Structure and properties of dispersion-strengthened-with-nanosized particles refractory hard material TiC–Ni-alloy

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Abstract

Some particularities of the effect of nanocomponents such as ZrO2, Al2O3, W, WC, WC–Co, NbC, Si3N4 on the combustion process, the structure, and mechanical properties of a novel electrode dispersion-strengthened alloy TiC–40% Ni have been studied. The refractory hard alloy based on titanium and a nickel alloy has been produced by the method of self-propagating high-temperature synthesis. It has been shown that introduction of a nanosized powder causes reduction of the combustion velocity depending on the specific surface area of the additive. It has been found that upon introduction of nanodispersed powders into the green mixture the product structure undergoes significant modification. The ZrO2 and NbC additives produce a positive effect on the main mechanical characteristics of the alloy (its strength, hardness, and crack resistance). In contrast, these properties are negatively affected by the Al2O3 and Si3N4 nanopowders. Enhancement of the material bending strength and crack resistance can be achieved by respective addition of WC–Co and W, WC.

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1. Introduction

The industry of today advances elevated requirements to the quality and mechanical characteristics of the materials used. Some of them are successfully overcome by employment of self-propagating high-temperature synthesis (SHS) or combustion synthesis. Physical–chemical and technological peculiarities and regularities of SHS are well known [1–4]. This method has a number of advantages over the conventional powder metallurgy, e.g. low energy consumption, low-cost equipment, short-term technological cycles, etc. At present, the use of nanosized powders as starting reagents and modifying agents to improve the product performance characteristics is of a great interest. Small amounts of nanosized powders added produce a rather positive influence on the material characteristics owing to their unique properties, large specific surface and small dimensions.

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The TiC–40% Ni-alloy used in the present study is an attractive electrode material for deposition of refractory, wear-resistant coatings on the articles of titanium and nickel alloys that are widely spread in the aircraft building [4–7]. High-temperature mechanical properties of Ni-based refractory alloys are determined by the presence of structural coherent formations of the γ'-phase (Ni3Al), which retains its stability up to relatively high temperatures. High solubility of alloying elements in the nickel matrix, which is characteristic of all nickel alloys, is of a particular interest. Nanopowder additives are known to exert a positive effect on the material properties [8–10].

Modifying agents used in the present study are nanosized powders produced by sol–gel and plasma-chemical methods [11]. The major criterion of their choice was a high melting point exceeding the combustion temperature. Since the combustion temperature of the green mixtures is of an order of 2000 °C, the ZrO2, Al2O3, W, WC, WC–Co, NbC, Si3N4 powders that have different wettabilities with the titanium and nickel melts were used as nanodispersed additives. Besides, ZrO2 micropowder with an averaged particle size of <20 μm was used to
compare the influence of nanosized particles on the properties of the given alloy.

The present study was aimed at investigation of the particularities of the influence of various nanosized powders on the process of combustion, the structure, and mechanical properties of the alloy TiC–40% Ni-alloy and development of new dispersion-strengthened electrode materials.

2. Experimental

The products were synthesized via the technology of forced SHS compaction. Exothermic mixtures composed of (48% Ti + 20% C + 40% Ni-alloy) and powders of nickel, chromium, aluminium, iron, titanium, carbon black and added with nanosized powders were used in the experiments. The characteristics of the starting materials and modifying additives are listed in Tables 1 and 2, respectively. Grain size (r) of nanopowders was calculated thought the experimental data of specific surface area (S) on follow very simple equation: $r = 3/(5\rho)$, where $\rho$ is density of nanosized particle materials. S was measured by standard method of BET.

The powders were fractionated after drying at 90 °C. The initial components were mixed for 6 h in a ball mill at the mixture/balls mass ratio of 1/6. The as-prepared mixture was preprocessed in a cylindrical mould up to the relative density of 55–60%. To have a poreless product the synthesis was carried out in sand reaction mould on a DA-1932B press under loading of 194 MPa. To determine the combustion velocity, the front propagation was registered with the use of photodiodes fixed directly in the reaction press-form opposite side to the initiating tungsten wire [1–4].

The experimental compositions and the combustion velocities are presented in Table 3. The nanosized components were introduced as 7 vol% $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, NbC, $\text{Si}_3\text{N}_4$ and 3.5 vol% W, WC, WC–Co. The adiabatic combustion temperatures calculated with the use of ‘TERMO’ program developed at the Institute of Structural Macrokinetics and Materials Science RAS [12] are also cited in Table 3.

The Vickers hardness of the resultant SHS materials was measured on the IT 5010 device under loading of 10 kg.

