ZIRCONIUM ALLOY POWDERS FOR MANUFACTURE
OF 3D PRINTED ARTICLES USED IN NUCLEAR POWER INDUSTRY

T. Ianko*, S. Panov*, O. Sushchyn’sky*, M. Pylypenko, O. Dmytrenko
*Public Joint Stock Company “Titanium Institute”, Zaporizhzhya, Ukraine
E-mail: titanlab3@rambler.ru;
National Science Center “Kharkov Institute of Physics and Technology”, Kharkov, Ukraine

Main methods of zirconium alloy powder synthesis have been reviewed. Powder applications for additive manufacturing were analyzed. Advantages and drawbacks of zirconium powder production and usage have been shown. Hydrogenation/dehydrogenation method was offered for zirconium powder production.

INTRODUCTION

Power consumption around the world grows a lot faster compared to its production. Usage of new prospective technologies in this field is envisaged not earlier than from 2030 due to the obvious technical complications. Lack of fossil energy resources is more and more growing problem. Possibilities of new hydro-power plant constructions are also very limited. Politically declared fighting against so called “greenhouse effect” considerably restricts oil product, gas and coal incineration at thermal power plants.

Cautiously evaluated power consumption at the planet will be doubled in the middle of XXI century. This will beacon sequence of world economy development, population growth and other geopolitical and economical factors. Thus more electric power will be needed. It will also include power consumption for hydrogen (the most prospective fuel) manufacture and fresh water supply.

Considering the above it is feasible to conclude that nuclear power industry still holds the leading position in the world and it will not be changed in the nearest time.

Nuclear power is the most important branch of the global electric power. Its notable contribution to the latter started a few decades ago. Production cost of nuclear power makes it highly competitive with that produced at other types of power plants. The obvious advantage of NPP: lack of atmospheric pollution by aerosols and “greenhouse” gases.

At present world nuclear power includes approximately 500 nuclear reactors in total. They are located in 31 countries (Fig. 1). Whole production capacity: 370 GW [1].

![Fig. 1. Percentage of operational nuclear reactors by country](image)

Even the most moderate forecasts of International Atomic Energy Agency (IAEA) show that up to 600 new power units will be constructed before 2030 in the world. According to World Nuclear Association (WNA) evaluation full power capacity of all power units will reach at least 1100 GW in 2060. This number could be increased to 3500 GW considering current nuclear power consumption growth.

Augmentations of power capacities will de finitely yield increasing in demand of nuclear fuel and its components.

Zirconium alloys are the main construction material for fuel element tubing used in nuclear reactors. Hafnium-free zirconium is particularly well-suited for these applications primarily because of low thermal neutron absorption, and low susceptibility to radiation. Nuclear fuel cladding and reactor core structural components are the principal uses for zirconium metal. This is the only material with unique physical and nuclear properties for effective fission of uranium. Replacement of zirconium by other metals is technically and economically impossible.

Objectives of nuclear power plant development: minimization of production cost due to high reliability of construction elements; effective work of main and auxiliary equipment. Safe work of operation units requires structural materials with definite mechanical, exploitation, and corrosion resistance properties. The parts of reactor hot zones must have high corrosion, radiation, heat resistance and also possess dimensional stability.
**ADDITIVE TECHNOLOGIES**

High demand in zirconium alloys [2–4] requests the following from metal manufacturers: decreasing of production cost, development of new technologies, using of resource-saving methods. Required level of mechanical properties combined with low production cost for zirconium alloys demands not only manufacturing improvements but also correct applications of the materials.

At present high grade zirconium sponge reduced by magnesium is the major raw material for zirconium alloy manufacture. This sponge contains small concentration of impurities. However, it does not have any alloying elements. Thus required level of mechanical and corrosion resistant properties cannot be achieved even for simple and widely used metallurgical zirconium alloys. Production experience for the alloys has demonstrated that usage of zirconium sponge with low content of impurities demands additional complex alloying.

Majority of known alloying methods for zirconium includes technological step of adding alloying elements from master alloys into zirconium batch [4]. This process stage along with technological complications does not yield full and homogeneous distribution of alloying elements in semi-products. Thus it causes increasing of a process step number for obtaining required zirconium semi-product [5]. In general more than 50 technological steps (in some cases) are necessary for manufacture of the final structural article.

Considering the above it is feasible to say that the main objective is development of new technologies. The latter must include cost reduction, minimization of a production step number, and environmental protection. One of the most perspective routes is Additive Fabrication or Additive Manufacturing (AM-technology). This method forms final article shape using layer by layer material addition and its melting in accordance with a computer digital model [6, 7].

The process is developed as step by step by bonding of the previous layer to the next one using 3 dimensional computer model yielding the final article [8, 9].

