Research of the effect of preliminary preparation on characteristics of powders for modification of nickel superalloys

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Abstract. To improve the mechanical and operational properties of nickel alloys, complex modification has become widespread, in which refractory compound powders are used as inoculants. However, industrial powders are distinguished by a significant scatter of the specific surface and particle dispersion values. The aim of the work was to study the effect of the preliminary preparation of powders on their dispersity and dimensional stability. A method is proposed for preparing ultradispersed powders of plasma chemical synthesis for introduction into a liquid metal, including high-temperature purification of particles using ultrasonic vibrations of $17 \cdot 10^3$ Hz with an input power of 20 W/cm^3 in the melt of alkali metal halides. It is established that the preliminary preparation of powders provides activation of particles and increases their dispersion by five times, dimensional stability by seven times, and the number of particles of nano-sized level increases to eight times.

1. Introduction

The development of blanking production of machine-building enterprises is inextricably linked with the improvement of the technology for manufacturing steel workpieces. Particularly relevant is the problem of manufacturing billets responsible destination of nickel-based alloys. The physicomechanical and service characteristics of foundry billets are mainly determined by the state of the metal structure. The processes of controlling the crystalline structure of a metal by changing only the thermophysical parameters of its crystallization at the present time do not provide for obtaining the required structure and, accordingly, physical and mechanical properties.

There are known technologies for improving the properties of castings from frying alloys on nickel base through the use of complex modification by dispersed synthetic refractory particles [1–5]. The main obstacle to the direct introduction of such particles into metal melts is the high values of the surface tensions of the melts and the presence of contaminants on the surface of these powders, which worsen their wettability with the metal. However, an increase in the melt temperature, the use of fluxes of optimal composition and, most importantly, preliminary special preparation of refractory particles can minimize the difficulties associated with the introduction of particles into the metal.

In order for the particles of refractory compounds to play the role of crystallization substrates, they must have certain and preferably the same size, be well moistened with molten metal and evenly distributed throughout its volume. Fulfillment of these requirements is connected with the necessity of preliminary preparation of powders before their use, since, as it was established, commercial powders of refractory compounds are characterized by a considerable difference in grain size and surface oxidation of particles, which deteriorates their wettability with molten metal [2].

2. Formilation of the problem

At present, ultradispersed powders obtained by the method of plasma chemical synthesis (PCS) are used as inoculators for complex modification of steels and alloys [6, 7]. Such powders are produced at the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences, the Center for Powder Technologies of the Siberian State Mining and Metallurgical Academy, the Institute of Metallurgy named after Academician A. A. Baikov and others. Table 1 shows the chemical composition and specific surface values of some PCS powders.

Table 1. Powder characteristics PCS

Powder	element, %						F_s, m^2/g
	Ti, Al, Mo, W, Nb	Si, B	N_2	C	O_2	impurities	
TiCN – 1	70 - 71	-	8 - 13	2 - 7	10 - 12	2,0	17
TiCN – 2	70 - 71	-	8 - 13	7 - 12	8 - 9	1,5	10
Si_3N_4 - 2	-	65,0	20 - 21	-	9 - 10	5,0	30
Si_3N_4 - 3	-	45 - 50	20 - 21	-	24 - 26	6,0	40
AlN	60 - 65	-	30 - 35	-	2	0,8	35
TiC	70 - 79	-	-	19 - 20	2,5	0,4	23
SiC		90-92	-	0,8	3,5	4,0	16
TiB_2	59 - 63	30 - 33	-	-	6 - 7	1,3	48
NbC	88 - 85	-	-	8 - 12	2,5	0,8	29
NbCN	80 - 83	-	4 - 9	4,0-4,5	3 - 5	2,3	35

Such a significant variation in the properties of the presented powders depends on the type of raw materials and features of the technological process of plasma-chemical synthesis.

Improving the processing efficiency of the refractory compound powder and facilitating its introduction into the molten metal can be achieved by cleaning particles with ultrasound in a liquid medium from a melt of metal halides, and plating these particles with metallizing additives dissolved in this melt.