### Table 1

| Material         | The mean particle size ($\mu$m) |
|------------------|---------------------------------|
| Nickel           | 63                              |
| Chromium         | 63                              |
| Aluminum         | 63                              |
| Iron             | 63                              |
| Titanium         | 45                              |
| Carbon (lamp soot)| $5 \times 10^{-2}$              |

### Table 2

| Nanosized powder additive | Produced by | Specific surface area (m$^2$/g) | The mean particle size (nm) |
|---------------------------|-------------|---------------------------------|-----------------------------|
| $\text{Al}_2\text{O}_3$   | Sol–gel     | 180                             | 17                          |
| $\text{ZrO}_2$            | Sol–gel     | 30                              | 4.2                         |
| W                         | Plasma chemistry | 0.9                  | 172.3                      |
| WC                        | Plasma chemistry | 30                              | 6.4                         |
| WC–Co                     | Plasma chemistry | 20                              | 9.9                         |
| NbC                       | Plasma chemistry | 30                              | 12.5                        |
| $\text{Si}_3\text{N}_4$  | Plasma chemistry | 49                              | 17.8                        |
| $\text{ZrO}_2$ (micropowder) | Electro-chemistry | 0.04                            | $<2 \times 10^9$            |

Their bending strength $\sigma$ was determined according to the method of three-point bending. The bar-shaped samples with the rectangular cross-section of 5 $\times$ 5 $\times$ 30 were tested on a universal approbation machine UTS-100 with a worm gear and the maximum tension–compression effort of 100 kN. Similar samples with thin lateral cuts-in made in the central part with a diamond disc were subjected to crack resistance ($K_{1c}$) testing according to the standard procedure [13]. The rate of deformation was found to be equal to 0.5 mm/min. The material density $\rho$ was determined by the method of hydrostatic weighing.

The phase composition of the samples was studied on a DRON-3 X-ray diffractometer (Co K\textalpha) in the scan-by-scan mode. To have the qualitative and quantitative phase data the obtained spectra were analyzed on an IBM according to the method described elsewhere [14]. The fracture microscopy was performed on a scanning electron microscope JSM-US furnished with the EDISON system involving WIDENS and DIPS and a scanning electron microscope HITACHI S-3000N with an EDAX supplement. The granular structure of the alloys was observed by variation of the image magnification.

The elemental analysis was used for the control over the chemical composition of all synthesis products.

3. Results and discussion

After the nanosized powder has been introduced, the combustion velocity in the green mixtures of different compositions diminishes from 1.42 to 0.52 cm/s (Table 3). This is an evidence for a relative chemical inertness of the additives and partial blocking of the reacting surface of the titanium–carbon black mixture.

Such a specific feature can be followed on an example with $\text{Al}_2\text{O}_3$, NbC, W nanodispersed powders. Addition of the tungsten powder with a low specific surface of 0.9 m$^2$/g
and a high thermal conductivity of 118 W/m K (at $T = 1500$ K) entails an insignificant decrease in the combustion velocity down to 1.16 cm/s, whereas the nanosized powder of alumina having a developed specific surface of 180 m$^2$/g and a low thermal conductivity (7 W/m K) at the same temperature decelerates combustion down to 0.52 cm/s. An analogous decelerating effect is observed at introduction of niobium carbide, which lowers down the combustion velocity to 0.81 cm/s.

The results of the X-ray phase analysis (XRD) are presented in Table 4. Their analysis leads to the conclusion on the changes in the period of the titanium carbide lattice, which is probably caused by the nanoadditive dissolution in TiC, essential grain dispersion, and varying tensile state of the material. The TiC–40% Ni-alloy structure consists of titanium carbide with the lattice period of 4.320 Å and a solid nickel–chromium–iron solution with the lattice period of 3.357 Å.

The products of close phase compositions are formed in the TiC–40% Ni-alloy + ZrO$_2$ and TiC–40% Ni-alloy + ZrO$_2$ (< 20 µm) compositions. Addition of nanosized zirconia and micropowder of zirconia results in the formation of complex titanium–zirconium oxycarbides (Ti,Zr)CO with the respective lattice periods of 4.338 and 4.336 Å. An also formed zirconium oxycarbide Zr(C,O) precipitates as a separate phase with the lattice period of 4.657 and 4.657 Å. Reduction of the lattice period of the solid solution Ni–Cr from 3.575 to 3.565 Å can be determined by partial dissolution of zirconia in Ni–Cr.

The volume content of the phase components has also changed in comparison with the initial composition and the volume shares of TiC and the binding phase Ni–Cr are approximately equal.