The main technological advantages of the technology are as follows:

1. Production of the articles with complicated shapes.
2. The production of the article requires three a dimensional model only.
3. Article geometry can be changed rapidly and efficiently.
4. High coefficient of raw material usage.

All existing additive technologies can be divided according to material feed in two types:

1. Direct deposition. Here the material is fed into the definite position where heat power is applied and the process of the article formation is conducted. Disadvantage: usage of special holders which prevent article deformation during its construction.
2. Bed deposition. In this method the material layer is initially formed by, for example, sprinkling of definite powder amount on the work platform. Then the powder is leveled by roller (“knife”) forming even layer of the material with definite thickness. Finally, the powder is selectively melted by laser or electron beam in accordance with three dimensional model cross-sections [10].

Different additive machines use various powder fractions. The latter are divided according to the size range into the following groups: nano-particles (diameter less than 0.1 μm), ultra-fine (0.1...1.0 μm), high-fine (1.0...10 μm), small (10...40 μm), medium (40...250 μm), large (250...1000 μm) [6, 9]. Usage of definite powder size often depends on heat energy feed to the powder layer. In a case of laser powder melting (SLM-Solution, EOS, Concept Laser and other equipment manufacturers) the material with size range from 10 to 60 μm is used. When electron beam is a heat power source the powders have size from 50 to 120 μm (ARCAM EBM). Here smaller metal particles will be dispersed by electron beam.

However the main problem for wide usage of all additive technology methods is absence of available raw materials.

Majority of produced zirconium (more than 70%) is used as structural material in nuclear power plants. The rest is utilised in chemical industry and metallurgy (Fig. 2) [11].

Insignificant amount of zirconium powder is used for pyrotechnics and micro-alloying. Also the powders are utilized as surface coatings and getters for purification of vacuum systems [12].

![Fig. 2. Zirconium alloy usage in different industries](image)

**METHODS OF ZIRCONIUM ALLOY POWDER SYNTHESIS**

Zirconium powders can be produced by the following methods:

- metal-thermal (magnesium, sodium, and calcium reduction);
- electrochemical (electrolysis);
- atomisation (gas or plasma spraying, plasma rotating electrode process – PREP);
- Hydrogenation/de-hydrogenation (HDH).

In metal-thermal processes zirconium compounds are reduced by more chemically active component to the powder. In a case of sodium-thermal production zirconium tetrachloride (ZrCl₄) is reduced by sodium. When calcium-thermal technology is employed zirconium fluorides are reduced by calcium hydride (CaH₂) or zirconium oxide (ZrO₂) is reduced directly by metallic calcium. Magnesium-thermal reduction of zirconium powders is still at the laboratory scale development. Zirconium powders produced according to the described methods have non-spherical shape,
uneven fractional composition (with the main content of large particles \(>100\mu m\)), and porous structure. Other disadvantages: difficulty in production of alloyed powders, insufficient quality for the level of impurities. Electrolysis yields zirconium powders with the required quality (low concentration of solid impurities). Alloyed powders can also be manufactured. However the powders have non-spherical shape and crystal structure (Fig. 3). They also have redundant content of gases and require additional treatment.

Fig. 3. External view of electrolytic zirconium: typical cathodic precipitate of electrolytic zirconium [13] (a); electrolytic zirconium powder [14] (b)

KCl, NaCl, NaF,

Salt preparation, drying, calcination

Electrolyte melting

Electrolysis

Used electrolyte

Hydrometallurgical treatment

Solutions

K\(_2\)ZrF\(_6\) production

Cathode product

Vacuum thermal treatment

Zirconium powder

Salt condensate

Fig. 4. Technological flow sheet for zirconium manufacture from its complex fluorides [15]
Technological flow sheet (Fig. 4) includes preparation of salt melt or solution followed by electrolysis and vacuum treatment of cathode product. Raw materials: individual or mixed chlorine-fluorine salt systems based on zirconium.

The main shortcomings of the described method are: complicated equipment, multi-step process, large equipment service and power costs. Also there is industrial safety problems bound to chlorine and fluorine emissions.

The most wide spread method for powder manufacture of metals with high melting points is atomisation. Advantage of this technology is feasibility of production spherical powders with insignificant porosity. Here each metal particle is a micro-ingot with required chemical composition. Chemically active metals can be processed under inert gas (gas atomisation) or vacuum atmosphere (Fig. 5).

![Fig. 5. Typical schemes for metal powder production using gas (a) [16] and plasma (b) [17] atomization](image)

Powder particles are cooling down when moving from the top to the bottom part of the work chamber. Finally they are sprinkled and collected at the bottom of the unit. Then powders are divided into fraction in vortex cyclones.

