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Production of cast electrodes from SHS-alloy based on NiAl in a metal shell, plasma rotating electrode process and getting composite microgranules for additive technologies

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Abstract. Implementing the latest additive technologies such as selective laser melting (SLM) and electron-beam melting (EBM), as well as direct metal laser sintering (DMLS) requires source materials (powders, or microgranules) of a specified chemical or granulometric composition. This paper describes a brand new technological process of obtaining composite microgranules that consists of three main stages: (1) synthesizing a NiAl-based intermetallic alloy of a specified chemical composition by centrifugal SHS metallurgy, (2) single-stage metallurgic processing (vacuum induction melting or inert-medium melting) of synthesized SHS materials (cast-charge materials, CCM) to be subsequently cast in a specially prepared steel tube for crystallizing; (3) centrifugal atomization (PREP) of the obtained steel-shell electrodes to make spherical composite microgranules. A NiAl-Cr-Co-Hf nickel-aluminide-based multi-component cast alloy was synthesized by that technology. We obtained the kinematic-viscosity dependency for this SHS alloy. Series of studies was conducted to optimize the vacuum-induction melting, and the melt was cast in a specially prepared steel crystallizer. We thus melted a double-layer electrode for plasma-rotating electrode process. The electrode was atomized to produce spherical microgranules and to study their morphology.

1. Introduction

Today, high-alloyed Ni-, Co-, or Fe-based alloys [1,2] are the basis for developing many materials used in heavy-duty applications (high temperatures and loads) in such industries as: aviation and marine engine engineering, rocket-space vehicle engineering, special equipment, nuclear power plants technology, etc. Solving the problems of meeting the operating requirements to modern technical devices has caused an increase in the operating performance of metal products while urging the development of new materials.

Many studies in this area aim at solving the problem of developing new alloys with improved physico-chemical properties while creating technology for making such alloys [2]. Special attention is paid to alloys based on equiatomic nickel aluminide, which feature a unique combination of chemical, physical, and operating properties such as high melting point (1640º C), chemical stability, low density, high heat and corrosion resistance. Despite these advantages, these alloys have so far not found any wide industrial application due to their lack of adaptability, low plasticity and strength at room temperature [2].

Castings made in induction and arc furnaces, when cast in molds, have such defects as shrinkage-caused porosity and cracks, uneven grain size and shape, non-homogeneous chemical composition, and uneven distribution of components. These defects manifest themselves to a far lesser extent in ingots produced by electroslag remelting and vacuum melting with consumable electrodes. However, even in the latter case cast NiAl-based alloys display chemical non-homogeneity, enrichment of grain boundaries with low-melting and brittle compounds that cause the material to be more brittle than desired and to develop cracks when machined.

Known technologies used for making such materials often do not generate a desired set of properties; besides, they are complicated, multi-staged, and energy-intensive. This combination of factors prevents wide commercial use of such materials.

Pellet metallurgy is one of the efficient ways to solve the problem of making products of brittle and hard-to-machine materials. Industrially developed countries including Russia currently seek to develop additive technologies such as selective laser melting (SLM), electron-beam melting (EBM), and direct metal laser sintering (DMLS).

Implementation of the latest technology requires use of source materials in the form of powders (microgranules) of a specified chemical and granulometric composition. The production of spherical powders from standard nickel superalloys, a number of titanium alloys, and Fe- and Al-based alloys has been partially implemented in Russia and abroad. This paper is the first to propose a method for producing composite microgranules consisting of an intermetallic alloy and the crystallizer-shell material (Me). Products made of such microgranules feature the properties of intermetallic alloys while retaining plasticity. The proposed method is demonstrated by casting the intermetallic alloy in a steel pipe for crystallization.

The process of making composite microgranules consists of three main stages: (1) synthesizing an NiAl-based intermetallic alloy (CCM) with a specified chemical composition by centrifugal SHS metallurgy, (2) single-stage metallurgic processing (vacuum induction melting or inert-medium melting) of synthesized SHS materials (CCM) to be subsequently cast in a specially prepared steel tube for crystallizing; (3) centrifugal atomization (PREP) of the obtained electrodes in steel shell to make spherical composite microgranules.

2. Experiment methodology

2.1. Synthesized cast CCM by SHS metallurgy

In this research, we studied the promising intermetallic alloy of the following composition: Ni as the basic component, Al 24.0%, Cr 11.5%, Co 6.5%, Hf 0.9 mass%. To synthesize CCM from the studied alloy, we used an SHS , method that is considered to be a basic SHS technology [3,4] and is based on using the heat energy of highly exothermic thermite-type SHS systems consisting of metal oxide powders, a reducing agent, and non-metals.

