Development of feedstock of tungsten-nickel-iron-polyformaldehyde for MIM technology

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Abstract. The article presents the results of the research and development of technology and formulation of the feedstock from domestic metal powders and polymers to fabricate complex-shaped components from heavy alloy of VNZh 7-3 brand (90 wt. % tungsten - 7% nickel - 3% iron) by Metal Injection Molding (MIM technology). The metal part of the feedstock is composed of powders of tungsten, nickel and iron, and the polymer part is composed of polyformaldehyde with the addition of low-density polyethylene and beeswax. The modes of mixing the components and the influence of the composition of the feedstock on the melt flow rate and the homogeneity of the feedstock were investigated. The optimal formulation of the feedstock was determined. Microstructure, density and hardness of control samples fabricated by MIM technology from the developed feedstock, correspond to, and in some respects are superior to the samples of VNZh 7-3 alloy fabricated by technology of traditional powder metallurgy.

Keywords: heavy alloy, metal powders, MIM technology, feedstock, polymers.

1. Introduction

Heavy composite pseudoalloys of tungsten-nickel-iron system (alloys of VNZh type in Russia) with a high specific weight and improved mechanical properties are well known and are used for manufacturing components and structures with special properties [1]. They are produced only by powder metallurgy methods: compaction of the powder mixture followed by sintering, hot pressing, infiltration of porous tungsten skeleton by molten metal binder [1]. However, these traditional methods of powder metallurgy allow the production of components of the simplest shapes only. In this connection, of interest is the use of MIM technology for the production of complex-shaped components from alloys of VNZh type. Technology of Metal Injection Molding (MIM) is a technology for injection molding of blanks of complex-shaped components from mixtures of melts of polymers with metal powders followed by removal of the polymer binder and sintering of metal powders [2]. This technology combines the capabilities of the technology of injection molding of thermoplastics by automatic molding machines and the technology of powder metallurgy and is widely used abroad for large-scale production of components for various purposes. The raw material
for the MIM-technology is a feedstock consisting of a mixture of metal powder and polymer binder. The most common binder for feedstocks is polyformaldehyde or polyacetal. The introduction of MIM technology at the factories of Russia is hampered by lack of feedstocks from domestic components, the development of which has just started [3, 4]. Therefore, it is important to develop the domestic MIM feedstocks and for heavy alloys of VNZh type.

The aim of this work is to develop a MIM-feedstock of VNZh 7-3 heavy alloy from domestic metal powders and polyformaldehyde as a binder.

2. Materials and methods

The chemical composition of the VNZh 7-3 heavy alloy is the following: 6.5-7.5 wt. % nickel (Ni); 2.5-3.5% iron (Fe); tungsten (W) is the base [1]. The most suitable for MIM technology are metallic powders of spherical shape, which are not larger than 20 µm with an average size of about 5-10 µm [2]. Therefore, for development of metallic part of the feedstock, the following powders of domestic production were selected: the powder of carbonyl nickel of PNK-1L8 brand, consisting of rounded particles with a size up to 1 micron; the powder of carbonyl iron of VM brand, which is a mixture of spherical particles of size from 0.1 µm to 10 µm; the powder of tungsten of PV-2 brand, consisting of rounded particles in the size range 1 to 5 microns. For development of polymeric part of the feedstock, the following materials were used: polyformaldehyde with processing additives of "Tekhnaset A-110" brand (main binder); low-density polyethylene of 15813-020 brand (additional binder to hold the structure of the porous skeleton after removal of the main binder); beeswax according to GOST 21179-2000 (surfactant).

Particle-size distribution of powders was determined by laser particle-size analyzer Analysette 22 Compact. Microstructure of the materials was investigated by scanning electron microscope (SEM) Jeol JSM-6390A, and phase composition of materials was determined by X-ray diffractometer (XRD) ARL X'TRA.

The modes of preparation of the mixture of initial metal powders, or a powder batch, were worked out in a ball mill with metallic grinding bodies in the form of balls with a diameter from 5 to 10 mm and rollers with a diameter of 5 to 8 mm and a length of 8-10 mm. The powder batch load ranged from 300 to 500 g. For the preparation of feedstock, a laboratory installation was used consisting of two main parts heated by ultrathermostat: a batch blade mixer of polymer and powder components with a volume of 0.2 dm³ and a hydraulic press with a die for extrusion a cord with a diameter of 5 mm followed by cutting it into granules 5 mm in length [3].

