Evolution of dispersion of high temperature chromium compounds

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Abstract. Chromium compound – boride \( \text{Cr}_3\text{B}_2 \) and carbide \( \text{Cr}_3\text{C}_2 \) are hard, wear-resistant, chemically inert materials, demanded for production of protective coatings of metals and cermets as components and alloying additives of tungsten free solid alloys. Future prospects for expansion of boride and chromium carbide usage are related to their production in the form of nanopowders. The researches into change of the particles shape and size of high-temperature chromium compounds in the conditions of plasma flow were carried out. There is coarsening of boride and carbonitride particles of nanoscale level at the reduction in the linear velocity of their growth.

1. Introduction

The priority directions of modern machine building require materials that can be used in the conditions of simultaneous exposure to high temperatures, high loads and corrosive environments. In this regard, the role and significance of high temperature synthetic superhard compounds – carbides, borides, nitrides, oxides and their combinations is constantly rising. Among them are chromium compounds – boride \( \text{Cr}_3\text{B}_2 \) and carbide \( \text{Cr}_3\text{C}_2 \) which are hard, wear-resistant, chemically inert materials, demanded for production of protective coatings of metals and cermets as components and alloying additives of tungsten free solid alloys. [1-3]. Future prospects for expansion of boride and chromium carbide usage are related to their production in the form of nanopowders. Boride and chromium carbide in the nanostate opens up new directions for their application, including for electroplating, surface and volumetric modification of metal alloys and polymers. All this demonstrates the need for further development of the technological base of boron – carbon-containing chromium compounds. Comparison of different technologies for producing powders of refractory compounds indicates that to achieve the nanoscale level, first of all, the technology based on the use of highly concentrated energy flows for the raw material gasification and formation of the desired product at a volume condensation from the gas phase is required. Among such techniques the plasma method is characterized by relative simplicity, and it is the most studied and competitive method [4].

Currently, the empirical approach to the study of nano-products enlargement in the conditions of plasma synthesis is the most informative, establishing the connection between the characteristics of dispersion with the temperature as the main factor controlling the dispersion, as another important factor – the mass of condensate concentration in the flow is maintained close to the maximum during the plasma processing of the powdered raw material.
The aim of this work is to study changes in the particles shape and size of high temperature compounds of chromium – boride \( \text{Cr}_3\text{B}_2 \) and carbide \( \text{Cr}_3\text{C}_2 \) in the conditions of plasma flow.

2. Experimental research and results
Considering plasma syntheses of diboride and chromium carbonitride as three-stage processes comprising transition of the initial raw material into the vapour state, the synthesis itself and formation of nano-disperse product (condensation, coalescence, crystallization, coagulation), it should be noted that the least studied of these stages is the latter. This is due to the short duration of the processes of nano-disperse product formation (up to 20-25 ms) and the absence of reliable diagnostic and monitoring tools operating in these conditions. In such circumstances, a model-mathematical approach is very promising.

In [5] the authors offered a generalized mathematical model of carbide formation during plasma synthesis of silicon carbide, which includes sub-models “Evaporation of raw materials” and “carbonization of raw materials” providing, in combination with the software complex, the execution of multiple research and engineering design calculations of the reactor parameters and the efficient plasma processing of various types of silicon-containing raw material into carbide. However, the model does not contain sub-models “Condensation”, responsible for the formation of nano-disperse product, which generally reduces the significance of the results achieved by the authors [7].

In [5, 6] a theoretical analysis of the possibility of building a condensing block of the model within the technological process of volume condensation was performed, providing quantitative predictions of dispersion for the obtained nano-products. The analysis is based on the scheme of formation of the desired nano-disperse product by converting the supersaturated single-component vapour into a disperse condensation followed by the evolution of its dispersed composition first by liquid-drop coalescence, and then – aggregate coagulation.

According to the authors [5, 6], the volume condensation can be described by the equation of Szilard-Farkas, but much simplified due to the theoretical and experimental indeterminacy of a number of factors included in it and adapted to the system without chemical interactions with spatially homogeneous conditions, i.e., far from reality. In [5, 6] there is no assessment of the results reliability for prediction of dispersion of solid particles of condensation origin, specific examples and simulation results, which limits the technological feasibility of this approach.

Taking into account the estimation nature of the results obtained in the result of theoretical modeling of condensation processes, the authors in [7 - 9] conducted for a number of substances an experimental study of the temperature dependence of the average sized particles as they rise in the plasma flow. The statistical processing of the results for the temperature conditions of coagulation was made in the form of dependence

\[
\bar{d} = A \cdot T^{-m}
\]

where \( \bar{d} \) – particle average size;
\( A \) – coefficient depending on physical properties of the condensate;
\( T \) – temperature.

The results, described in [6, 7], are shown in Table 1.

