Hydride technologies in porous metals production

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Abstract. The experience of RFNC–VNIIEF in application of hydride technologies in porous metals production is presented. Using metal hydrides as pore-forming agents for foaming of metal melts, as raw materials for obtaining porous samples by sintering of powder compacts and as intermediate products in processes of hydride grinding of metals for further sintering of compacts are considered.

1. Introduction

Porous metals are widely used in various fields of science and technology first of all due to unique combination of low density and mechanical strength (for example, [1–3]). There are a lot of technologies for producing porous metals, and in particular case the optimal technology depends on nature of the metal and the requirements for the end-product. Porous metals can be produced by passing gas through a metal melt, by pouring the metal melt into a matrix of porous spheres, by depositing metal vapors from the gas phase and so on [1–3]. At the same time a number of advantages are provided by using hydride technologies which often make it possible significantly simplify technological processes and reduce the cost of porous metal samples.

Based on experience of RFNC–VNIIEF in relation to porous metals production hydride technologies can be used in the next cases. Firstly metal hydride powders can be used as pore-forming agents that decompose in a metal melt with the hydrogen release and provide obtaining porous structure of the end-product after cooling [4, 5]. In comparison with bubbling gas through the metal melt, using hydrides powders allow significantly increase the technological efficiency and make it possible to obtain end-products with regular porous structure. Secondly metal hydride powders can be used directly as raw materials in porous metals production [6, 7]. Thermal decomposition and further sintering of metal hydride powders in a form of a set geometry allows achieving the end-product density close to the bulk density of the initial hydride powder. Thirdly hydride grinding technology can be used to produce fine metal powders [8–10] whose are the raw materials for porous metals production by sintering of powder compacts. First of all using effect of hydrogen embrittlement makes it possible to obtain fine powders of different plastic metals, which are difficult to obtain by mechanical grinding.

The following are specific problems related to porous metals production, which were solved in RFNC–VNIIEF using hydride technologies.

2. The experience of RFNC–VNIIEF in application of hydride technologies in porous metals production

2.1. Production of porous aluminum samples using metal hydrides as pore-forming agents
The goal of this work carried out in collaboration of RFNC–VNIIEF and All-Russian Institute of Light Alloys ("VILS", Moscow, Russia) was to develop a cost-effective technology for obtaining aluminum porous samples with uniform structure. The well-known method (for example, [2, 3]) based on mixing a powder of pore-forming agent into a molten metal was taken as a basis. A pore-forming agent actively decomposed and released gas foams the molten mass. Subsequent cooling of the melt makes it possible to obtain porous metal samples. In this work the titanium hydride powder [4, 5] was used as a pore-forming agent as widespread and cheap material with high hydrogen specific content.

Trial experiments carried out according to this scheme show the following difficulties:

- Non-uniform distribution of pore-forming agent in molten aluminium due to poor wettability of titanium hydride and high viscosity of melt;
- Rapid loss of gas by titanium hydride during mixing in molten metal due to fast decomposition at the temperatures close to the aluminum melting point, which negatively affects the homogeneity of the porous samples;
- Non-cost-effective technology if there is a stage of mechanical processing of the obtained porous aluminum.

In order to overcome these difficulties and to achieve the goal the following tasks had to be solved:

- Choose the best way to modify pore-forming agent to increase its heat resistance;
- Ensure uniform distribution of the modified pore-forming agent in the molten aluminum;
- Exclude porous aluminum mechanical processing to reduce the cost of end-products;

In this work these tasks were solved as follows.

The best solution to increase the thermal stability of the pore-forming agent in this work was the passivation of titanium hydride powder with air oxygen. According to [11] passivation with air oxygen leads to formation of oxide and oxohydride coatings on the particles’ surface that prevent fast releasing of hydrogen during mixing the pore-forming agent in the aluminum melt. It was necessary to determine the optimal technological oxidation mode for titanium hydride, which allows increasing the heat resistance of powder and saving initial specific hydrogen content as much as possible. It was found that the optimal and well-reproducible result is achieved when the fine titanium hydride is oxidized with air oxygen in thin layers of powder at about 440 °C for one hour [4, 5, 11]. The rate of thermal decomposition of partially oxidized titanium hydride is significantly reduced, while the specific hydrogen content remains high enough, which significantly improves its properties as a pore-forming agent.