The chemistry of synthesizing the studied alloy can be generally represented as

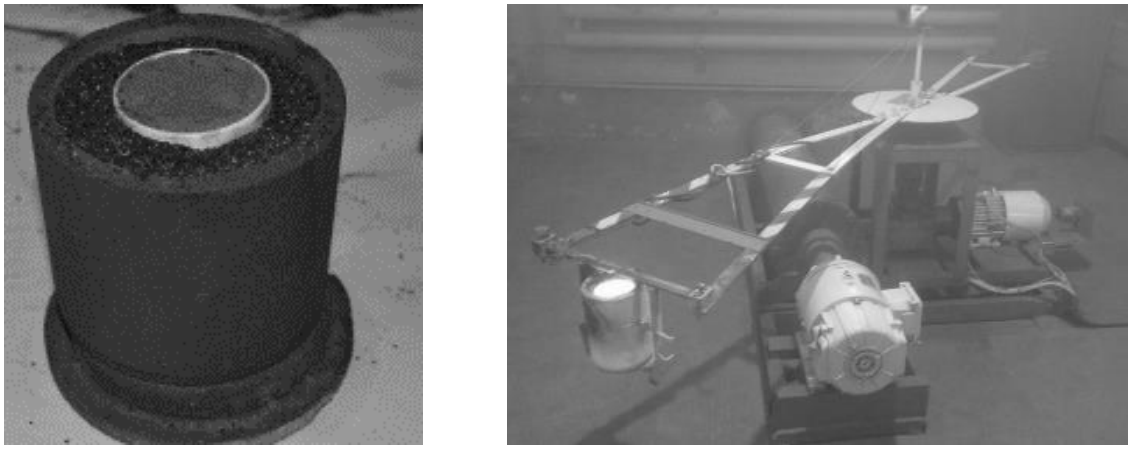
$$(1\text{-}\alpha)\ NiO + \alpha Al + (\mathbf{AA}) + (\mathbf{FA}) \rightarrow [Ni_xAl_y\text{–}\mathbf{AE}] + Al_2O_3 + Q,$$

Where: **AA** – alloying / modifying additives (Cr_2O_3, Co_3O_4, Hf),
FA– functional additives (Al_2O_3, ($Na_3[AlF_6]$),
AE – alloying / modifying elements (Cr, Co, Hf).

The basic components of the source mixture are metal oxides with ≥ 99.6 % purity and 20 to 60 μm particles; a reducing metal (Al) of Aluminum-Powder 4 grade with the main-fraction particle size of 140 to 160 μm and ≥ 98.0 % purity; AR-grade Co_3O_4, extra-pure-grade NiO, pure-grade Cr_2O_3, and HFM-1 grade powder Hf.

The exothermic composition preparation procedure included dosing the components, mixing them in a planetary mixer for 15 minutes, and filling graphite molds (40 to 60 mm in diameter) with the charge. The prepared mixture was placed in a graphite mold coated internally with a protective refractory layer made of corundum-based infusible inorganic compound. To intensify the gravitational separation and convective mixing of the melt, the alloy was synthesized in a centrifugal SHS unit (Figure 1a) being exposed to an overload from 15 to 150 (±5g). To minimize the chemical interaction

of the liquid intermetallic alloy with the mold during the SHS synthesis process, we used alundum crucibles placed into the graphite molds with intermediate alundum chippings as coating (Figure 1b).



