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METALLURGICAL PROCESS FOR THE PRODUCTION OF POLYVALENT METALS AND THE COATING OF ARTICLES THEREWITH

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This invention is for a metallurgical process for the production of titanium, zirconium and other di, tri and quadravalent metals, and especially those which, like titanium and zirconium, are not economically reducible from their natural oxide state by usual smelting or reducing furnace procedures.

Titanium, for example, is abundant in various compounds over the earth's surface, and is in wide demand. It is, however, expensive to produce because of the difficulty in reducing it from the compounds in which it occurs. Its oxides are highly refractory, and at elevated temperature it reacts with oxygen, nitrogen, hydrogen and carbon dioxide, so that normal metallurgical reducing operations are entirely unsuitable and inoperative, on a practical scale at least, for its production.

Zirconium is likewise difficult to produce, as are many of the polyvalent metals, other than the more familiar commercial ones.

An object of the present invention is to provide a new and more economical process for the production of these metals, and a further object is to provide a method for the coating of articles with a surface film or layer of these metals.

It is well known that organic compounds of titanium, zirconium and other polyvalent metals may be prepared, including esters. Referring for example to titanium, esters have been prepared from both the lower and higher alcohols. Important among these, for my purpose, is butyl titanate, which has more stability than ethyl and propyl esters, although these may also be used. Likewise, esters of alcohols higher than butanol could be used.

These esters are relatively inexpensive to produce, and have heretofore found use in varnishes and coatings. TiO_2, for example, may be reacted with hydrochloric acid to produce titanium tetrachloride, from which orthotitanic acid is secured by hydrolysis, this acid then being reacted with the alcohol, all of which procedures are well known and form no part of my invention.

If butyl titanate is heated, it decomposes, leaving TiO_2 as a residue. I have discovered, however, that if a relatively small amount of metallic iodine be mixed with the butyl titanate it may then be heated in an inert atmosphere, first to release the butanol and subsequently to sublimate the iodine, leaving the titanium sponge as a residue. It would be expected that iodine would be required in an equivalent mol ratio to form TiI_4 as an intermediate compound, but this is not the case and the ratio does not appear to be critical. I have discovered that as little as 10% of the mol equivalent is satisfactory. The iodine apparently functions as a catalyst or stabilizer rather than as a reagent.

As indicated above, butyl titanate is a desirable ester, rather than the esters of either the higher or lower alcohols, because of the stability of this compound, and the fact that butanol is commercially available and less expensive than the esters of the higher alcohols.

In the practice of my invention, the mixture of butyl

titanate and iodine is heated in an atmosphere of water vapor. At a temperature of 300° to 350° F., the alcohol or other organic components of the compound are removed, along with some of the iodine. Heating is thereafter continued in an inert atmosphere to a temperature above 711° F., this being the boiling point of titanium tetra iodide, and in the region of 800° to 850° F., all of the iodine will be removed by sublimation. The alcohol and iodine removed in this manner may be condensed and recovered for reuse, so that the reagents, except for small amounts, are not lost. The cost of their recovery is, of course, low, and the required equipment is known. Helium or argon may be used to provide an inert atmosphere above 350 F. or the operation may be carried out in a vacuum.

As an alternative procedure, some water, as for example about 2% by weight, may be added to the btuyl-iodine mix, which, upon agitation, causes a polymerization and thickening of the mass. This is not necessary, but such polymerized material may be thickly spread over an object, such for example as a ferrous body or sheet. The coated object is then heated as above to remove butanol and iodine, after which the temperature is raised to 2000° to 2200 F. or more to fuse the resulting metal residue to the surface of the object, this all being done in an inert atmosphere or environment. The polymer, because of its better covering properties, will coat the surface more evenly and be less likely to run or flow off the coated sheet. The polymer also may be reduced to metal sponge the same as the unpolymerized mixture in the same manner.

The same procedures may be followed using the zirconium ester to produce zirconium sponge and zirconium coated objects. Silicon and other polyvalent metals may also be produced by this process, especially metals of the class which are too reactive for reduction by furnace smelting processes.

Bromine may be used in place of iodine, but with no apparent advantage, and greater difficulty is involved both in recovery of the bromine and from corrosion of equipment.

My invention, as herein disclosed, is much faster and more economical than present methods and lends itself to a continuous process.

While I have disclosed the oxide as the starting material, these being the most prevalent natural compounds of titanium and zirconium, other compounds may be used and converted to a chloride, as is now generally known to the art.

I claim:

1. The metallurgical method which comprises mix-iodine into the ester of a polyvalent metal and thereafter heating the mix to break down and remove the organic constituents of the compound and sublimate the iodine, leaving the sponge metal of said polyvalent metal as a residue.

2. The metallurgical method as defined in claim 1 in which the esterified polyvalent metal is one of the group consisting of titanium and zirconium.

3. The metallurgical method as defined in claim 1 in which the esterified metal is one of the group consisting of titanium, zirconium and silicon.

4. The metallurgical method as defined in claim 1 in which the esterified metal is titanium.

5. The metallurgical method as defined in claim 1 in which the esterified metal is zirconium.

6. The metallurgical method as defined in claim 1 in which the esterified metal is silicon.

7. The metallurgical method as defined in claim 1 in which the iodine is added in an amount substantially less than the theoretical mol ratio to convert the metal of the esterified compound to a tetra iodide of the metal.

8. The metallurgical method as defined in claim 1 in which the heating is effected in an environment inert to the metal being reduced.

9. The metallurgical method as defined in claim 1 in which about 2% by weight of water is added to the ester-iodine mix to polymerize the same.

10. The metallurgical method defined in claim 1 in which the ester is butyl-titanate.

11. The metallurgical method as defined in claim 1 in which the esterified metal is one of the group which reacts with oxygen and hydrogen at elevated temperatures and is not amenable to reduction from its oxide by reducing gases or smelting.

12. The metallurgical method as defined in claim 1 in which the ester-iodine mix is applied to the surface of an object and the heating is continued after sublimation of the iodine to a temperature where the residue metal is fused to the surface of the object.

13. The metallurgical method as defined in claim 3 in which the ester-iodine mix is applied to the surface of an object and the heating is continued after sublimation of the iodine to a temperature where the residue metal is fused to the surface of the object.

14. The method defined in claim 1 in which the organic constituents and iodine are recovered for reuse.

No references cited.