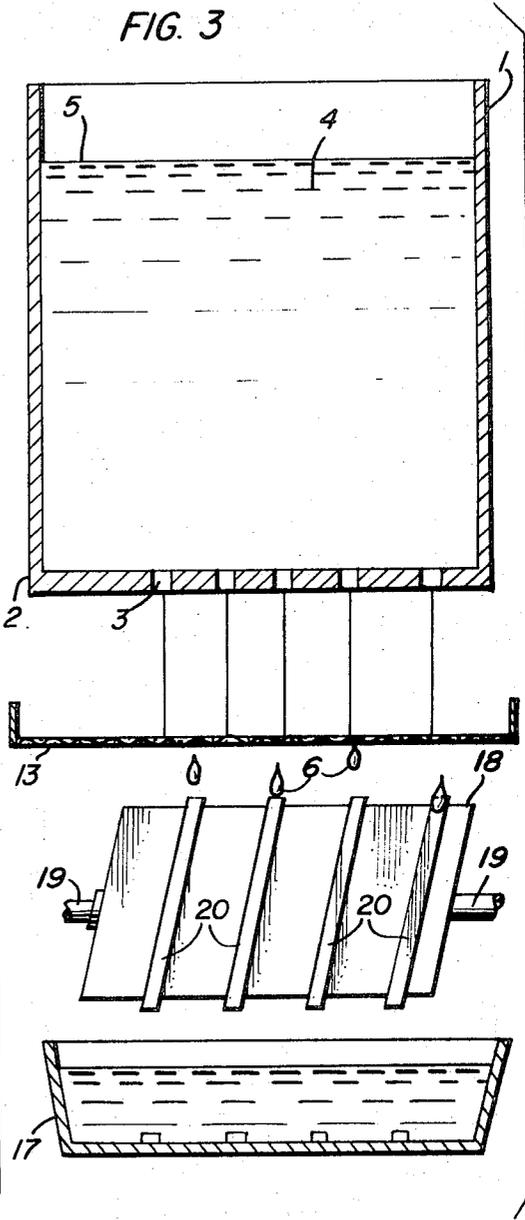


FIG. 3



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23 Claims

ABSTRACT OF THE DISCLOSURE

This invention comprises methods for producing shaped aluminum alloy particles. These particles can range from 1-99 percent aluminum, although for subsequent use as active metal catalysts, the concentration ranges from 50 to 90 percent aluminum and 10 to 50 percent of nickel, cobalt, copper or iron. These shaped particles are produced by a melt drop technique whereby individual drops of alloy are dropped into a water bath or onto a cold flat plate. In one preferred embodiment, a steady stream is segmentally cut by a vibrating wire or screen to produce drops prior to contacting the water bath or plate.

BACKGROUND OF THE INVENTION

This invention relates to the formation of shaped aluminum alloy particles. These particles are then leached to produce fixed bed Raney nickel, cobalt, copper or iron catalysts of high activity.

Various metallic materials have been produced in various shapes. Metals and alloys have been cast, extruded, forged, rolled and otherwise shaped. A further art technique has been shotting to produce essentially solid spherical particles for use as gunshot. Prior art patents in regard to shotting are 2,113,279, and 2,919,471. The first two patents concern producing lead and lead alloy shot using high dropping towers of up to 150 feet. The particles as they fall down the tower acquire a spherical shape and cool sufficiently to maintain their shape. These particles are then quenched in a water tank in the base of the tower. U.S. Pat. 2,919,471 sets out a shotting technique useful for aluminum, and one which does not require the large shot tower. This technique comprises semisolidified aluminum dropping through an orifice to form a teardrop particle which solidifies on its short drop. These techniques, however, do not disclose methods for shaping aluminum alloys in a high surface area condition and alloys which can subsequently be leached to form highly active Raney nickel, cobalt, iron or copper catalysts. This melt drop technique is a new way to form Raney catalysts, and results in catalysts of unexpectedly high activity. It is further a very convenient and comparatively inexpensive method for shaping these highly ductile alloys. Further, it produces a convenient fixed bed catalyst in contrast to the commonly used powdered catalysts which require the addition of a filtering step for removal from a product stream. Therefore, in essence the present process produces aluminum alloys in shapes which, when leached to produce a Raney nickel catalyst, yield a catalyst of unexpectedly increased activity while also having the advantage that catalyst filtration steps are not required. This is a consid-

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erable contribution to the process industries which carry out continuous hydrogenation reactions.