The temperature dependence of the composition and dispersion of the condensed products of diboride and chromium carbonitride synthesis were based on probe selection of condensate from different areas of the reactor. Sampling was carried out in the temperature range 2600-2000 K.
Table 1. Temperature dependence of the particles size of various substances during their growth in the plasma flow.

| Substance    | Temperature range, K | Variation $d \cdot 10^9$, m | Coefficients in equation $d = A \cdot T^{-m}$ | Information sources |
|--------------|----------------------|-----------------------------|-----------------------------------------------|---------------------|
| Ni           | 2200–800             | 70–121                      | A $(2.413\pm0.559) \cdot 10^{-6}$, $m 0.451\pm0.090$ | [6]                |
| W            | 3000–2200            | 30–46                       | A $(1.023\pm0.246) \cdot 10^{-4}$, $m 1.423\pm0.297$ | [6]                |
| W            | 2300–1800            | 43–85                       | A $40.231\pm5.112$, $m 2.401\pm0.554$          | [6]                |
| Si+$\text{Si}_3\text{N}_4$ | 2200–1650         | 28–59                       | A $(0.924\pm0.193) \cdot 10^{-4}$, $m 1.304\pm0.251$ | [6]                |

The temperature of synthesis products in different zones of the reactor was assumed to be equal to the average weight temperature of the flow. At each temperature level, the samples were taken from the central zone of the plasma flow, i.e., along the reactor axis, three times at intervals of 10 minutes, and the results of quantitative determinations were averaged.

The phase and chemical composition of the synthesized condensed products diboride and chromium carbonitride were studied by the methods of X-ray and chemical analysis, and their morphology and dispersibility were determined by transmission and scanning electron microscopy. In the first case the studies were conducted using a transmission electron microscope EF/4-M/P “Karl Zeis” with an accelerating voltage 65 kV.

While preparing the material the weight 0.1 g was mixed with 500 ml of 50% ethanol solution and treated by ultrasound in the disperser 3 DH-1 for 15-30 min. A drop of the resulting slurry was applied on the coal substrate with thickness 0.10-0.25 µm and dried at a temperature of 323 K. During work with the nanopowders the magnification was 40000. In the second case a scanning electron microscope JSM-6700F with an accelerating voltage 0.5-30 kV and resolution 0.1 nm at 15 kV and 0.22 nm at 1 kV was used. For preparation of the material on the preliminary rolled indium plate of size 10x8x1 mm a nanopowder was sprayed; the sprayed layer was pressed in, and the remains were removed by surface blowing. Further with the magnification up to 300000 the particles were examined impregnated into the metal matrix. The specific surface area of nanopowders was determined by the thermal desorption of argon in the installation IPM NAN made in Ukraine in accordance with the State Standards (GOST) 23401-78 (with some changes introduces after January 01, 1985). The essence of the method consists in determining the argon amount adsorbed on the surface of nanopowders from the flow of an argon-helium mixture with the predetermined concentration (usually argon 5-7%, helium 93-95%) at a liquid nitrogen temperature, followed by its desorption into the same mixture at a temperature increase up to 293±5 K. Sample weight is 0.05-0.10 g. The samples treatment is performed by argon blow at a rate $(0.5-0.8)\cdot 10^{-6} \text{m}^3/\text{sec}$ at a temperature 673 K for 40-50 min. The error of the surface area measurement does not exceed 5%. The average particle size was calculated by the formula

$$d = \frac{6}{0.8 S_{\text{spec}} \rho}$$

$S_{\text{spec}}$ – the specific surface of the sample, $\text{m}^2/\text{kg}; \rho$ – material density, $\text{kg/m}^3$.

The experimental studies were carried out for three technology variants of chromium boride synthesis $\text{CrB}_2$ in the nitrogen-hydrogen plasma flow of powder mix containing chromium – boron, chromium chloride – boron, chromium oxide – boron, and one the most optimal technological variant of chromium carbonitride $\text{Cr}_3(\text{C}_{0.80}\text{N}_{0.20})_2$ – carbonization of chromium powder with natural gas in the plasma flow of nitrogen [9].
Micrographs of chromium diboride nanopowder obtained by TEM with the use of the prepared material (Figure 1) provides visualization of individual particles, definition of their size and statement of nanoscale, confirmation particles shape close to spherical.

![Micrographs of chromium diboride nanopowder](image)

**Figure 1.** Micrographs (TEM) of chromium diboride of plasma synthesis from chromium (a), its chloride (b), oxide (c) and the magnesium-thermal synthesis from chromium (d).

Analysis of the micrograph also helps to establish the basic nano-particle size range corresponding to 20-50 nm. The average and maximum size of nano-particles of chromium diboride is 42.0 and 90.0 nm. The spherical shape of nanoparticles suggests that the boride formation proceeds according to the mechanism “vapour- melt-crystal”.