To achieve the uniform distribution of the pore-forming agent in the molten aluminum mixing time must be quite long. During prolonged mixing time titanium hydride loses the main part of the gas, which negatively affects the porous sample structure. To solve this problem a method for injection the pore-forming agent into the molten aluminum was proposed [12]. This method consists in previous injection the titanium hydride in an "auxiliary" aluminum-based alloy (for example, the Al-Mg alloy) that has a lower melting point than pure aluminum. Due to the lower melting point the degree of decomposition of the pore-forming agent after mixing in "auxiliary" alloy is significantly lower. After cooling and grinding the "auxiliary" alloy' particles injected into the aluminum melt. Because of close properties of "solvent" and "soluble substance" the uniform distribution of pore-forming agent in the aluminum is achieved in a short time. As a result this approach makes it possible to reduce the degree of decomposition of the pore-forming agent and to ensure its uniform distribution in the metal matrix. Finally it provides a positive effect on homogeneity of the porous samples structure.

To exclude porous aluminum mechanical processing and to reduce the cost of end-products using semi-aggregates (so-called "precursors") was proposed. This approach consists of extrusion of melt with uniformly distributed pore-forming agent and fast cooling down of obtained aluminum granules (Figure 1) to prevent their active foaming. To produce porous sample with required shape the granules containing partially decomposed titanium hydride are placed into a form of a set geometry where the final foaming of the "precursors" is performed [4, 13]. As an example, the cylindrical samples obtained according to this method at the experimental base of "VILS" are shown in the Figure 2.
As a result, a promising technology for obtaining porous aluminum samples with uniform pore structure and different types of pore morphology using partially oxidized titanium hydride as a pore-forming agent was developed (Figure 3).

In addition it was found that porous structure and morphology of aluminum samples can be regulated by changing the pressure over the metal melt [4]. In particular, increasing the pressure of hydrogen or inert gas over the melt leads to formation more uniform porous structure because of slowing the rate of pore "swelling" at the initial stages of foaming and reducing the probability of pore coagulation at the final stages of foaming.

2.2. Production of porous uranium samples using uranium hydride
The goal of this work was to develop a technology for obtaining uranium porous samples for high-pressure shock compression experiments (for example, [14]) to study properties of metal uranium in conditions of high concentration of thermal energy. Samples must have a set geometry, uniform porous structure and relative porosity at least 60 %.

Due to the relatively high melting point of uranium (1133 °C) working with molten metal is undesirable. In addition, using of water-soluble pore-forming agents in this case is complicated by the possibility of chemical interaction of uranium with water. At the same time, porous uranium samples could be produced by uranium powder sintering, but due to material "shrinkage" during sintering this method does not allow obtain the required porosity.
As a result, for experimental verification a method for obtaining uranium porous samples by heat treatment of fine uranium hydride powder placed into a form of a set geometry was chosen (Figure 4). It was assumed that hydrogen released during hydride thermal decomposition would prevent material "shrinkage" during sintering. Thus, in this case uranium hydride used as a feedstock for obtaining porous metal, and porosity of samples can be varied by using the initial hydride powder with different particles’ size. It should be noted that there are references to similar methods for obtaining a number of porous metals [15, 16]. However, these methods cannot be directly used to achieve the goal first of all due to requirement of high porosity of samples. In addition, we must take into account the requirements for working with toxic and pyrophoric materials, which include fine uranium hydride, therefore all technological operations must be carried out in a closed volume in inert atmosphere.

![Figure 4. Obtaining of porous uranium samples using uranium hydride](image)

Trial experiments to check the efficiency of the chosen method were carried out using small masses of fine uranium hydride powder. The powder was placed into a reaction chamber in a glove box with dry argon. After that the reaction chamber was evacuated and then the heat treatment of the material with continuous pumping of releasing hydrogen was carried out. The results of trial experiments confirmed the possibility of achieving the required porosity of the samples, but for full-scale practical implementation of this method it was necessary to solve the following tasks:

- Exclude increasing the sample volume above the set dimensions due to mechanical stresses caused by heat treatment of the material;
- Reduce local overheating of the powder which can lead to sharp uncontrolled surges of hydrogen pressure in the reaction chamber that negatively effects on the sample structure.

In this work these tasks were solved as follows.

To exclude increasing the sample volume above the set dimensions and reducing formation of cracks and voids in the sample structure due to fast gas release, the initial powder was placed into a special designed collapsible form of a set geometry with rigidly fixed dimensions made of hydrogen-resistant alloy (Figure 5) [6]. As a result the dimensions of sample kept unchanged throughout all stages of the technological process.

