Nitriding during Powder Production and Study of the Structure of EP741NP Alloy Doped with Nitrogen

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\textbf{Abstract}—The development of modern equipment is limited by the physical and mechanical characteristics of the produced alloys, properties of which are often determined and enhanced by introduced alloying components. One of the alloying elements that have been very actively introduced in recent years is nitrogen. As a rule, alloying with nitrogen is carried out by ferroalloys, less often by gaseous nitrogen, which has significant advantages. In the processes of special electrometallurgy, alloying with nitrogen can be performed using, for example, nitrogen-containing plasma. Such a method may be feasible in the production of powder metal by spraying the ingot with nitrogen-containing plasma. It is known that performance properties of the products made of powder metal are significantly higher than those of cast metal. This stimulated the investigation of the properties of a product obtained from nitrided EP741NP powder alloy. In this work, a study of changes in the chemical composition, microstructure and microhardness of EP741NP alloy samples was carried out. The studied material was nitrided metal powders made on a plasma centrifugal atomization unit (PCAU) and ingots from granules obtained by hot isostatic pressing (HIP). The chemical composition of the obtained samples was determined by wave dispersion X-ray fluorescence spectrometry. In order to study the microstructure of metal powders and ingots, the methods of scanning electron microscopy with EDXS were used. Microhardness of the samples was assessed using a microhardness tester by the Vickers method. The analysis of gas impurities was carried out on a gas analyzer. It is shown that nitriding of heat-resistant EP741NP nickel alloy is possible at the stage of metal powder production, without significant loss of alloying components and a sharp change in chemical composition. An increase in microhardness of the obtained nitried samples was noted in comparison with the initial one.

\textbf{Keywords:} nickel-based alloys, nitrogen, powder metallurgy, plasma centrifugal atomization

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\textbf{INTRODUCTION}

Development of modern equipment requires metallurgists to produce the workpieces possessing increased mechanical and operational characteristics. An increase in the heat strength and reliability of the essential components operating at high temperatures and aggressive environment was mainly achieved by improvement and increase in complexity of the chemical composition of alloys, which resulted in the development of modern superalloys \cite{1, 2}. However, ingots of such alloys lose ductility due to the presence of a large number of elements and could not be processed using conventional methods. An increase in the amount of dendritic and zonal segregation and formation of cracks and pores due to a large number of alloying additives \cite{3} shows that the methods and technologies of iron and steel making are at the high at this stage of development.

At present, additive manufacturing is the technology, which could solve such problems and produce high-tech workpieces from hardly workable materials. Additive technologies could fabricate integral complex parts and units without welding, soldering, and other processes and provide low dendritic and zonal segregation thus increasing mechanical characteristics of the product \cite{4, 5}.

Technologies of melting of spherical powder materials, such as direct laser growth (DLG), selective laser melting (SLM), selective electron-beam melting (SEBM), and hot isostatic pressing (HIP) became widespread \cite{6–16}. Approaches to the preparation of metal powders, such as gas-jet and centrifugal atomization, are well known. Gas-jet atomization is often carried out in ceramic crucible, which leads to the observation of a high content of nonmetallic inclusions in the finished metal. Production of metal powders due to plasma centrifugal atomization involves the preparation of a round ingot (electrode) through
remelting of charge materials in vacuum-induction furnace (VIF) and subsequent vacuum arc remelting (VAR). Metal powder is produced through the fusion of the end of rotating electrode with plasma, composition of which can be varied with the aim to increase mechanical and operational characteristics of the produced grains on the plasma centrifugal atomization unit (PCAU). Preparation of metal powder along with nitriding of the melt by the plasma consisting of the mixture of inert gases and nitrogen can represent an integrated process, which could fabricate complex profiled parts without weld joints possessing increased hardness [17, 18].

The stages of formation of a solid metallic grain on PCAU are following:

— formation of film on the end of the ingot at the site of plasma heating;
— transfer of the liquid film from the center of ingot to the peripheral part due to centrifugal forces;
— formation of the drop of melt;
— detachment of drop of the melt from the ingot as a result of exceedance of centrifugal acceleration over surface tension;
— and crystallization of drop during free-flight motion.

The described mechanism of formation allows one to obtain dense metal powders with the minimum weight fraction of inert gas [19–24].

### MATERIALS AND METHODS

In this work, variation of chemical composition, microstructure, and microhardness of the specimens (metal powder and pellets) of the EP741NP alloy doped with nitrogen was investigated. Doping of the alloy with nitrogen was carried out at the stage of the fabrication of metal powders on the PCAU by using the plasma consisting of the mixture of argon and helium inert gases with nitrogen at varying percentage ratio.

