Selection of composite material composition for non-evaporable getters of new generation

M V Aleksandrova¹, Y V Nikolyukin² and Y A Kurganova¹

¹ Bauman Moscow State Technical University, 2-nd Baumanskaya, 5, b.1, 105005, Moscow, Russia
² IP “Nikolyukin Y.”, Ryazan, Russia

E-mail: kurganova_ya@mail.ru

Abstract. The article is devoted to the issue of synthesizing materials of non-evaporable getters of the new generation with enhanced operational properties. The promising compositions of getter materials are considered, their basic properties are analyzed, and parameters that have a significant effect on their size are selected. According to the results of the literature analysis and patent search, a strategy was developed, on the basis of which three experimental compositions of the material for the non-evaporable getter were determined on the basis of the Ti-Zr system, a visualization-calculation model of the structure was constructed. Based on the traditional technology, the technology for the final product was developed. The results of studies of experimental samples of the material selected composition are presented and the level of acquired operational properties is predicted.

Keywords: getter, sorption, activation temperature, titanium, zirconium, powder metallurgy, mechanical activation.

1. Introduction

Objects that can adsorb and chemically bind all gases, except inert gases, are called getters. They are used in various fields of technology for pumping and maintaining a high vacuum. Performance of the relevant devices depend on the performance of getters [1]. Monitoring the market for such products has demonstrated a monopolization of the domestic manufacturer, which indicates the relevance of creating a competitive product of decent quality. Activity to all gases except inert, present in the atmosphere of an electrovacuum device, regardless of the nature of these gases (oxidizing or reducing), is assessed by sorption versatility, while the volumes and rates of gas evolution are important parameters in the design of the getter [2]. Traditionally, metals that have the ability to chemically react with non-inert gases are considered as getter materials. Inert in air material should be easily activated by heating under pumping during the manufacture of the device, with low vapor pressure at operating temperatures [3]. Gas absorbers are divided into unsprayed and evaporating [4]. The first ones are selected as the subject of study of this work. When activated, they remain in a solid state, have a longer lifespan, can be easily removed or replaced with new ones, which are significant advantages over evaporating ones.

It is known that increasing the maximum sorption capacity plays a key role in creating the most efficient material of the non-evaporable getter, since it is responsible for its performance, i.e. contributes to an increase for gas absorbed under these conditions for a certain operating period [5]. The sorption rate
parameter is interrelated with the sorption capacity, it is similar to the so-called “pumping rate”: at higher rates of gas sorption by the getter material, the evacuation process is accelerated, which indicates an increase in the productivity of both the product and the entire vacuum system as a whole. Lowering the temperature of material activation allows using the getter at less high temperatures, which expands the range of operating temperatures [6, 7].

Particularly widespread are the so-called porous getters based on transition metals of groups IV and V of the Periodic System of Chemical Elements: titanium, zirconium, vanadium. High sorption properties are provided by an increased specific surface, which contributes to a more intensive chemical reaction between the getter metal and the gas of the medium.

The choice of composition of the getter alloy is based on a number of conditions, the main of which are the final performance characteristics and total porosity. It is obvious that a highly porous structure can be rationally obtained by powder metallurgy methods. Materials, the total value of porosity which ranges from 30 to 55% received distribution in the technique. Alloys of this type are highly porous [8].

Currently, there are a number of successful combinations of such alloys gas getters: Zr-Al [9], Zr-V-Fe [10], Zr-Mn-Fe, and compositions Zr-V-Ca, Ti-Cr-Ca [11].

The effective performance of the composition is provided by the rational choice of the elemental composition [12]. The first component must include at least one element from the group of transition metals Ti, Zr, V, ensuring the sorption properties of the finished product. The second component is chosen from the group of Al, Mn, Fe, Ni, providing a level of mechanical properties, as well as "solidity" of the alloy. According to studies, the preferred mass ratio between the components of the alloy powder is from 5: 1 to 1: 2. The degree of chemical heterogeneity is determined based on the fact that the arithmetic average of the ratios of the concentrations of each of the elements of the first and second components in a randomly selected several pairs of points should not exceed 30 [5].

The purpose of this study is to obtain a prototype of an unsprayed getter of a new composition with a low activation temperature and enhanced performance properties.

2. Materials and research methods

Based on the analysis of technical literature and responses of the effective use of getters, Ti, Zr were selected as metals to create a prototype of an unsprayed getter, as elements providing enhanced sorption properties of the final product, and Al as a binder. The choice of a composition of two transition metals, rather than the use of only one of them, is due to the need to lower the activation temperature of the getter. It is known that gas absorbers made by sintering a powder of a single transition metal are high-temperature, their activation temperature exceeds 800°C. It is possible to lower the activation temperature using a combination of materials [1].