In this work, the powder was mixed with ultrasound and cleaned in the melt with a composition of 30 % KCl – 70 % $BaCl_2$, which has a relatively low melting point (about 800 ºC) and at the same time a rather high density at this temperature (about 3 g/cm^3). The processing of powder particles was carried out with ultrasonic vibrations at a frequency of 17 kHz with an input power of 20 W/cm^3. Mixing and uniform distribution of the powder, which constituted 25 % of the volume of the melt, was carried out for 15 minutes. Melting of salts is carried out in a metal crucible placed in a heating furnace. After melting and reaching a predetermined temperature, the end of the ultrasonic tool – emitter is immersed in the melt and the powder of the refractory compound is poured in small batches.

The task of the work is to study the effectiveness of the proposed technology of pretreatment of ultrafine particles of the powders of the modifying complexes.

3. Object and research methods

The object for research in the work is the powder TiCN-1, which has found application for modifying steels and alloys [1, 4, 5].

The dispersion of particles was determined by the method of diffraction (scattering) of laser radiation on particles of the dispersed phase in ethanol using a SALD-2101 laser analyzer.

Evaluation of the appearance of the powder was carried out on a Carl Zeiss AXIO Imager A1m optical microscope.

The method of transmission electron microscopy (TEM) on the JEM 2010 apparatus was used to evaluate the morphological and crystallographic characteristics of the powder under study. For this purpose, a polymer film with a thickness of 10–20 nm was placed on the copper mesh, onto which TiCN powder previously ground in an agate mortar was sprayed.

Non-destructive analysis of the powder elemental composition was carried out on an OPTIM'X ARL wave dispersion spectrometer using X-ray fluorescence analysis using the WinXRF «Thermo» software [8].
To determine the physicochemical parameters of the powder, depending on the temperature, thermogravimetric and differential thermal analyzes were used on a NETZSCH STA449C instrument equipped with a mass spectrometer.

4. Results of experiments and discussion

The results of the particle dispersion study are shown in figure 1. The X axis shows the values of particle diameters, the Y axis shows the volume fraction in percent of particles of a given size.

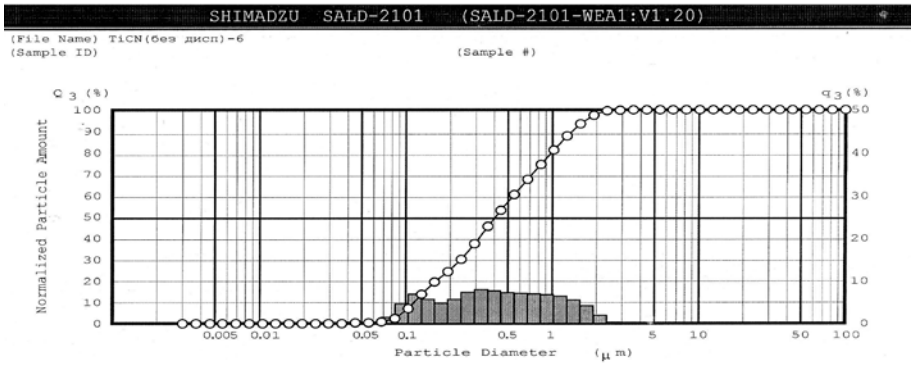


Figure 1. The distribution (in %) of the particles of the investigated powder size.

Studies have shown that the dispersion of particles of TiCN powder, obtained in industrial production, has a variation in a wide range – from 0.03 to 3.5 μm. At the same time, the volume fraction of nanoscale particles is insignificant. The average particle size for a series of two measurements is in the range from 0.402 to 0.419 μm and 50 % of the particles of the powder under study have sizes of 0.407–0.427 μm (figure 2).