The cast ingots employed for atomization and production of metal powder were produced through double remelting on VIF and VAR. The produced electrode that is 75 mm in diameter and 670 mm in length was transferred to the PCAU. The fabrication of metal grains due to nitrogen-containing plasma can be separated into following stages:

— fusion of the end of rotating electrode;
— formation of liquid drop on the end of ingot and its detachment from the electrode surface;
— and cooling and crystallization of grains in the mixture of inert gases and nitrogen.

The rotation speed of the ingot was 20000 rpm and the time of remelting of one electrode was ca. 20 min. The fractional composition of the produced metal-powder composition varied from 40 to 140 μm and the obtained powders were exposed to HIP.

Chemical composition of the specimens under study was determined on a Rigaku Primus ZSXII wave-dispersive X-ray fluorescent spectrometer. X-ray studies were carried out on a Rigaku MiniFlex 600 diffractometer (CuKα-radiation) equipped with a D/teXUltra 1D position-sensitive detector. Experimental diffractograms were processed using Rietveld method on a Rigaku PDXL 2 program and the ICDDPDF-2 database of inorganic compounds. Metallographic study of the specimens was performed on an Olympus PME-3 optical microscope at 100–500× zoom. Additional studies of structural features of granulated (powder) specimens were performed using a Tescan Vega 3 SB scanning electron microscope (SEM) at the accelerating voltage of 30 kV, which is equipped with an Oxford Instruments equipment for energy-dispersive elemental microanalysis.

The concentration of hydrogen, oxygen, and nitrogen in the specimens was measured through reducing melting in the graphite crucible in pulse resistance furnace in inert gas flow (argon and helium). Evolved hydrogen and nitrogen were determined using heat-conductivity detector; and oxygen, by the amount of evolved CO2 using infrared absorption. Analysis was performed in Rhen–602 and TC-600 gas analyzers of Leco Company.

Microhardness of the specimens was measured using the Vickers method; measurement was carried out on a LecoM-400-H microhardness meter, loading was 0.1 N, and the time under loading was 20 s.

### RESULTS AND DISCUSSION

The metal powders were prepared using plasma centrifugal atomization with a different composition of plasma-forming gas. Fig. 1 shows example images of the metal powders at different zoom. Composition of the plasma-forming gas is given in Table 1. Images of the grains in secondary-electron mode obtained by scanning electron microscope reflect the morphology of the surface of produced metal powders. As follows from Fig. 1, the grains are spherical, with a small number of satellites. Investigation of the microstructure of the EP741NP alloy specimens shows the presence of
dendritic segregation near large grains, which can be associated with the fact that crystallization of grains occurs at high rate.

Table 2 shows the chemical composition of the specimens after HIP.

Figure 2 shows the image of the microstructure of the specimens at different zoom recorded on the scanning electron microscope in reflected-electron mode after HIP from metal powders with a different nitrogen content.
Table 2. Chemical composition of EP741NP alloy samples after HIP, wt %

| Element | Al  | Si  | Ti  | Cr  | Fe  | Co  | Ni  | Nb  | Mo  | Hf  | W  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| HIP 1   | 7.56| 0.04| 1.83| 9.41| 0.10| 14.87| 54.16| 2.94| 3.82| 0.26| 5.02|
| HIP 2   | 7.77| 0.05| 1.81| 9.35| 0.09| 14.85| 54.01| 2.97| 3.83| 0.26| 5.00|

Table 3. Results of EDXS, %

| Element | Spectrum no. |
|---------|--------------|
|         | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ni      | 55.2 | 54.9 | 54.4 | 54.3 | 55.3 | 54.6 | 56.3 | 54.0 | 55.1 | 54.6 |
| Co      | 16.1 | 15.7 | 16.7 | 16.1 | 16.5 | 16.3 | 16.5 | 14.8 | 16.4 | 16.1 |
| Cr      | 9.5  | 9.5  | 9.6  | 9.7  | 9.7  | 9.7  | 9.5  | 9.5  | 9.6  | 9.7  |
| W       | 6.4  | 5.7  | 6.7  | 6.0  | 6.7  | 6.2  | 6.8  | 4.4  | 6.7  | 7.1  |
| Al      | 4.4  | 3.6  | 4.8  | 5.1  | 4.2  | 5.1  | 4.2  | 5.8  | 4.3  | 4.7  |
| Mo      | 3.7  | 4.0  | 3.6  | 4.1  | 3.7  | 4.0  | 3.3  | 4.4  | 3.7  | 4.0  |
| Nb      | 2.5  | 3.6  | 1.6  | 2.6  | 2.1  | 2.1  | 1.6  | 4.5  | 2.3  | 2.0  |
| Ti      | 2.1  | 2.4  | 1.6  | 2.1  | 1.8  | 1.9  | 1.8  | 2.6  | 2.0  | 1.9  |