The quality of the feedstock was controlled for the following characteristics: a melt flow index of the feedstock on plastometer MELT INDEXER MI-2 at a temperature of 190°C, with inner diameter of capillary of 2 mm and a load of 21.6 kg; the homogeneity (uniformity) of the feedstock on a helium pycnometer AccuPyc II 1340.

Blanks of control samples for testing were molded in injection molding machine MicroPower 5/7.5 (obtaining green blanks). The removal of the polymer part from the feedstock (obtaining brown blanks) was conducted in a stepwise mode, close to that adopted for feedstocks on polyformaldehyde base. Sintering of the control samples was conducted in the environment of hydrogen with temperature up to 1440°C.

The hardness of the sintered samples of the VNZh 7-3 alloy was determined by the method of Brinell, the density was determined on a helium pycnometer AccuPyc II 1340.

3. Results and discussion

A study of particle-size distribution of the initial metal powders showed that the powders of nickel and tungsten are composed of particles with size of 1-5 µm, but these particles are combined into agglomerates with size of 40-70 µm. To prepare a homogeneous mixture of these powders, it is necessary to achieve the destruction of the agglomerates. To determine the optimal preparing time of the powder batch, the experiment was conducted on the dynamics of grinding components of the batch...
for four hours with sampling every half hour. The results of this experiment are presented in table 1 in the form of the change of wt. % different size fractions with time.

Table 1. The change of particle-size distribution with time of grinding, wt. %.

| Grinding time, hour | Size fraction of powder mixture, µm |
|---------------------|-----------------------------------|
|                     | 0-40     | 0-30     | 0-20     | 0-10     | 0-5      | 0-2      | 0.5-1.0  | 0.3-0.5  |
| 0.5                 | 2.5      | 9.8      | 30.7     | 30.1     | 21.2     | 4.5      | 0.74     | 0.33     |
| 1.0                 | 4.3      | 26.9     | 36.0     | 26.4     | 5.1      | 0.91     | 0.42     |
| 1.5                 | 2.2      | 23.4     | 37.8     | 29.4     | 5.6      | 1.04     | 0.46     |
| 2.0                 | 1.4      | 20.8     | 38.6     | 31.5     | 6.1      | 1.13     | 0.50     |
| 2.5                 | 0.5      | 18.0     | 39.6     | 33.7     | 6.4      | 1.24     | 0.53     |
| 3.0                 | 1.7      | 13.7     | 41.8     | 36.0     | 6.8      | 1.18     | 0.63     |
| 3.5                 | 0.2      | 15.9     | 39.8     | 35.7     | 6.7      | 1.28     | 0.58     |
| 4.0                 | 0.1      | 14.4     | 39.7     | 36.7     | 7.1      | 1.40     | 0.59     |

These results show that the intensive milling of the components of the batch occurs within the first three hours, when the fraction greater than 20 µm completely disappears. Further reduction in size does almost not happen, but on the contrary, there is agglomeration of particles. Thus, the optimum preparing time of the powder batch in a ball mill is 3 hours. (In the case of using other equipment, e.g., an attritor, the grinding time can be reduced, which requires additional study.)

The microstructure of the powder batch of VNZh 7-3 alloy, ground in a ball mill in the course of 3.0 hours, is presented in figure 1.

![Figure 1. SEM image of powder batch after grinding during 3.0 hours.](image)

It is seen that the mixture of powders is homogeneous and has no large agglomerates of particles larger than 10 µm.

The prepared powder batch was transferred into the chamber of the heated blade mixer, where the polymer components were added, and mixing was performed for 35 minutes in the temperature range 160-195°C with increasing temperature at a rate of 1 °C/min. Obtained metal-polymer composition, or feedstock batch, was placed into a preheated die for extruding and forming a cord with subsequent cutting of granules. In the course of the study, five experimental batches of the feedstock of VNZh 7-3
heavy alloy with different content of components were made, the composition of which is presented in table 2.