In the plasma atomisation method one or a few plasmatrons are used for heating of local zone. Metal wire of definite composition passes over this area [17] yielding metal powder. This method produces the powder with size range from 1 to 200 μm almost ideally spherical with minimum porosity (Fig. 6).

![Fig. 6. External view of zirconium alloy powder synthesized by atomization methods: gas atomisation [18] (a, b); plasma atomization [19] (c)](image)

Another method for manufacture of chemically active metal powders is plasma rotating electrode process (PREP). In this case preliminary prepared electrode with certain chemical composition is fixed in the spindle and rotates with definite angular speed. The electrode is melted by high temperature plasma discharge and sprayed into the work chamber (Fig. 7).

Main drawbacks of the above atomisation methods are: complicated technologies, sufficiently low final product actual yields, high cost of raw materials (zirconium alloys), usage of semi-products for metal spraying (wire, electrode, ingot, etc.).

![Fig. 7. Synthesis of metal powders by PREP method [20]](image)
At present the major industrial method for zirconium powder manufacture is HDH technology. However this technique is mainly used for pure irregularly shaped zirconium powders (Fig. 8).

![Fig. 8. External view of zirconium powders produced by HDH method [21]](image)

The process is based on hydrogen ability of embrittlement metallic zirconium. At first zirconium hydride is synthesised (reaction 1) then hydrogen is released during ZrH\textsubscript{2} grinding (process 2):

\[
\begin{align*}
\text{Zr} + \text{H}_2 &\rightarrow \text{ZrH}_2, \\
\text{ZrH}_2 &\rightarrow \text{Zr} + \text{H}_2.
\end{align*}
\]

This technology allows production of zirconium and its alloy powders with low impurity contents and practically of any fractional compositions. It is also possible to synthesize globular powders using plasma spheroidizing [22].

Alloyed zirconium powders can be manufactured from available zirconium sponge blocks alloyed during their reduction process [23]. In addition modern additive technologies allow usage both spherical and non-spherical powders of metals with high melting points as raw materials [24]. Technology of zirconium alloy manufacture using waste from the conventional production methods looks promising as well. This method envisages waste division by chemical composition, metal surface cleaning from various contaminants and oxides, hydrogenation, grinding, and degassing. This scheme is the cheapest one for the powder production.

CONCLUSION

Thus, according to authors’ opinion, the most prospective method for zirconium alloy powder manufacture is a hydrogen embrittlement method with alloyed zirconium sponge as raw material.

Advantages:
- possibility of powder manufacture with wide frame of size ranges;
- low content of impurities;
- short and relatively simple production cycle which includes: zirconium sponge reduction, vacuum-thermal treatment of a sponge block, hydrogenation, grinding, degassing, and screening of final powders;
- obtaining of both spherical and non-spherical powders;
- powder synthesis from industrial waste.

Considering powder production of different shape and sizes it is feasible to conclude that electron beam melting in 3D printing has the brightest future. Usage of electron beam as a heat source allows employing of deep vacuum. Here the particles with size range from 50 to 150 μm will be melted to sufficiently large depth. Also high power multi-beam systems can be employed. Final articles can be treated by electron beam instead of their machining.

REFERENCES

8. E.V. Balaka. Main influence factors for article shaping process in technologies of layer by layer growing (rapid photocopying) // High technologies in machine building. 2011, N 1, p. 29-36.

Article received 22.11.2017

ПОРОШКИ ИЗ ЦИРКОНИЕВОГО СПЛАВА ДЛЯ ПРОИЗВОДСТВА 3D-ПЕЧАТИ ИЗДЕЛИЙ, ИСПОЛЬЗУЕМЫХ В АТОМНОЙ ЭНЕРГЕТИКЕ
Т. Янко, С. Панов, А. Сущинский, Н. Пилипенко, А. Дмитренко

Рассмотрены основные способы получения порошков циркониевых сплавов. Проанализированы применения порошков в аддитивных производствах. Показаны преимущества и недостатки способов получения и применения порошков циркония. Для производства порошков циркония предложен метод гидрирования/дегидрирования.

ПОРОШКИ З ЦИРКОНИЕВОГО СПЛАВУ ДЛЯ ВИРОБНИЦТВА 3D-ДРУКУ ВИРОБІВ, ЩО ВИКОРИСТОВУЮТЬСЯ В АТОМНІЙ ЕНЕРГЕТИЦІ
Т. Янко, С. Панов, О. Сущинський, М. Пилипенко, О. Дмитренко

Розглянуто основні способи отримання порошків цирконієвих сплавів. Проаналізовано застосування порошків в аддитивних виробництвах. Показано переваги та недоліки способів отримання і застосування порошків цирконію. Для виробництва порошків цирконію запропоновано метод гідрування/дегідрування.