

UNITED STATES PATENT OFFICE.

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METALLURGICAL METHOD.

1,088,909.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that we, HANS KUZEL, a subject of the Emperor of Germany, residing at Baden, near Vienna, Empire of Austria-Hungary, and EDGAR WEDEKIND, a subject of the Emperor of Germany, residing at Strassburg, Germany, have invented certain new and useful Improvements in Metallurgical Methods, of which the following is a specification.

Our invention relates to a method of obtaining metals from their compounds and more particularly from their oxids and also comprises a metal now for the first time produced in a condition of substantial purity.

We have found this method particularly applicable to the production of pure zirconium, thorium, titanium, cerium, vanadium, uranium, chromium, tungsten and molybdenum from the oxids and especially advantageous for the production of zirconium, thorium, titanium, vanadium and cerium. It has heretofore not been found possible to reduce the oxids of these metals to pure metal directly (as by means of light metals, such as magnesium, or by carbon), although they occur in nature in a condition of comparative purity and are in some cases relatively inexpensive. The processes heretofore used for the production of these metals have for the greater part been based upon the action of alkaline metals, principally sodium on halogen compounds or double halogen compounds of the metals to be produced. The results of these processes have been very unsatisfactory, and their product has been of a low degree of purity. These methods are particularly disadvantageous when employed on a large scale, the alkaline metals readily distilling off at the high reaction temperatures necessary to the reaction; or, if the reaction is carried out in closed apparatus, giving rise to a dangerously high pressure. By the use of our invention, these metals may be readily and directly produced from their oxids in a condition of purity.

For the purpose of effecting reduction of these oxids, we employ metallic calcium. We find that metallic calcium reacts with the oxids of the refractory metals referred to very energetically. The calcium practically does not distil at all at the reaction

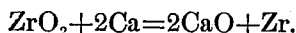
temperatures; and at such relatively high temperatures (for example, 800° C. or more) becomes more active and shows a greater affinity for chlorine, oxygen, etc., and seizes upon them even more eagerly than sodium, for example. By our method, the refractory metals referred to are obtained in an extremely finely divided and amorphous state, even when the reaction goes on slowly. This makes possible a very thorough cleansing of the product and facilitates its transformation into the colloidal state.

To enable those skilled in the art to practise our invention to the best advantage, we will describe in detail its application to the production of pure zirconium and we will then indicate what considerations must be borne in mind when it is used for the production of other metals.

In a suitable mixing or grinding device, we make an intimate mixture of 50 grams zirconium oxid and 72 grams of metallic calcium, the calcium for this purpose being preferably in the form of the finest possible chips or in the still finer form of metallic sponge or powder. This amount of calcium is considerably in excess of that which enters into reaction with the zirconium oxid; but the excess insures complete reduction of the oxid and is easily removed. The mixture thus obtained is placed as quickly as possible in a vessel suitable for the reaction, the oxygen and nitrogen of the air being preferably excluded during the transfer. For this purpose may be employed a cylindrical crucible or bomb which may be closed air tight by a cover furnished with a metal cock; or, if preferred, a spherical apparatus may be used. The apparatus used should be made of the most refractory metals that can conveniently be employed, such metals as platinum, steel, and the like, being suitable. After it has been charged and closed, the apparatus is exhausted with a vacuum pump to an absolute pressure of from 0.5 to 0.1 mm. of mercury. The cock is then closed and the bottom of the apparatus heated by means of a strong flame until the reaction between the zirconium oxid and calcium begins. The beginning of this reaction may usually be easily recognized by the glowing of parts of the apparatus which are not in contact with the flame. As soon as this

glowing begins, the external heating is stopped. The finer the powder of the mixture, the more lively is the reaction, and the more readily does it occur. Under some circumstances, it may be caused by electric ignition, as, for example, by the use of a platinum wire heated to incandescence by current or by a high voltage spark. Spontaneous ignition has repeatedly been observed, even when the mixture was in contact with the air.