**Table 2.** Compositions of experimental batches of the feedstock of VNZh 7-3 alloy.

| Number of feedstock batch | Content of components, wt. % | Powder batch | Technaset A-110 | Low-density polyethylene | Beeswax |
|---------------------------|-----------------------------|--------------|----------------|-------------------------|---------|
| No. 1                     |                             | 90           | 8              | 1.0                     | 1.0     |
| No. 2                     |                             | 91           | 8              | 0.5                     | 0.5     |
| No. 3                     |                             | 92           | 7              | 0.5                     | 0.5     |
| No. 4                     |                             | 93           | 6              | 0.5                     | 0.5     |
| No. 5                     |                             | 94           | 5              | 0.5                     | 0.5     |

The properties of the produced feedstocks were evaluated by the melt flow index and the deviation from homogeneity of the granules, the values of which are presented in table 3.

**Table 3.** Properties of experimental batches of the feedstock of VNZh 7-3 alloy.

| Feedstock batch number | Average density, g/cm³ | Deviation from homogeneity, % | Melt flow index, g/10min |
|------------------------|------------------------|-------------------------------|--------------------------|
| No. 1                  | -                      | -                            | 1150                     |
| No. 2                  | 8.42                   | 1.1                          | 430                      |
| No. 3                  | 8.87                   | 0.87                         | 365                      |
| No. 4                  | 9.76                   | 0.5                          | 230                      |
| No. 5                  | 10.11                  | 0.79                         | 60                       |

The melt flow index (MFR) shows the possibility of application of the feedstock to injection molding machines, as well as the correct ratio of metal and polymer parts. The melts of the feedstock batches No. 1 and 2 flowed easily out the die even under its own weight, wherein the cord grew thin and heterogeneous. When reducing the amount of polymer part in the feedstock, the cord coming out under pressure up to 5 MPa, however, he had a uniform cylindrical shape. But the feedstock batch No. 5 contained deficient polymer part and the cord was formed with difficulty. The feedstock batches No. 3 and 4 were the most suitable, their values of MFR correspond to the typical values of MFR of feedstocks on the base of polyformaldehyde (200-500 g/10min), i.e. the optimal ratio between the metal and polymer parts in the feedstock is in the range of 92-93 wt. % metal powders.

Homogeneity shows the degree of uniformity of distribution of metal powders in a polymer binder. As follows from table 3, the feedstock batches No. 3 and 4 have deviation from homogeneity of less than 1%, which is an indicator of high uniformity.

In the study of the microstructure of the feedstocks on electron microscope, pores and voids, large and small inhomogeneous inclusion were detected. Figure 2 shows the microstructure of the feedstock of batch No. 4. The structure of the feedstock is rather uniform, the maximum particle size of the metal phase does not exceed 6 µm.

Four feedstock batches No. 2-5 were used to make control samples by MIM technology to determine mechanical properties and structure of sintered material corresponding to composition of VNZh 7-3 heavy alloy. The results of measuring Brinell hardness of the samples are the following: 285, 310, 333 and 308 HB for batches No. 2, 3, 4 and 5 correspondingly. The hardness of the samples fabricated by MIM technology is 10% higher the hardness of the samples of VNZh 7-3 composition made by technology of traditional powder metallurgy (260-280 HB). The results of measuring the density of the control samples made by MIM technology are the following: 17.0546, 17.0957, 17.0840 and 17.1245 g/cm³ for batches No. 2, 3, 4 and 5 correspondingly. These values of the density of the
MIM samples are even slightly higher than the density values (16.6-17.0 g/cm³) specified for VNZh 7-3 heavy alloy, made according to traditional technology of powder metallurgy [1].

![Figure 2](image1.png)

**Figure 2.** SEM magnification of feedstock of batch No. 4.

The microsections were made of sintered control samples, obtained at MIM-technology and traditional technology of powder metallurgy (PM), and their microstructure was analyzed (figure 3).

![Figure 3](image2.png)

**Figure 3.** Microstructure of sample sintered from feedstock of batch No. 4.

The microstructure of the MIM samples is fully consistent with the microstructure of the PM samples: rounded tungsten grains surrounded by a Ni-Fe binder. The grain size is 30-40 µm, the individual grains reach 50-70 µm in size.

**4. Conclusion**

As a result of the study, the technology and composition of the feedstock from domestic metal powders and polymers are developed to manufacture complex-shaped components from VNZh 7-3 heavy alloy by the technology of injection molding and sintering (MIM technology). Microstructure, density and hardness of control samples fabricated by MIM technology from developed feedstock, fully meet, and in some respects superior to the samples of this alloy produced by the technology of traditional powder metallurgy.
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