Micrographs of raster electron microscopy of chromium diboridenano-powder are shown in Figure 2, from which it follows that the nanopowder in the as-received condition is presented by aggregates of spherical shape with various sizes – from 150 to 500 nm, formed by spherical particles of a wide sizes range – from 20 to 80 nm, the number of which in the aggregate depends on its size.
Figure 2. The micrographs (raster electron microscopy) of chromium diboride nanopowder of plasma synthesis from chromium boron-containing mix: a – in the as-received condition; b – morphological pattern of the aggregate; c – the ensemble of particles and aggregates; d – the individual particles.

Nano-level and morphology of the particles can be considered as products of chromium microdroplets boriding, produced during the volume condensation of its vapour, liquid-drop coalescence and crystallization, and the presence in the examined samples of aggregates of various sizes indicates a high likelihood of further nanoparticles coarsening at the lowered temperatures by their coagulation [10].

Indeed, in the studied temperature range (2600-2000) K we can see coarsening of boride particles with the reduction of linear velocity of their growth (Figure 3a). Linear velocity of the nanoparticles growth is $(0.86 \div 2.65) \cdot 10^{-6} \text{m} \cdot \text{sec}^{-1}$.

The average size of the diboride nanoparticles increases from 46 to 52 nm and varies with the temperature as follows:

$$d = (2.30 \pm 0.04) \cdot 10^{-6} T^{(0.471 \pm 0.105)}.$$

(3)

Consequently, the diboride nanopowder coarsens in 1.15 times.
Figure 3. Dependence of particle size (d) of chromium boride (a), chromium carbonitride (b) and the linear velocity of their growth (I) on the flow temperature (T).

The micrographs of chromium carbonitride, obtained by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) using the prepared materials, are shown in Figures 4 and 5, respectively.

Figure 4. Micrograph (TEM) of nano chromium carbonitride.

Nanopowder of chromium carbonitride is represented by aggregates of spherical shapes with a size from 600 to 150 nm, formed by globular particles with a rather wide size range – from 20 to 80 nm, the number of which in the aggregate depends on its size. Nano-level and morphology of particles allow us to consider them as products of chromium microdroplets carburizing, generated during volumetric condensation of its vapor, liquid-drop coalescence and crystallization, and the presence in the examined samples of aggregates of various sizes indicates a high likelihood of further coarsening of the nanoparticles at the lower temperature by their coagulation. Indeed, in the studied temperature range (2600-2000) K we can see a steady carbonitride particles coarsening during natural decrease of linear velocity of their growth (Figure 2b). The linear velocity of the nanoparticles growth is \((2.96\pm6.04)\times10^{-6}\text{ m sec}^{-1}\).
The average size of the carbonitride nanoparticles increases from 41 to 90 nm and varies alongside with the temperature:

\[ d = (726 \pm 35.1) \cdot T - (2.96 \pm 0.44). \] (4)

Consequently, carbonitride nanopowder coarsens in 2.2 times.

The results analysis of the dispersion evolution of high-temperature chromium compounds indicates the increased influence of the temperature on the processes of coarsening during transition from the liquid-drop coalescence to aggregate coagulation. The linear velocity of the particle growth was \((0.2-1.2) \cdot 10^{-6} \text{ m} \cdot \text{sec}^{-1}\), and the achieved level of dispersion did not exceed 80-120 nm. Such behaviour of the dispersion change with the temperature for high temperature chromium compounds may be due to a special energy state of nano-dispersed systems.

**Figure 5.** The micrographs (SEM) of nano- chromium carbonitride: a – exterior view; b – morphological pattern of the aggregate; c – ensemble of particles and aggregates; d – the individual particles.

Nano-sized level of the powder provides increased stresses in the crystal lattice, accumulation of line and point defects, and defects of a grain boundaries type. The boundary is the major defect in the nano-dispersed systems. In such systems, in contrast to conventional powder systems and polycrystals the ratio of the total area of boundaries to their volume is by 4-5 orders of magnitude greater than, for example, in the polycrystal with a grain size \(\approx 100 \mu\text{m}\).

### 3. Conclusions

Researches of the change in the particles shape and size of high temperature chromium compounds in the conditions of plasma flow were conducted. There is a coarsening of boride and carbonitride particles of a nanoscale level at the reduction of the linear velocity of their growth. Such behaviour of the dispersion variation of carbide and chromiumboride nano-powders might be due to the capacity of
the initial nanoparticles of metallic compounds to the solid phase coalescence (primary recrystallization) inside the aggregates. The results showed that the achieved level of dispersion of high temperature chromium compounds does not exceed the nano-scale level (80-120 nm), which opens up new areas of their application, including electroplating, surface and volumetric modification of metal alloys and polymers.

4. References

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