To reduce local overheating of the material during heat treatment which was observed mostly at the initial stages of decomposition of uranium hydride even at relatively slow heating rate, it was decided to increase temperature in the reaction chamber in the step-by-step mode [7]. From the beginning of gas release the temperature was incrementally increased by 10–20 °C per step with a delay at the each step until hydrogen release was stopped. When the gas release from the sample stopped, the reaction chamber was heated up to 760 °C and kept at this temperature for a several days to sinter the uranium. The sintering temperature was selected based on the analysis of properties of uranium and its compounds. In addition to prevent surges of pressure in the reaction chamber, as well as to exclude the removal of powder particles by the hydrogen flow that leads to experimental setup pollution, two compressed metal filters were placed in the outlet of the collapsible form (Figure 5) [7]. The filters throughput was selected in such a way as, on the one hand, to limit the maximum rate of gas removal during decomposition of hydride and, on the other hand, to ensure an acceptable rate of vacuuming the powder material before heating.
According to this method it was possible to obtain uranium samples with relative porosity up to \(~ 70 \%\) which according to X-ray analysis had a fairly uniform porous structure \([6]\). However, the main disadvantage was the long duration of the process carried out in a continuous mode, which created an inconvenience in practice. In order to realize this method discontinuously over several stages of heat treatment, the additional experiments were carried out to obtain porous samples with interrupting the thermal decomposition of uranium hydride every six hours at the end of the working shift. At the beginning of the each next working shift the reaction chamber, cooled down up to room temperature during the break, was reheated again in the step-by-step mode.

Processing of experimental data of hydrogen release in different stages using equations of formal kinetics of heterogeneous non-catalytic processes \([17]\) has shown that the transition from kinetic to diffusion mode of uranium hydride thermal decomposition reaction took place at the each stage of the heat treatment (figure 6). As shown in the figure, the temperature of the transition from kinetic to diffusion mode naturally increased from stage to stage in proportion to increase the degree of decomposition of uranium hydride. The values of the "apparent" activation energy of dehydrogenation reaction for all stages were in the range of \(~ 66–83 \text{ kJ/mole}\) which is in a good agreement with the data \([18]\) where this parameter was \(~ 79 \text{ kJ/mole}\).

Taking into account the uniform structure of samples obtained in a discontinuous technological process, it was concluded that proposed method could be realized in several working shifts. Some of the samples with relative porosity in the range of \(~ 60–70 \%\) obtained according to this method were successfully used in shock compression experiments carried out in RFNC–VNIIEF.

2.3 Producing of fine metal powders using hydride grinding

Hydride grinding commonly used in RFNC–VNIIEF for obtaining fine powders from bulk titanium, zirconium, yttrium, scandium and other metals (for example, \([8–10]\)). Producing fine powders by mechanical grinding of these metals is difficult due to their plasticity. In addition mechanical grinding of metal leads to significant increase of impurities in the end product. At the same time using hydride grinding is much more effective. Then fine metal powders can be used to produce porous samples by sintering of compacts. So, in this case metal hydrides are intermediate products in porous metal obtaining technology.

Hydride grinding includes three main stages (Figure 7): hydrogenation of bulk metal, mechanical crushing of brittle metal hydride and thermal decomposition of obtained powder. The main stages can
be supplemented by grinding or sifting of obtained metal powder (in case of particles’ sintering during thermal decomposition of metal hydride) or by repeating of hydrogenation-dehydrogenation cycles (in case when hydrogen content in the hydride phase increases during repeated cycles).

**Figure 7.** Obtaining of fine metal powder using hydride grinding

In relation to porous metals production hydride grinding allows obtaining fine metal powders with a narrow particles’ size distribution. Sintering of pressed powders leads to obtaining porous samples with uniform porous structure and required pore sizes. Another way of porous metal production is mixing the obtained fine metal powder with a powder of blowing agent [2, 13]. Porous samples obtained by compaction and foaming of such powder mixtures are characterized by high structural homogeneity. In particular, foaming of compacts obtained by pressing fine aluminum powder with an admixture of titanium hydride makes it possible to obtain high-quality aluminum foam. However, in practice, this approach is rarely used first of all due to high cost of the initial fine metal powder.

3. Conclusion
The experience of RFNC-VNIIEF in application of hydride technologies in porous metals production is presented. A technology of obtaining porous aluminum samples with uniform porous structure based on using modified titanium hydride as a pore-forming agent is developed. A method of obtaining porous uranium samples using step-by-step thermal decomposition and further sintering of uranium hydride powder is described. The main principles of obtaining fine metal powders using hydride grinding technology for further production of porous samples by sintering of powder compacts are considered.

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