It is an object of this invention to produce aluminum alloy shaped particles by a melt-drop technique.

It is also an object of this invention to produce fixed bed Raney nickel cobalt, copper or iron catalyst from these aluminum alloy shaped particles.

It is further an object to produce highly active Raney nickel, cobalt, copper and iron catalysts of comparatively low nickel, cobalt, copper or iron contents.

It is additionally an object of this invention to provide a fixed bed Raney catalyst not requiring any filtration from a product stream when in process use.

BRIEF SUMMARY OF THE INVENTION

This invention comprises a process for producing shaped aluminum particles having preferred alloy concentration ranges of from 50 to 90 percent aluminum and 10 to 50 percent of either nickel, cobalt, copper or iron or mixtures of these components. These particles are produced from a melt by allowing discrete liquid or semi-liquid particles to fall onto a cooled surface or into a cooled liquid. Subsequent to particle shaping, the aluminum can be leached to yield the shaped Raney nickel, cobalt, copper or iron catalyst particles.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevational assembly view illustrating the apparatus for producing at least partially hollowed particles.

FIG. 2 is an elevational assembly view illustrating the apparatus using a vibrating screen and a grooved rotating drum.

FIG. 3 is an elevational assembly view illustrating the apparatus using a vibrating screen and a cooled plate having raised ribs.

FIGS. 4 and 5 illustrate some of the shapes of the resulting particles.

Broadly, this invention comprises methods of forming aluminum-nickel, aluminum-cobalt, aluminum-copper and aluminum-iron alloys, or mixtures, into shaped particles of comparatively high surface area. This property of high surface area is of concern, since the preferred end use for these shaped particles is in the formation of highly active metal catalysts of the Raney type. As used in this application, a Raney nickel, cobalt, copper or iron catalyst is one in which the nickel, cobalt, copper or iron has been put in a high surface area, highly active condition via the technique of alkali leaching the aluminum content out of the alloy. In the process of this invention, the end Raney catalyst has essentially the same shape as the form of the shaped aluminum alloy. This technique allows for the shaping of the catalytic material in the unactivated form, and then activating for subsequent use while maintaining the predesigned shape.

The forming of these alloys into high surface area shapes has proven to be of a formidable problem. The final activated (Raney) particle does not lend itself to shaping due to its high friability. On any application of shaping forces, it will crush to a powder consistency. It was, therefore, required that the activated catalyst be shaped prior to activation, that is prior to leaching any of the aluminum content. However, these alloys from which the catalyst is formed, and particularly those of

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low nickel, cobalt, copper or iron contents (about 20 percent) are soft and ductile and cannot be shaped by art recognized crushing techniques useful when these metals are in about a 40 percent content. And extrusion techniques require a considerable capital outlay. Confronted with this dilemma, the present invention solved this problem. By this invention, these soft, ductile alloys can be shaped into high surface area active catalyst particles at a low cost for equipment and alloy. This is a significant advance in the art, permitting hydrogenation reactions to be more easily carried out by the use of fixed bed catalytic reactors.

In essence, therefore, and in a particular mode, this invention is directed to a means for producing a fixed bed Raney catalyst material. In order to produce such a material, the shape, size and other features of the catalyst particles would have to be such that they would not become entrained in the product stream, would further have to be crush resistant, while having a high surface area and being highly active. These problems have been solved using the unique methods of this invention, with these techniques further yielding the unexpected result of permitting a lower nickel, cobalt, copper or iron content in the final catalyst if desired, while maintaining activities equivalent to higher active metal contents when the powdered forms are used.