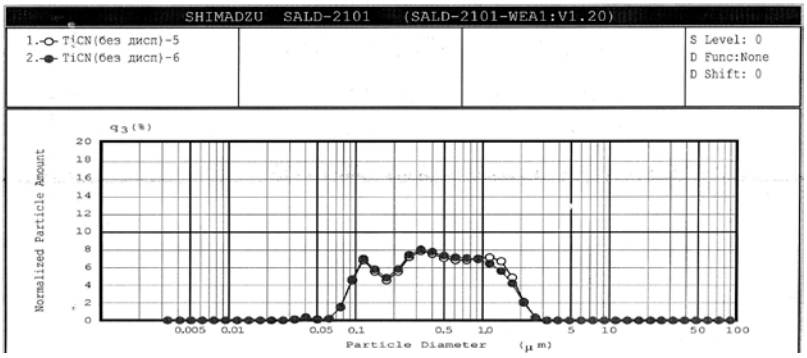
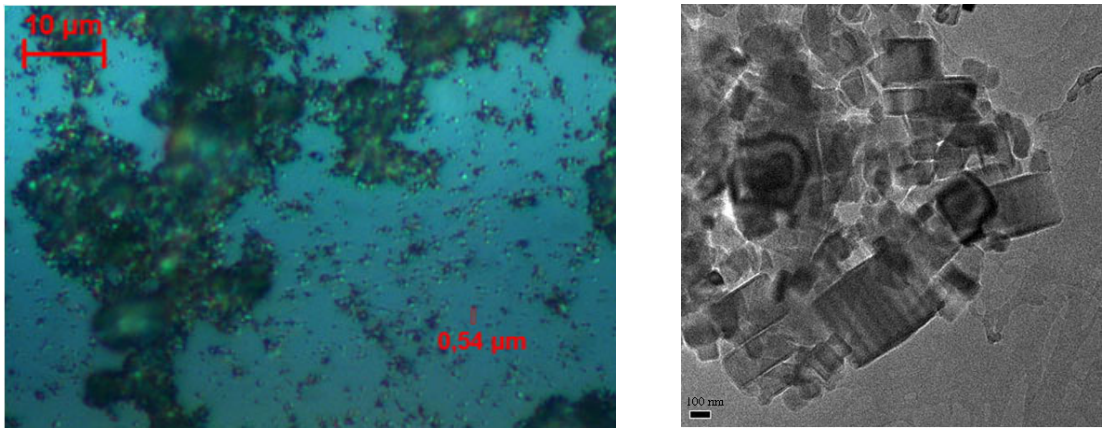


Figure 2. Differential distribution curves of particle size powder.

The appearance of the powder particles is shown in figure 3, a. The image shows that the powder consists of both individual particles and their conglomerates of 2–40 μm in size.



(a) (b)

Figure 3. Appearance (a) and granular composition (b) of the investigated powder.

Studies by the method of transmission microscopy (figure 3, b) showed that the bulk of the TiCN powder consists of particles larger than 100 nm in size and having different geometric shapes. Individual particles reached a size greater than 1000 nm. Particle crystals have cut elements with angles close to 90 °, i.e. cubic symmetry, and more rarely cut elements with angles close to 120 °, i.e. hexagonal symmetry. Such forms are characteristic of titanium nitrides and carbonitrides. At the same time, particles of rounded shapes are observed in the powder, which can be attributed to conglomerates of small particles.

X-ray fluorescence analysis (figure 4) showed the presence of titanium with chromium impurities in the sample. Vanadium may be present, but this indication may occur due to the overlapping of peaks from titanium and chromium.