a ***b***

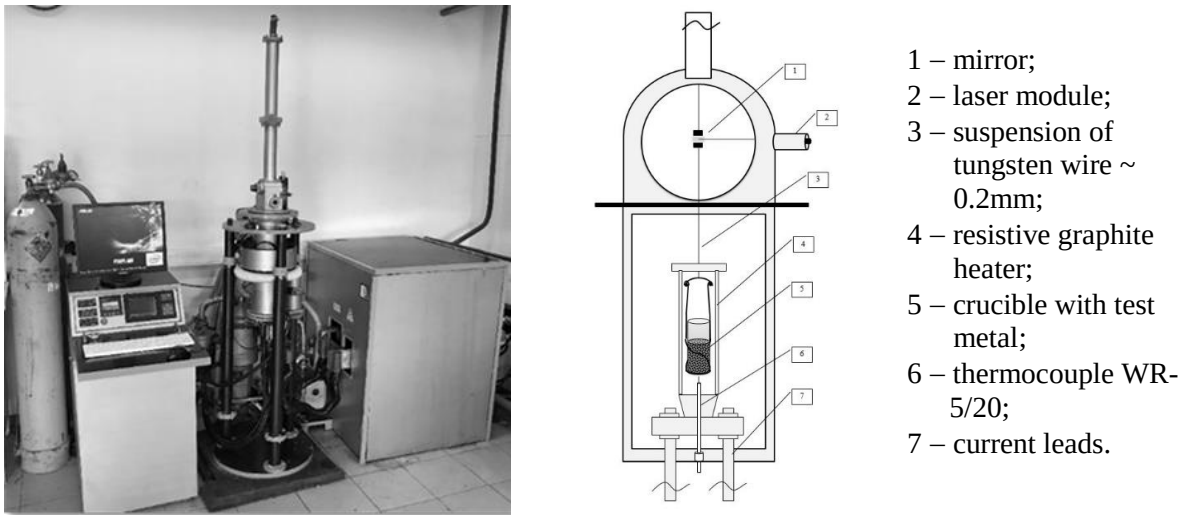
Figure 1. Appearance of the mold before combustion (a) and a multipurpose experimental centrifugal SHS installation (b).

After finishing the SHS process, the product was cooled down and removed from the mold. The product was a double-layer ingot: an upper layer of corundum based oxide solution (slag), and a lower layer of a heat-resistant NiAl-based alloy (the target product) of a specified composition.

2.2. Changes in the CCM melting point and melt viscosity during remelting.

Testing the parameters of subsequent metallurgical conversion of the produced CCMs requires precise selection of the temperature and time of melt overheating. To that end, we used a high-temperature measurement system for measuring the viscosity of metal melts (HTV) [5] that enabled experimentation in a wide temperature range (up to 2100 °C) in vacuum or in an inert-gas atmosphere, which was why we were able to precisely identify the melting point (solidus-liquidus).

Figure 2 presents a schematic of the system.



a ***b***

Figure 2. General schematic of the high-temperature system (*a*) and the overhead system (*b*) for measuring the viscosity of metal melts (HTV).

The HTV operates on the basis of registering the kinematic viscosity by determining the logarithmic decrement of attenuation, empty-system oscillation period, and liquid-system oscillation

period. The relation between the observable oscillating-system parameters and the viscosity of the liquid under analysis is mathematically substantiated in [5].

2.3. Smelting the electrode in shell in a vacuum induction furnace.
The authors had earlier discovered that VIM could enable efficient degassing of the CCM of the obtained SHS alloys [6]. To remelt the CCM for subsequent casting in a metal tube in a protective inert atmosphere (highly-pure-grade (Rus: ВЧ) argon (99.995% Ar)) that the induction-furnace chamber was filled with after being evacuated to a diffusion vacuum (10-5 Pa), at a pressure of 0.95×105 Pa. The induction heating rate was 150 (±30) °C/min. To remove gaseous impurities, the obtained melt was cured at 1680-1700 °C for at least 3 minutes. With the inductor on, the produced melt was cast in a specially prepared steel crystallizer (60 mm internal diameter) that had been pre-mounted in the furnace chamber; the crystallizer was used to crystallize the ingot. Upon completion of the casting process, the inductor would be switched off. The produced double-layer ingot of NiAl-based heat-resistant alloy and the metal shell were cooled down in the induction-furnace chamber in an argon atmosphere for 3 to 5 hours.

2.4. Centrifugal atomization (PREP)
Centrifugal atomization of the Fe/NiAl electrode was done using a UTsR-9I unit at a workpiece rotation speed of 20,000 rpm and a plasma torch power of 85 kW.

2.5. Studying the phase composition and microstructure
The microstructure of the synthesized SHS alloy and microgranules was studied by scanning electron microscopy using Ultra 55-based Zeiss Ultra plus high-definition microscope.

3. Experimental results and discussion

3.1. Patterns of product combustion in SHS and production of CCM.
We initially conducted a series of experiments to optimize the conditions of synthesizing the multi-component intermetallic alloy. Sample analysis in the studied g range showed that alloy ingots synthesized at 50 to 150 (±5g) had a close-to-calculated mass (~ 98 mass %), whereas its loss (dispersion) to combustion did not exceed 1.5 mass %. All the samples produced at this overload had a cast appearance with clear division into 2 layers, one of the target alloy and one of the oxide (Al_2O_3). It could be seen that the transverse cleavage of the ingot synthesized at > 50g did not have any residual porosity (figure 3).