Homogeneity of the powder under study was confirmed by the results of X-ray microanalysis of several grains, elemental composition of which varied marginally (Fig. 3, Table 3).

Fig. 2. SEM BSE images of microstructure of EP741NP alloy after HIP, nitrogen content in granules is (a) 0.021, (b) 0.026%.
ANALYSIS OF GAS IMPURITIES

The metal powders produced as a result of plasma centrifugal atomization represented the objects of study of the content of gas-forming impurities in the specimens of EP741NP alloy. Results of analysis are given in Tables 4 and 5.

These data show that employment of PCAU with the nitrogen-containing plasma could provide the concentrations in the melt, which are 40–50 times as large as the initial nitrogen content. These results conditionally agree in practice with previously calculated theoretical data from [25] (calculated nitrogen content is 0.073% upon treatment with plasma-forming gas at \( R_{N_2} = 0.2 \text{ atm} \)). This indicates the possibility of the process and formation of the nitrided alloy at the stage of the production of metal powders.

| Table 4. Chemical analysis of the initial samples for the content of gaseous impurities, wt % |
|------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Element                            | Hydrogen        | \( S_d \)       | Oxygen          | \( S_d \)       | Nitrogen        | \( S_d \) |
|------------------------------------|-----------------|-----------------|-----------------|-----------------|
| EP741NP                            | 0.00006         | –               | 0.0010          | 0.0005          | 0.0005          | 0.0001 |

\( S_d \) is the standard deviation.

| Table 5. Results of chemical analysis of EP741NP alloy samples obtained in the presence of nitrogen in plasma, wt % |
|------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Element                            | Oxygen          | \( S_d \)       | Nitrogen        | \( S_d \)       |
|------------------------------------|-----------------|-----------------|-----------------|-----------------|
| EP741NP no. 1.1                    | 0.0069          | 0.0005          | 0.021           | 0.001           |
| EP741NP no. 1.2                    | 0.0065          | 0.0005          | 0.020           | 0.001           |
| EP741NP no. 2.1                    | 0.0063          | 0.0005          | 0.025           | 0.001           |
| EP741NP no. 2.2                    | 0.0064          | 0.0005          | 0.026           | 0.001           |

MICROHARDNESS MEASUREMENT

Figure 4 shows the results of microhardness measurement (in HV\(_{0.01}\) units) of the EP741NP alloy specimens in various states. As follows from the diagram, microhardness of the considered metal grains with the nitrogen content of 0.021 and 0.026% increased as compared to initial specimen. An increase in the microhardness of the specimens after HIP as compared to the initial state can be associated with an increase in the density of the specimen and additional strengthening at accelerated phase-structural transformations.

Figure 4 shows the microhardness values of the specimens obtained as a result of plasma centrifugal atomization of the nitrogen-containing plasma and subsequent HIP. The diagram shows that an increase in the nitrogen content results in the increase in...
microhardness by 10% as compared to the standard EP741NP specimen.

CONCLUSIONS

Technology of production of nitrogen-containing metallic powders at the stage of their production using the mixture of plasma-forming gases consisting of argon, helium, and nitrogen on PCAU has been studied. It has been shown that employment of nitrogen as a plasma-forming gas on the equipment of special electrometallurgy, in particular, on PCAU, could increase the concentration of nitrogen from 0.0005% in the ingot to 0.025% in the finished metal. Study of the microstructure and chemical composition of the grains has shown that employment of nitrogen-containing plasma does not notably alter the structure of the alloy and its homogeneity. The metal powder under study, fractional composition of which was 40–140 μm, has been exposed to HIP and microhardness measurement via Vickers method. These results have demonstrated an increase in the measured microhardness from the factor of 539 in the case of the cast alloy to 594 HV,0.01 in the case of the specimens after HIP. This could indicate that an increase in the concentration of nitrogen in the melt affects positively the characteristics of the powder alloy under study.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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