The basic technique most useful for alloy shaping is melt forming, that is, putting the alloy into a shape while in a melt condition with subsequent cooling to ambient temperatures. The shapes of preferred importance are those of FIGS. 4 and 5, although essentially any shape can be utilized. The aim of any shape, however, is to attain a high surface area while maintaining crush resistance and still minimizing pressure drop on the fixed bed reactors. The shapes of this invention are produced by dropping molten alloy into or onto a cooled medium. When dropped onto a cold medium such as a plate, the drop will spread to the form of a disc. If a shaped cold surface is used, the drop will form a shape complementary to the cold surface to which it was contacted. When dropped into a cold medium, which can be water or some surface, the drop deforms to form a novel shape depending on the liquid, the energy of the falling drop, and its melt condition. The preferred particle shape from this technique is an essentially hollow, partially spherical particle. Particles of any of these types have proven to subsequently yield very active Raney catalysts.

The processes of this invention will be elaborated on in greater detail with reference to the various views of the drawings. Also, for simplicity and clarity, the description will be directed to aluminum-nickel alloys and Raney nickel catalysts, although the process is fully operable, and very useful, with aluminum-cobalt, aluminum-copper and aluminum-iron alloys to produce Raney cobalt, Raney copper and Raney iron catalysts respectively. Further, these alloys and catalysts may be mixtures of the nickel, cobalt, iron and/or copper components, and may also contain promotional amounts of chromium or molybdenum. These promotional amounts of chromium and molybdenum are in the range of from about 1 to 15 percent by weight. FIG. 1 illustrates the embodiment of dropping molten Ni-Al particles into a liquid. 1 here is a containing vessel of a material which can withstand temperatures of 650° C. to 1000° C. 2 is the base plate of vessel 1, and 3 the holes in the base plate to allow flow of the alloy melt. 4 is the liquid alloy, and 5 the molten metal level. When in operation, molten drops 6 are formed which fall into vessel 7 which contains cooling liquid 8. As the molten drops strike the liquid surface 10, they are slightly deformed, and in some instances they trap liquid therein which is then usually vaporized out of the hot particles, which vaporizing appears to hollow out the particle. The cooled, shaped particles then fall to the bottom of the vessel.

Of importance in the embodiment of FIG. 1 are several

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factors. The alloy should be maintained in the range of 10° C. to 100° C. above its melting point. The holes 3 should range in size from 1/32 inch to 1/8 inch, and the molten metal head 5 should be about 2 inches to 24 inches. These parameters insure a flow of metal through the base plate 3 to form drops or a stream which can be subsequently cut. The height of the vessel 1 above level 10 of vessel 8 is also of importance. This should range from 3-24 inches so that the drops 6 will not be solidified prior to striking liquid level 10. These parameters are given as definitely operable ranges, with adjustments from these parameters also operable as long as the inventive concept is being followed. That is, the level 5 can be greater than 24 inches if smaller holes 3 are used, or if the temperature is maintained at near the alloy solidification range. Further, if a superheated metal is used, the distance of base plate 3 from surface 10 can be greater without any likelihood of particle solidification. Other variations are also possible, but these are considered to be within the present concept.

The liquid in vessel 7 is preferably water, but can also be an organic solvent, or a mixture of organic solvents and water. The function of this liquid is to aid in forming the particle to a shape. The liquid aids in forming the particle by flattening the molten drop as it strikes the surface, and by the liquid being partially encapsulated by the cooling drop, so that as it cools it vaporizes this encapsulated liquid and causes the formation of at least partially hollow particles. This dual function of cooling and shaping is an essential feature of this invention.