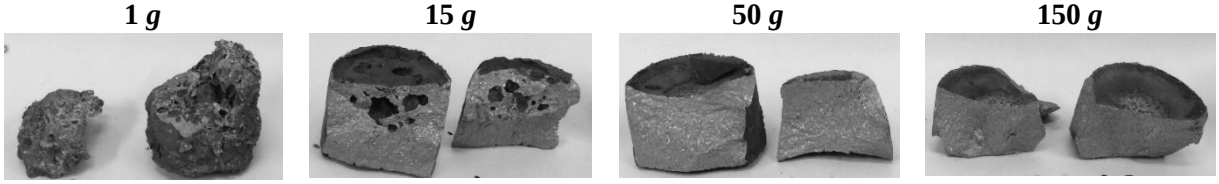


Figure 3. Appearance of transverse-cleft samples produced at various g values.

The effect of centrifuge-generated high gravity suppresses the dispersion of combustion products during the synthesis, intensifies the phase separation of the metallic (alloy) and the oxide (corundum) phases while facilitating the homogenization of the alloy composition and the formation of a finer-grained structure of generated products [6].

Detailed analysis of the structural components and the results of the X-ray diffraction analysis (XRD) of the synthesized products, the obtained CCM, had been presented in earlier studies [6].

3.2. Studying the double-phase region by means of HTV

For the second stage of this research, we melted the synthesized SHS alloys in a high-temperature viscometer (HTV) to find the exact melting point of the alloy, which amounted to 1520 °C. Melting was done in an Ar atmosphere with an excessive pressure of 0.3 atm.

Experimental melting of the synthesized SHS workpieces by means of an HTV unit helped obtain the dependency of the melt kinematic viscosity on the temperature in heating and cooling (Figure 4). Such considerable reduction in viscosity could be deemed a positive outcome for making complex-configuration castings.

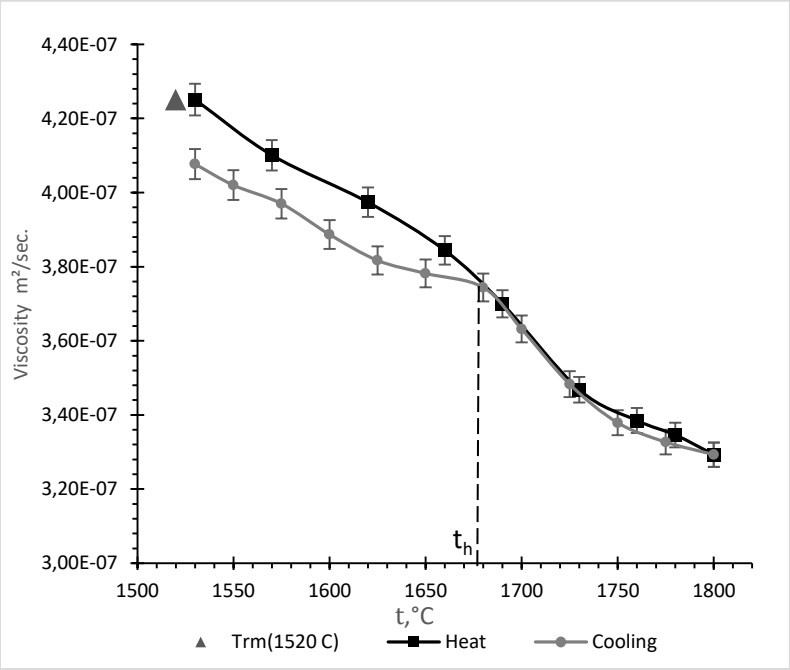


Figure 4. Dependency of the kinematic melt viscosity (v) on the temperature.

The experiment showed that the viscosity polytherm featured hysteresis. The melt heated from the melting point to the hysteresis-onset temperature t_h was not in the equilibrium. Such heating increased the energy of chaotic atom motions, accelerated the diffusion and other restructuring processes. [5] The melt reached equilibrium at t_h. The reverse branch obtained by measuring υ while the system was cooling down matched its equilibrium state. Such hysteresis is observed in heterogeneous systems when it is related to the completed solution or surfacing of the intermetallic inclusions.

Earlier papers also presented the study of the reproducibility of SHS alloy microstructures at various overheat temperatures above the melting point [7]. This information enabled us to move on to the next stage of our research.