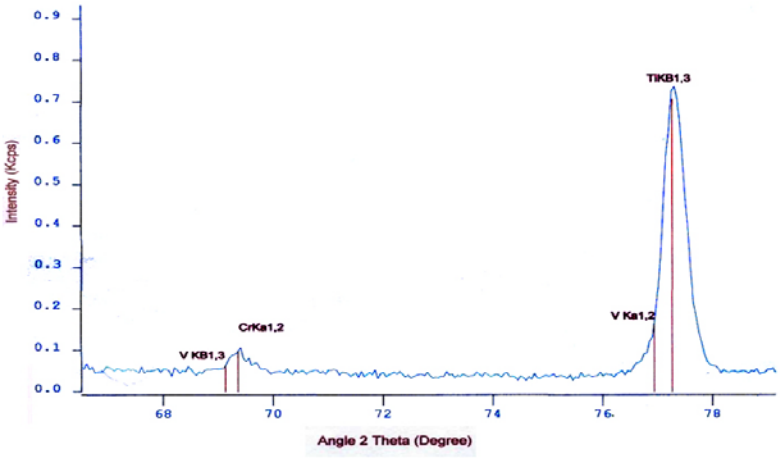


Figure 4. X-ray fluorescence spectrum of the investigated powder.

In figure 5 shows the results of thermogravimetric and differential thermal analyzes.

Analysis of the TG and DTG curves shows that during the heating process, a general increase in the sample mass occurs, which reaches up to 31 % up to 1000 °C.

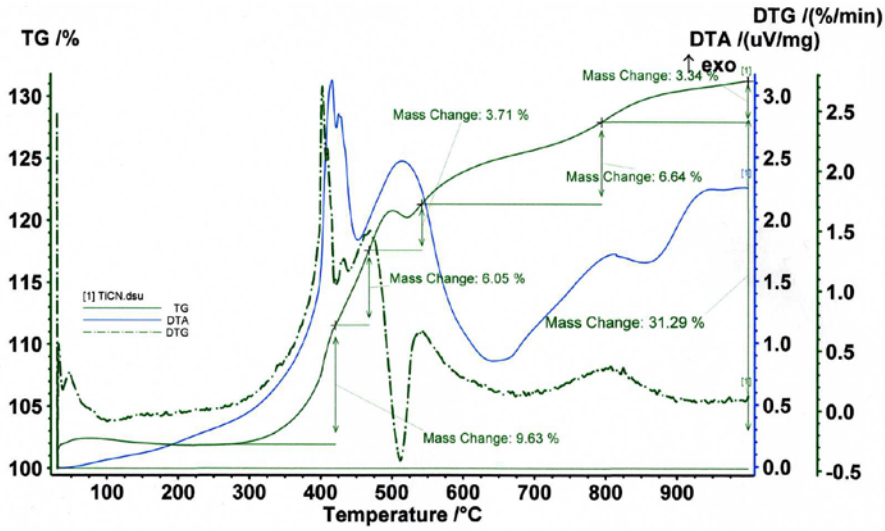


Figure 5. The results of thermogravimetric and differential thermal analysis of the investigated powder.

In the temperature range from 250 °C to 450 °C, an increase in the mass of the powder with a complex exothermic effect is clearly visible. When this occurs, the release of NH_2 and NH_3 (figure 6). When heated in the range from 440 °C to 600 °C, the release of CO, CO_2, N_2 is observed.

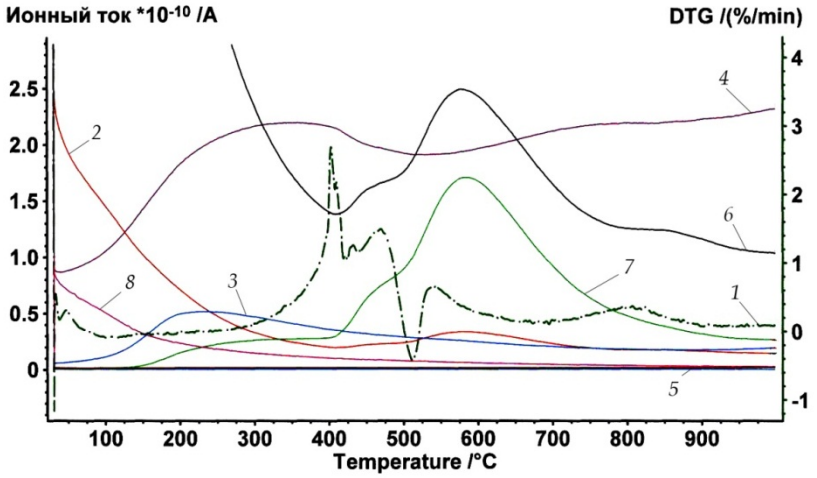


Figure 6. The results of thermal (1) and mass spectral (2-8) analyzes: 1 – DTG (1); 2 – CO; 3 – NH_3; 4 – NH_2; 5 – H_2; 6 – CO_2; 7 – N_2; 8 – O_2.