The phase compositions of TiC–40% Ni-alloy + WC and TiC–40% Ni-alloy + WC–Co are practically identical. The lattice period of titanium carbide does not practically change as compared to that of the initial additive-free alloy; they are, respectively, equal to 4.324 and 4.320 Å. At the same time, the lattice period of Ni–Cr is somewhat reduced from 3.575 to 3.566 and 3.558 Å. Like in the case of

| Material                          | Phase composition | Amount (vol.%) | The lattice parameter, $a$ (Å) |
|-----------------------------------|-------------------|----------------|-------------------------------|
| TiC–40% Ni-alloy                  | TiC               | 92             | 4.320                         |
| TiC–40% Ni-alloy + ZrO$_2$        | Ni–Cr             | 8              | 3.575                         |
| TiC–40% Ni-alloy + ZrO$_2$ (< 20 µm) | Ti,Zr(C,O)       | 85             | 4.338                         |
| TiC–40% Ni-alloy + Ni–Cr          | Ti,Zr(C,O)       | 85             | 4.338                         |
| TiC–40% Ni-alloy + ZrO$_2$ (< 20 µm) | Ni–Cr             | 13             | 3.565                         |
| TiC–40% Ni-alloy + ZrO$_2$ (< 20 µm) | Zr(C,O)          | 2              | 4.645                         |
| TiC–40% Ni-alloy + Ni–Cr + ZrO$_2$ (< 20 µm) | Ti,Zr(C,O)       | 78             | 4.336                         |
| TiC–40% Ni-alloy + Ni–Cr + ZrO$_2$ (< 20 µm) | Ni–Cr             | 20             | 3.561                         |
| TiC–40% Ni-alloy + Ni–Cr + ZrO$_2$ (< 20 µm) | Zr(C,O)          | 2              | 4.657                         |
| TiC–40% Ni-alloy + Ni–Cr + ZrO$_2$ (< 20 µm) | TiC               | 81             | 4.318                         |
| TiC–40% Ni-alloy + Ni–Cr + Al$_2$O$_3$ | Ni–Cr             | 19             | 3.580                         |
| TiC–40% Ni-alloy + Ni–Cr + W      | TiC               | 44             | 4.309                         |
| TiC–40% Ni-alloy + Ni–Cr + WC     | TiC               | 91             | 4.324                         |
| TiC–40% Ni-alloy + Ni–Cr + WC–Co  | TiC               | 9              | 3.566                         |
| TiC–40% Ni-alloy + Ni–Cr + NbC    | Ni–Cr             | 13             | 3.558                         |
| TiC–40% Ni-alloy + Ni–Cr + Si$_3$N$_4$ | TiC             | 16             | 3.559                         |
| TiC–40% Ni-alloy + Ni–Cr + Si$_3$N$_4$ | Ni–Cr             | 14             | 3.541                         |
zirconia, addition of niobium carbide results in the formation of a complex titanium–niobium carbide (Ti,Nb)C with the lattice period of 4.337 Å. However, a slight decrease in the lattice period from 3.575 to 3.669 Å is also observed for Ni–Cr. Upon introduction of a silicon nitride additive, the lattice periods of both TiC and Ni–Cr are reduced from 4.320 to 4.311 Å and from 3.575 to 3.541 Å, respectively. This allows the supposition to be made on possible interaction of silicon nitride and titanium and partial dissolution of silicon nitride in the Ni–Cr melt in the combustion wave of the given system.

The microstructures of the TiC–40% Ni-alloy, TiC–40% Ni-alloy + ZrO2, TiC–40% Ni-alloy + ZrO2 (≤ 20 μm), TiC–40% Ni-alloy + Al2O3, TiC–40% Ni-alloy + W, TiC–40% Ni-alloy + WC, TiC–40% Ni-alloy + WC–Co, TiC–40% Ni-alloy + NbC, and TiC–40% Ni-alloy + Si3N4 alloys were recorded at two different magnifications (Figs. 1–9). In each case, the mean grain size was calculated according to the standard program.

Fig. 1 shows the microstructure of TiC–40% Ni-alloy consists of rounded grains of titanium carbide and an interlayer of the binding phase of the solid chromium–nickel solution. The mean size of the basic phase is equal to 3.0 μm. The structures of the alloys added with zirconia of various dispersities and aluminia are shown in Figs. 2–4. The alloy structure is seen to be significantly modified by introduction of the given nanosized powders into the green mixture. A (6–8)-fold decrease in the grain size of titanium
Fig. 4. The microstructures of the TiC–40% Ni-alloy + Al₂O₃.

Fig. 5. The microstructures of the TiC–40% Ni-alloy + W.