3.3. VIM and casting in a steel crystallizer

The next stage of the technology chain consisted in the vacuum induction melting (VIM) of the SHS alloy workpieces. Based on the experimental studies conducted by means of the viscometer, the main criterion was the slight overheating of the alloy and casting at ~ 1650°C. The main objective was to find the minimum mold wall thickness to cast the experimental alloy into it so as to obtain a solid long sample. At the same time, the comparison of thermal expansion coefficients for the NiAl alloy and the crystallizer also made an important property. In this case, we used an industrial grade: Steel-10. We made preliminary theoretical calculations and selected an optimum range of crystallizer tube wall thickness, which was 3 to 8 mm. However, it is known that the jet of the liquid melt entering the mold can scour some sections of the crystallizer tube, which was why we conducted a series of meltings. That experimental series helped us optimize the wall thickness of the crystallizer tube for melting these SHS intermetallic-alloy workpieces (figure 5).

a ***b*** ***c***

Figure 5. Experimental crystallizers of different wall thickness. (a) 3 mm, (b) 5 mm, (c) 6 mm.

We first cast in Tube 1 with 3 mm walls, Figure 5(a). The figure shows how the tube walls were scoured by the liquid metal jet. Then we cast in the 5-mm tube. Figure 5(b) shows no scouring penetration, but one can still see clear fusing of the wall, which might have caused the final phase separation of the chemical composition along the electrode. Figure 5c shows no fusing of the walls; this sample was cut at five sections along its entire length of 650 mm. It was found out that casting caused no chemical interaction of the NiAl-based alloy with the inner walls. The alloy was retained in the tube by the TEC and the mechanical interaction facilitated by pre-made incisions on the inner walls.

3.4. Centrifugal atomization (PREP)

By parametric study of the centrifugal atomization of the consumable workpiece, we obtained microgranules [8] of high sphericity and homogeneous microstructure, see figure 6.

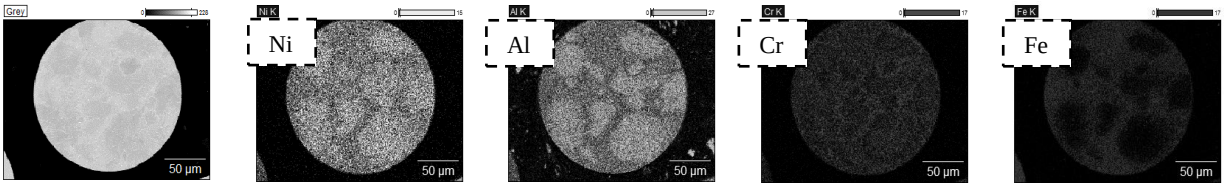


Figure 6. Distribution of elements in the microgranules obtained.

The microgranules had four structural components (Figure 6). The basic structural component of any microgranules was a NiAl dendritic grain. Dendritic branches had a typical size of 2 to 15 µm. Solid chromium-based solution was crystallized in the interdendritic space (the light-gray structural component in Figure 6). The solid chromium-based solution layer had a typical thickness of 0.5 to 2 µm. Fe was distributed across the entire volume of microgranules. We must note that after obtaining the cast electrode in a steel shell, the electrode was turned prior to centrifugal atomization. At this stage, we were able control the presence of the second component of composite microgranules (in this case, it was steel, thus Fe). Note that the microgranules had minimum shrinkage porosity, while the structure of microgranules was homogeneous for all the studied.

4. Conclusions

Single-stage centrifugal SHS casting method was used to synthesize a multi-component cast alloy based on NiAl-Cr-Co-Hf. The rapidness (combustion time 3 to 8 seconds) of the SHS process and the subsequent protection of the target product (alloy) from oxidation thanks to the Al_2O_3 slag layer enable the production of a cast alloy in air atmosphere, which would be difficult when using alternative metallurgy technologies or powder metallurgy. These obtained alloys were highly pure in terms of impurity (0 to 0.005, N – 0.0001 mass%); the entire volume of ingots featured a homogeneous structure.

We obtained a dependency of the kinematic viscosity of the studied melt on the heating/cooling temperature. Considerable reduction in viscosity was observed at greater temperatures, which is a

positive outcome when it comes to forming geometrically complex castings, where melt is cast in molds of varying shape.

A series of experiments was carried out to optimize the vacuum induction melting (VIM) of the SHS alloy, and the alloy was cast in a steel crystallizer tube. Therefore, we produced a double-layer electrode for plasma-rotating electrode process. The electrode was atomized to produce spherical microgranules, the microstructure whereof was analyzed.

The obtained results can be used to develop a comprehensive technology for producing composite microgranules consisting of an intermetallic alloy and the crystallizer-shell material (Me). Products made of such microgranules will have all the advantages of intermetallic alloys while retaining plasticity; such combination of properties might considerably reduce the energy and material costs of producing microgranules for selective laser melting (SLM) and electron-beam melting (EBM).

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