Summarizing the above recommendations, alloy compositions with a Ti: Zr ratio of 7:3, 5:5 and 3:7 by volume, respectively, were selected as prototypes. To improve the accuracy of calculation and estimate the required amount of aluminum binder, while maintaining the alloy's porosity at the required level, the package of titanium and zirconium powder on the 40 × 40 µm area was designed in the COMPAS-3D program (Figure 1).
Figure 1. Estimated packing scheme of an experimental alloy Ti-Zr-Al (large grains - titanium Ø 10 microns, small grains - zirconium Ø 4 microns, color sections - aluminum bundle), area size - 40 × 40 microns.

Geometrical calculations have established that the aluminum content at the 5% level is sufficient for bonding powders of the selected chemical and fractional composition of the getter material alloy, provided that aluminum powder with a size of about 100 nm is used. Taking into account the presented data, three model compositions of the alloys of the unsprayed getter prototypes were selected, which are presented in Table 1.

Table 1. Chemical composition of alloys for the manufacture of prototypes unsprayed getter with high sorption properties

| Alloy Number | Ti content, vol% | Zr content, vol% | Al content, vol% |
|--------------|------------------|------------------|------------------|
| 1            | 47.5             | 47.5             | 5                |
| 2            | 66.5             | 28.5             | 5                |
| 3            | 28.5             | 66.5             | 5                |

To obtain a getter, we considered a standard technology for obtaining powder non-evaporable gas getters (Table 2).
Table 2. Process map of the production of non-evaporable getters

| Number | Process operation     | Equipment                  | Mode          | Notes                                                                 |
|--------|-----------------------|----------------------------|---------------|----------------------------------------------------------------------|
| 1      | Powder preparation    | Scales                     | 20 t, °C; 0.5 τ, h | Percentage of components is determined by the particle size           |
| 2      | Powder mixing         | Drum type ball mills       | 20 t, °C; 36 τ, h | In polyvinyl alcohol                                                  |
| 3      | Drying                | Furnace                    | Up to 60 t, °C; | The end of the drying is determined by the absence of sticking of the mixture on the cold spatula |
| 4      | Screening              | Sieve                      | 20 t, °C; - τ, h | -                                                                    |
| 5      | Molding               | Auto press                 | 20 t, °C; - τ, h | -                                                                    |
| 6      | Assembly of the charge| Special trays              | 20 t, °C; 0.5 τ, h | -                                                                    |
| 7      | Sintering             | Furnace                    | According to the mode; | Cooling with furnace to room temperature |
| 8      | Control               | -                          | 20 t, °C; 2 τ, h | As per TU 1190                                                        |
| 9      | Mechanical restoration| CNC machine                | 20 t, °C; - τ, h | Turning and grinding                                                  |

Given the stated objectives, the technology was upgraded with the addition of a low-temperature component to the technological chain of the process of mechanical activation (Fig. 2).

The task of increasing the sorption capacity and reducing the activation temperature is realized through the mechanical activation of the combined base: titanium powder of micron size and zirconium powder of submicron size. In our case, more plastic zirconium in the process of mechanical activation, in contrast to the more durable titanium powder particles when exposed to the shear forces of the interaction of powder particles, goes into a more dispersed state, significantly increasing its surface activity, as well as the sorption capacity and activity at lower temperatures.

As a result of the subsequent sintering, the obtained structure of the porous composite skeleton makes it possible to obtain the effect of increasing the sorption capacity of the getter with a decrease in its activation temperature.

As a result of testing modernized technology on selected compositions (Table 1), samples were obtained in the form of sintered discs with a diameter of 11–13 mm and a height of 2–3 mm (Fig. 3).
Figure 3. Photos of prototypes.

Comparative analysis of the structure of the sintered samples of the second alloy, obtained using scanning electron microscopy in the laboratory of thin physical methods for studying the structure of materials of the MSTU named N.E. Bauman at the scanning electron microscope TESCAN VEGA.
Figure 4. Photographs of the structure of a) sintered titanium powder, b) sintered titanium powder with an aluminum binder (developed composition), obtained using scanning electron microscopy at magnification $\times 500$.

It is seen that the structure of the sample with the addition of aluminum is more ordered, the grains are arranged integrally and monolithically, periodically interconnected.

In order to predict the performance properties of getters from the material, the proposed composition carried out an assessment of the porosity and density of the experimental samples obtained. The porosity and density of the experimental samples were carried out according to the generally accepted method using a hydrostatic weighing method [13]. The measurement results are presented in Table 3.

Table 3. Average density and porosity of experimental samples

| Density, g/cm³ | Open porosity, % | Closed porosity, % | Total porosity, % |
|---------------|------------------|--------------------|------------------|
| 1.221         | 54.4             | 8.1                | 62.5             |

On the basis of the obtained data, the level of acquired operational properties is predicted, which is presented in Table 4.