It is known that ultradispersed powders absorb oxygen and water vapors upon contact with air, the amount of which depends on the specific surface area of the particles [11]. When an inoculator is introduced into the melt, the particles of the powder interact with these gases during heating, which may cause a decrease in the effect of modification. Desorption of dissolved gases during heating is characterized by the process of their molecular isolation at the interface. In this case, the powder particles float to the surface of the melt, where they are oxidized and subsequently not wetted. The composition of the desorbed gases includes nitrogen, oxygen, hydrogen, and water vapor [9]. The latter are actively removed when heated already at 200-300 °C.

Analysis of the chemical composition of ultrafine powders of refractory compounds showed that with thermal vacuum treatment, there is no decrease in the O_2 content, the amount of which remains in the range of 4-26 % in the form of chemical compounds (oxycarbides, oxynitrides, oxycarbonitrides).

These compounds form films with a thickness of up to 2.0 nm in the surface layers of the particles and impair their wettability by the melt [10].
Analysis of the dispersion of powder particles after ultrasonic treatment showed that the particle size is in the range from 0.029 to 0.547 μm (figure 7).

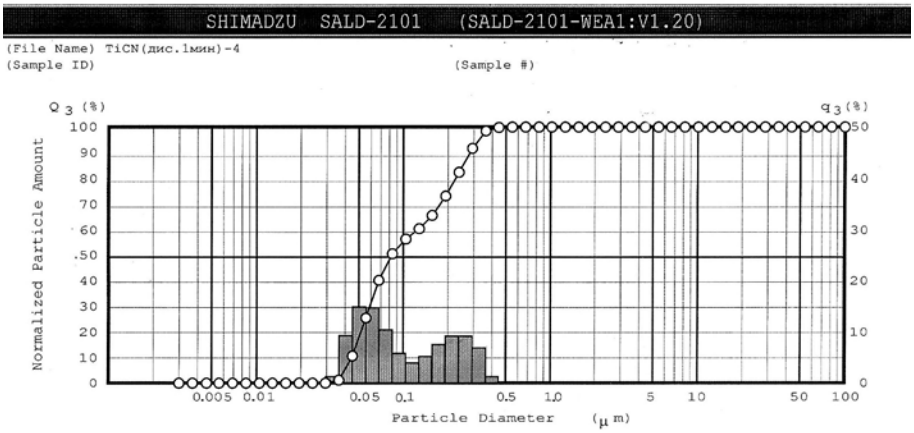


Figure 7. The size distribution (%) of the particles of the investigated powder after ultrasonic treatment.

50 % of the powder particles have a size in the range of 0.078–0.083 μm, while the average particle size is determined to be 0.097–0.102 μm (figure 8). Thus, compared with industrial powders, the average size has decreased by more than four times, and the proportion of nano-sized particles has increased almost eight times.