The reaction appears to take place according to the equation



The reaction being finished, the closed apparatus is first cooled in the air, then with water, and finally with ice-water. It is then opened, preferably in an environment from which nitrogen and oxygen are excluded, and the slightly coherent contents are treated with water in an acid-proof vessel until the excess of calcium is eliminated, and then with suitable dilute acids, for example, acetic or muriatic acid, in order to bring all the calcium into solution. The insoluble portions of the reaction product are then ground, collected in a suction filter, and washed with water until a reaction indicating the presence of calcium can no longer be obtained. The water is in turn driven off by alcohol and ether, and the powder is thoroughly dried, preferably in a vacuum. The drying may be rendered complete by heating the product for several hours in a high vacuum at about .1 mm. of mercury pressure to a relatively high temperature of, for example, 300 or 400 degrees C. If the product is also to be completely deprived of gases, it must be further heated to about 1000° C. and maintained at this temperature until the vacuum gage shows a constant pressure. If the heating is carried above this temperature, the metal powder sinters or welds itself into granules and small compact lumps. The metallic zirconium thus obtained shows a content of 96 per cent. free zirconium, the remainder consisting of zirconium oxid, about 3 per cent. of iron from the apparatus in which the reaction was carried on, and traces of zirconium nitrid. Using the method of this invention, it has even been found possible to obtain a product containing as much as 97 to 98 per cent. zirconium. If access of oxygen and nitrogen to the metal is prevented throughout, a metal free from oxid or nitrid is obtained. The metal has a brilliant metallic appearance, has a specific gravity of about 6.2, and a normal atomic heat of about 6.4. It is a good conductor of electricity and is very resistant to chemical re-agents,—with the exception of hydrofluoric acid. All these properties differ substantially from those hitherto ascribed to zirconium. This is owing to the fact that

the alleged zirconium hitherto produced contained very high percentages of impurities, as for example, oxid and carbid.

If the treatment of the mass resulting from the reaction in the bomb with acids is often repeated, it is very easy to obtain the metal in colloidal form, so that the process described is exceedingly well adapted for the manufacture of articles of the refractory metals named, such as filaments, by colloidal methods.

The oxids of titanium and thorium can be reduced with calcium according to this process in the same manner as zirconium oxid. It is to be noted that the reduction of products are less stable against treatment with water and acids. With the metals which are less susceptible to the components of the atmosphere, such as chromium, tungsten, and molybdenum, the reaction may be carried on in apparatus which has not been evacuated, tightly closed crucibles being quite satisfactory.

The new method offers considerable advantages over old methods in the case of these metals for various reasons, such as the ready reaction of calcium with water, the easy solubility of calcium and of its oxid and hydroxid in water and in dilute acids, and the facility with which salts may be washed out of the product by water as well as alcohol.

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

1. The method of producing refractory metals which consists in reducing oxygen compounds of such metals with metallic calcium in an inert environment.
2. The method of producing pure refractory metals which consists in reducing metallic oxids of such metals with calcium in a vacuum.
3. The method of producing metal which consists in heating an intimate mixture of a compound of the metal to be reduced and metallic calcium to cause reaction, and excluding oxygen and nitrogen from the reaction zone during the process of the reaction.
4. The method of producing substantially pure zirconium which consists in reducing zirconium oxid with calcium in an inert environment.
5. The method of producing pure zirconium which consists in reducing zirconium oxid with calcium and treating the reaction product to eliminate all substances except the metal, the reactions and treatment being effected in the absence of nitrogen and oxygen.
6. The method which consists in forming a mixture of zirconium oxid and finely divided calcium, inclosing this mixture in a vessel adapted to exclude oxygen and nitrogen, applying heat to the vessel to cause

reaction, cooling the same, and treating the products of reaction to eliminate all except zirconium.

5 7. The method of producing metal which consists in heating a metallic compound to be reduced in contact with calcium in a substantial vacuum.

In witness whereof, I, HANS KUZEL, have hereunto set my hand this 10th day of May, 10. 1910, and I, EDGAR WEDEKIND, have here-

unto set my hand this 17th day of May, 1910.

DR. HANS KUZEL.
PROF. DR. E. WEDEKIND.

Witnesses to Kuzel:

ANDREUS HIPCK,
AUGUST FUGGER.

Witnesses to Wedekind:

FRITZ WEDEKIND,
J. M. BOWCOCK.