The temperature of the cooling liquid, and the condition of the surface and subsurface can vary widely within the bounds of this process. When water is to be used as the liquid, this may range in temperature from 1° C. to 99° C. The higher the temperature, the greater will be steaming to produce hollowed types of particles. Further, this solution may be mixed under mild to vigorous agitation, turbulently or symmetrically, to further shape and produce uniquely characteristic particles. These are some modifications which can be used to vary the shapes and characteristics of the particles.

FIG. 2 sets out an apparatus and technique similar to that of FIG. 1. The differences are essentially that the molten alloys flows from the baseplate holes 3 in continuous streams, these streams being continuously cut by the vibrating wire grid 13. This grid 13 has a series of wires 14 which may be in the form of a screening grid, but preferably are solely in one direction. This grid is then vibrated at frequencies of from 2 c.p.s. (cycles per second) to 100 c.p.s., depending on the number of wires in the grid. The amplitude of each vibration is such that each stream is cut twice by a wire 14 of the grid during each complete vibration cycle. It is preferred that the molten stream be cut from 24 to 100 times per second. After being cut by the grid, the drops fall on cooled drum 15, and are collected in container 17. The particles which fall onto drum 15 are given a hat shape by grooves 16 in drum 15. On rotation of drum 15, the particles will fall into container 17. Further, container 17 can have an incorporated hopper or other device for further handling of the formed particles.

FIG. 3 illustrates an essentially flat cooling plate 18 onto which the molten droplets fall. 19 are the inlets and outlets for the plate or drum cooling fluids. This embodiment provides a means whereby the slope of the plate causes the particles to fall into the collection container. Raised ribs 20 serve to shape the drops which strike the plate 18. In this embodiment, as in the embodiment of FIG. 2, which uses a rotating drum, the particles may be formed from drops falling from apertures 3 in base plate 2, or by use of the vibrating grid molten stream slicing technique. Also, in each of these embodiments, the energy of the falling particle will determine the degree of spread when the drop hits the plate. Therefore, in a preferred technique, the vessel 1 is maintained at a height of from

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6 inches to 12 inches above the forming and cooling plate or drum.

Also in the embodiment of FIGS. 2 and 3, the surface of the plate or drum may be dimpled, grooved, or otherwise shaped so as to produce a particle of a shape of other than a flat disc. FIG. 4 illustrates a particle formed from a grooved plate or drum. This shape is preferred over a flat disc in fixed bed catalyst use, since there is a decreased tendency to pack tightly, with a resulting loss of effective surface area and increase in pressure drop. The particles of FIG. 5 are those produced by the technique of FIG. 1 of dropping the alloy into a cooled water tank.

In producing the Raney catalyst from the alloy, any of the known techniques can be used. This consists essentially of leaching from 10 to 50 percent of the aluminum content from the particle with sodium hydroxide. The amount of aluminum leached is determined from the volume of hydrogen evolved. 1 mole of aluminum will evolve 1.5 moles of hydrogen gas on leaching. Once activated, the catalyst can be immediately used or stored in various media. The shaped particles comprise an aluminum content of about 50 to 90 percent by weight and a nickel content of about 10 to 50 percent by weight, with the shaped active catalyst particles comprising an aluminum content of about 33 to 91 percent by weight and a nickel content of about 9 to 67 percent by weight. Alloys of from 1 to 99 percent aluminum can be shaped using the instant technique, but due to the friability after leaching of those particles greater than 90 percent aluminum, these are not as useful. Further, the catalyst particle should contain at least 10 percent of the nickel cobalt, copper or iron component.

The following examples are set out to further amplify the present invention.

EXAMPLE I

A molten Ni-Al alloy (20 percent Ni, 80 percent Al) at about 800° C. is poured into a graphite crucible tube which has a series of twelve $\frac{1}{16}$ inch holes in a base plate area. The crucible is maintained at about 800° C., and a head of molten alloy at 10 inches. At this head of molten metal discrete drops form and fall into the water containing vessel. The height of the baseplate to the water surface is 12 inches. A kilogram of particles are produced, the shape being essentially that of FIG. 5.