Table 4. Projected performance characteristics of new generation gas absorbers

| Characteristic | Properties of the existing analog | Predicted properties of the new material |
|---------------|----------------------------------|-----------------------------------------|
| Activation temperature, ° C | 350 – 400 | 300 – 350 |
| Specific maximum sorption capacity for hydrogen, m³ * Pa / g | 7.1 ± 0.2 | 7.5 ± 0.2 |
| Hydrogen sorption rate, l / s * g | 6.6 | 6.9 |
The calculations demonstrate that the selected composition and the modernized manufacturing technology of the new non-evaporable getter are capable of meeting the requirements, with a certain increase in the operational properties.

3. Conclusions

Thus, as a result of the research work, a model composition of a composite material for a non-evaporable getter was chosen: with a ratio of Ti powder with a size of 10 μm to a Zr powder with a size of 4 μm 7:3 by volume correspondence. Calculations have found that 5% of aluminum powder with a size of about 100 nm is sufficient for adhesion of powders of the selected chemical and fractional composition of the alloy. Modernization of the traditional technology by introducing the operation of mechanical activation ensures the achievement of a given porosity. Evaluation of the latter allowed to establish the feasibility and effectiveness of the technological changes made. Gas absorbers made from the selected material have higher performance characteristics than the existing compositions today.

References

[1] Aleksandrova M V 2018 The choice of the composition of the material of the non-evaporable getter with enhanced sorption properties. All-Russian Scientific and Technical Conf. “Student Scientific Spring: Engineering technology. conference materials URL: http://studvesna.ru/?go=articles&id=2167.

[2] Bychkova M S 2018 Getter pumping of electrovacuum devices. All-Russian Scientific and Technical Conference “Student Scientific Spring: Engineering technology. conference materials: http://studvesna.ru/?go=articles&id=1268.

[3] Glebov G D 1965 Gas absorption by active metals. M.: Energy. 184 p.

[4] Korzh I A 2016 The design and manufacturing technology of evacuated devices with unsprayed gas getters. Radio communication technology. Is.3. p.121-128.

[5] Reutova N P, Manegin S Yu, Pavlov V N 1989 Creation and study of metallic powder materials with an activation temperature below 550°C. TsNIICHM named after I.P. Bardin. Moscow. Final report on the D-713-88.

[6] Avakumov E G 1980 Mechanical methods of activation of chemical processes. Novosibirsk: Science. 297 p.

[7] Kachenyuk M N and Smetkin A A 2014 The evolution of the structure of composite particles during the mechanical activation of powder mixtures based on titanium, silicon carbide and carbon. Modern problems of science and education. Is.6. URL: https://science-education.ru/ru/article/view?id=15969.

[8] Reutov N P, Manegin S Yu, Akimenko V B 1998 The method of obtaining non-evaporated getter and getter, obtained by this method. The patent №2118831 of the Russian Federation. NTO "Technovak.

[9] Hendrik Johannes, Reinierus Perdijk, Johann Diedrich Fast, Jan Josephus Bernardus Fransen 1958 Method of producing a non-vaporizing getter. Patent №2.855.368 USA. US Patent Office.

[10] Claudio Boffito, Aldo Barosi, Alessandro Figini 1982 Non-evaporable ternary gettering alloy and method of use for the sorption of water, water vapor and other gases. Patent №4.312.669 USA.

[11] Claudio Boffito, Massimo Bolognesi 1993 Recovery of tritium deuterium from their oxides and intermetallic compound useful therein. Patent №4.312.669 USA.

[12] Kurganova Yu A and Kolmakov A G 2015 Structural metal matrix composite materials: a textbook. M.: Publishing House of MSTU named after N. E. Bauman. 141 p.

[13] GOST 18898-89. Powder products. Methods for determining the density, oil content and porosity. Eff. 1989-12-20 M.: Publishing house of standards, 1989.— 12 p.

[14] Adducts to produce self-healing thermosetting epoxy polymer from a widely used epoxy monomer. Polymer Chemistry. 4 724-30.
[15] Bai N, Simon G P and Saito K 2013 Investigation of the thermal self-healing mechanism in a cross-linked epoxy system. *RSC Advances*. 3 20699-707.

[16] Yuan Y, Yin T, Rong M and Zhang M 2008 Self healing in polymers and polymer composites. Concepts, realization and outlook: A review. *Express Polymer Letters*. 2 238-50.

[17] Chen X, Dam M A, Ono K, Mal A, Shen H, Nutt S R, Sheran K and Wudl F 2002 A thermally re-mendable cross-linked polymeric material. *Science*. 295 1698-702.

[18] Homer A and Winans C F 1939 Preparation of furfurylamines. *US Patent*, 2175585 A.