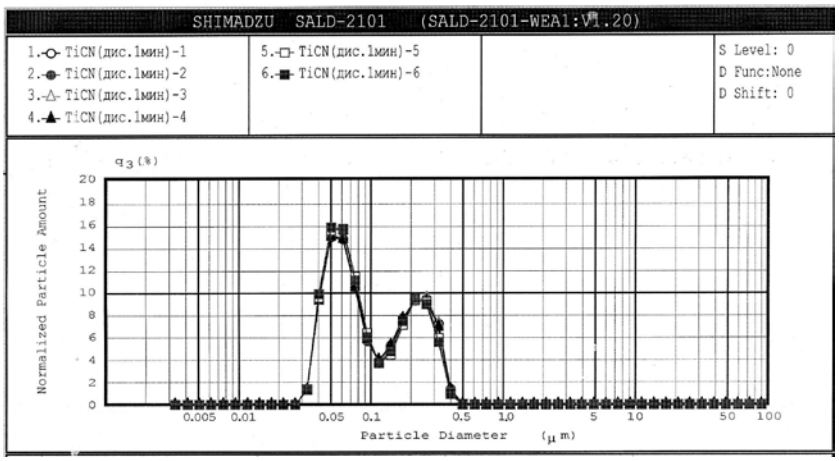
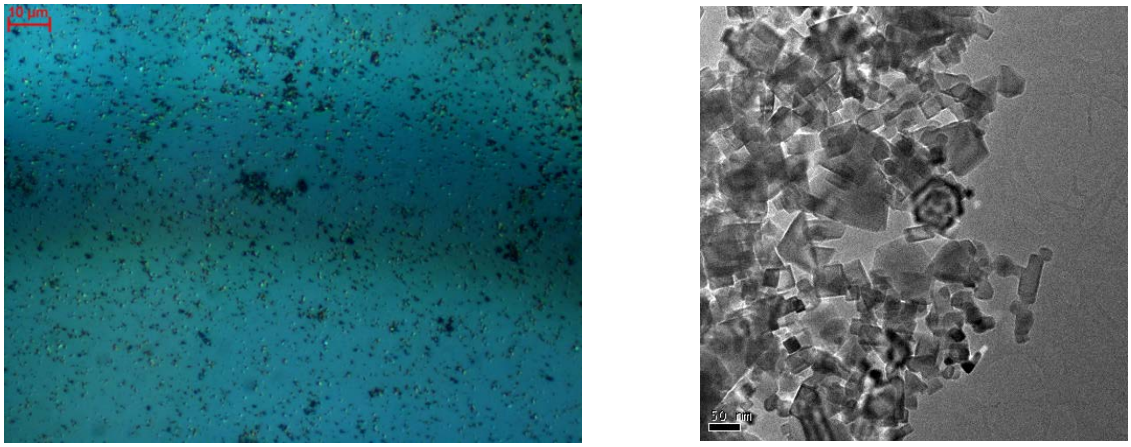


Figure 8. Differential distribution curves of the particle size of the powder after ultrasonic treatment.

The investigated powder after ultrasonic treatment is mainly individual particles of small size (figure 9, a). At the same time, conglomerates of particles are almost not observed.



(a) (b)

Figure 9. Appearance (a) and granular composition (b) of the powder after ultrasonic treatment.

Electron-microscopic analysis of the powder after ultrasonic treatment showed that most of the particles are 50–100 nm in size (figure 9, b). The geometric shape of the powder particles is varied.
The results show that the preliminary preparation of powders provides activation of particles and increases their dispersion by five times, dimensional stability by seven times, and the number of particles of nanoscale level increases up to eight times.

5. Conclusions

It was established that the particle size of industrial-grade TiCN powder produced by plasma-chemical synthesis is 0.03–3.5 µm, with an average size of 0.402–0.419 µm. The composition of the desorbed gases when the powder is heated includes NH_2, CO, CO_2, N, O_2 and water vapor. This indicates the need for pre-treatment of the particles of an inoculum, which ensures their degassing and dispersion, before entering the melt.
A method is proposed for preliminary preparation of particles of powders of refractory compounds, including the high-temperature treatment of particles in a molten metal salt using ultrasonic vibrations of $17 \cdot 10^3$ Hz. It was shown that as a result of processing, the particle size of the powder under study is in the range of 0.02–0.547 µm, with an average size of 0.097–0.102 µm, that is, more than four times less than that of powders without treatment.
The effectiveness of the preliminary preparation of powders allows us to recommend it in the technology of modifying with complex modifiers of superalloy nickel-based alloys.

6. References

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