EXAMPLE II

The procedure of Example I is repeated, but using a Co-Al alloy of 30 percent cobalt and 70 percent aluminum content. The temperature of the molten metal is maintained at 950° C., with the height of the baseplate above the water being 12 inches. Particles of essentially the same shape as FIG. 5 are formed.

EXAMPLE III

In this example, a series of Ni-Al alloy particles are formed using the apparatus of FIG. 1, but with a vibrating screen included to cut the molten alloy streams.

The alloy series of the table are each heated to about 800° C. and poured into a graphite crucible so as to maintain a molten metal head of about 20 inches. A Tyler 3 mesh screen, that is a screen having $\frac{1}{4}$ inch openings, is used as the vibrating grid. The screen vibration rate is 4 c.p.s. This vibrating grid is placed about 3 inches below the grid. On impact with the water, particles shaped essentially as shown in FIG. 5 are formed, these particles having a diameter of from about $\frac{1}{4}$ to $\frac{1}{2}$ inch.

These particles are collected and leached with a 10 percent sodium hydroxide solution to the percent aluminum removal set out in the table. The percent of aluminum removed is determined volumetrically from the hydrogen evolved. These catalysts were then washed with distilled

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water, and tested for activity by the ability to convert acetone to isopropanol at 25° C. and 1 atmosphere hydrogen pressure in a fixed bed reactor. An activity value of 1.00 is given to a commercial granular Raney nickel catalyst from a 42 percent Ni-58 percent Al alloy, from which about 15 percent of the aluminum has been leached.

TABLE

Alloy composition	Percent Al removed	Relative activity
Ni-Al:		
40-60-----	10	1.12
40-60-----	20	1.00
20-80-----	15	1.00
20-80-----	30	1.50
20-80-----	50	0.93
10-90-----	13	0.70
10-90-----	27	1.00
10-90-----	50	0.73
Standard alloy-----	15	1.00

EXAMPLE IV

The procedure of Example I is repeated, but using Cu-Al alloy of 30 percent copper and 70 percent aluminum. The temperature of the molten metal is maintained at 800° C. with the height of the baseplate above the water being 12 inches. Particles of essentially the same shape as FIG. 5 are formed.

These particles are then leached with a 10 percent sodium hydroxide solution to remove 50 percent of the aluminum content. The final product is an active Cu-Al catalyst composition having an aluminum content of 54 percent and a copper content of 46 percent.

EXAMPLE V

The procedure of Example I is repeated, but using an Fe-Al alloy of 80 percent by weight aluminum and 20 percent by weight iron. The temperature of the molten metal is maintained at 950° C. with the height of the baseplate above the water being 10 inches. Particles of essentially the same shape as FIG. 5 are formed.

What is claimed is:

1. A method for producing shaped active catalyst particles comprising:

providing a melt consisting essentially of an alloy selected from the group consisting of aluminum-nickel, aluminum-cobalt, aluminum-iron and aluminum-copper, said melt being maintained in the range of 10° C. to 100° C. above the melting point of said alloy;

forming said melt into discrete droplets; simultaneously shaping and cooling said droplets by dropping said droplets into a vaporizable liquid whereby said droplet partially encapsulates said liquid which on vaporization at least partially hollows said droplets to form hollowed shaped particles; and leaching at least a part of said aluminum content from said shaped particles, whereby shaped active catalyst particles containing at least 10 percent of the non-aluminum component of said alloy are formed.

2. The method as in claim 1 wherein said melt is formed into discrete droplets by passing said melt through orifices capable of forming the melt into said droplets.

3. The method as in claim 1 wherein said melt is formed into a continuous stream with said stream being segmentally cut by vibrating wires to form said droplets.

4. The method of claim 1 wherein said alloy further contains from about 1 to 15 percent of a promotional material selected from the group consisting of chromium and molybdenum.

5. The method of claim 1 wherein said vaporizable liquid is water.

6. The method of claim 1 wherein said shaped particles are subjected to a leaching with alkali hydroxide

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to remove at least part of said aluminum content and produce said shaped active catalyst particles.

7. The method of claim 6 wherein said shaped particles are shaped aluminum-cobalt alloy particles containing about 50 to 90 percent aluminum and 10 to 50 percent cobalt. 5

8. The method of claim 6 wherein said shaped particles are shaped aluminum-copper alloy particles containing about 50 to 90 percent aluminum and 10 to 50 percent copper. 10

9. The method of claim 6 wherein said shaped particles are shaped aluminum-iron alloy particles containing about 50 to 90 percent aluminum and 10 to 50 percent iron.

10. The method of claim 6 wherein said shaped particles comprise an aluminum content of about 50 to 90 percent by weight and a nickel content of about 10 to 50 percent by weight, with said shaped active catalyst particles comprising an aluminum content of about 33 to 91 percent by weight and a nickel content of about 9 to 67 percent by weight. 15 20

11. The method of claim 10 wherein said shaped active catalyst particles are essentially hollow, partially spherical particles.

12. A method for producing shaped active catalyst particles comprising: 25

providing a melt consisting essentially of an alloy selected from the group consisting of aluminum-nickel, aluminum-cobalt, aluminum-iron and aluminum-copper, said melt being maintained in the range of 10° C. to 100° C. above the melting point of said alloy; 30

forming said melt into discrete droplets;

simultaneously shaping and cooling said droplets by dropping said droplets onto a cooled metal surface to form disc like shaped particles; and 35

leaching at least a part of said aluminum content from said shaped particles, whereby shaped active catalyst particles containing at least 10 percent of the non-aluminum component of said alloy are formed. 40

13. The method as in claim 12 wherein said melt is formed into discrete droplets by passing said melt through orifices capable of forming the melt into said droplets.

14. The method as in claim 12 wherein said melt is formed into a continuous stream with said stream being segmentally cut by vibrating wires to form said droplets. 45

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15. The method of claim 12 wherein said alloy further contains from about 1 to 15 percent of a promotional material selected from the group consisting of chromium and molybdenum.

16. The method of claim 12 wherein said cooled metal surface is a cooled plate having raised ribs.

17. The method of claim 12 wherein said cooled metal surface is a cooled grooved metal drum.

18. The method of claim 12 wherein said shaped particles are subjected to a leaching with alkali hydroxide to remove at least part of said aluminum content and produce said shaped active catalyst particles.

19. The method of claim 18 wherein said shaped active catalyst particles have a disc like shape.

20. The method of claim 18 wherein said shaped particles are shaped aluminum-cobalt alloy particles containing about 10 to 90 percent aluminum and 10 to 50 percent cobalt.

21. The method of claim 18 wherein said shaped particles are shaped aluminum-copper alloy particles containing about 10 to 50 percent aluminum and 10 to 50 percent copper.

22. The method of claim 18 wherein said shaped particles are shaped aluminum-iron alloy particles containing about 10 to 90 percent aluminum and 10 to 50 percent iron.

23. The method of claim 18 wherein said shaped particles comprise an aluminum content of about 50 to 90 percent by weight and a nickel content of about 10 to 50 percent by weight, with said shaped active catalyst particles comprising an aluminum content of about 33 to 91 percent by weight and a nickel content of about 9 to 67 percent by weight.

References Cited

UNITED STATES PATENTS

2,268,888	1/1942	Mericola	264—13
3,579,721	5/1971	Kaltenbach	264—13
3,347,798	10/1967	Baer et al.	264—13
2,872,361	2/1959	Siefen	156—2

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U.S. Cl. X.R.

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