Fig. 6. The microstructures of the TiC–40% Ni-alloy + WC.

Fig. 7. The microstructures of the TiC–40% Ni-alloy + WC–Co.
carbide, i.e., down to 0.3–0.5 μm, is observed. The highest effect is exerted by zirconia obtained by the sol–gel method. The averaged size of the grains of complex titanium–zirconium oxycarbide does not exceed 0.4 μm. The grains are of a rounded shape and are tightly bound to the Cr–Ni matrix. When zirconia micropowder with the particle size of less than 20 μm is added to the green mixture, the grain size of complex titanium oxycarbide is also reduced (0.55–0.6 μm) but along with that formation of pores of 0.2–0.3 μm is observed. Similarly to the case of a larger-grained zirconia additive, the grain size of the carbide phase is equal to 0.55–0.6 μm at introduction of alumina powder. However, the structure uniformity is distorted by formation of pores and nanodispersed powder aggregates.

The structures of the alloys added W, WC, WC–Co and Si3N4 do not differ much. The structure formed is uniform enough and the titanium carbide grains are of a regular rounded shape. In the case of the WC and WC–Co additives, the respective average size of the TiC grains is equal to 0.7 and 1.1 μm (Figs. 6 and 7), i.e., their size is 2–3 times less than that of titanium carbide contained in the basic composition. At addition of tungsten (Fig. 5), the grain size of the resultant main phase is commensurable with that of the basic composition without additives and is of an order of 2–2.5 μm.

The structure of the alloy added with niobium carbide is depicted in Fig. 8. Unlike the other nanosized powders, niobium carbide promotes formation of a complex titanium–niobium carbide and insignificant structural modification, the mean size of the complex carbide grains being equal to 1.75 μm. Fig. 9 shows that at addition of the silicon nitride powder, like in the case of niobium carbide, the grain size is slightly reduced to 1.85 μm, pores and nanodispersed powder aggregates are observed in the alloy microstructure.

The data obtained suggest the conclusion that addition of nanosized and fine-fraction powders will cause the effect of structure modification (Table 5), which is determined by the following factors. First, nanoadditives are relatively inactive materials and act as thermic inerts in the combustion wave, thus lowering down its temperature and velocity. At the same time, the rate of the carbide grain growth is also reduced in the zone of structure formation inside the combustion wave. Second, the increase in the number of the crystallization centers induced by introduction of nanosized powders at the early stages of structure formation facilitates the process of heterogeneous nucleation. The most pronounced structure-modifying effect is observed in the compositions added with 7 vol% ZrO2, ZrO2 (<20 μm), Al2O3 and 3.5 vol% WC.

The mechanical characteristics of the obtained SHS materials are summarized in Table 5. The nanosized powders exert an ambiguous influence on the properties of the TiC–40% Ni-alloy material (e.g., its strength, crack resistance, and hardness). Thus, the presence of nanosized zirconia and niobium carbide enhances the materials strength from 699 to 767 and 710 MPa, respectively. Other additives either do not affect the alloy strength or
exert a negative effect as in the case of alumina. A sharp decrease in the alloy strength down to 344 MPa can be probably caused by an enhanced porosity of the material and the possibility of formation of brittle components, which negatively affect the strength characteristics of the alloy. The crack resistance of the alloy is significantly increased at introduction of zirconia, tungsten, and tungsten carbide from 9.5 up to 10.6, 13.2, and 11.3 MPa m$^{1/2}$. The nanodispersed powders of alumina, silicon nitride, and tungsten carbide exert a negative effect on the crack resistance and decrease it down to 8.0, 7.9, and 8.0 MPa m$^{1/2}$, respectively. The other nanosized powders do not essentially affect the material strength.

The most positive influence on the hardness of the initial alloy is observed at addition of ZrO$_2$, when the alloy hardness increases from 1404 to 1722 kg/mm$^2$. This is an additional evidence for the positive effect of the given nanosized powder on the mechanical properties of the alloy. At introduction of WC–Co and NbC additives the material hardness is, respectively, enhanced to 1513 and 1557 kg/mm$^2$. The alloy hardness is not essentially affected by the other nanosized powders, but alumina, which lowers it down to 1098 kg/mm$^2$.

Analysis of the data of Table 5 leads to the conclusion that nanosized zirconia has a positive influence on all mechanical properties of TiC–40% Ni-alloy. Nanodispersed niobium carbide is also a positive additive, although its influence is less pronounced. The mechanical properties of the alloy become noticeably worse at addition of alumina and silicon nitride. As for the other additives, they either produce a positive effect on only one of the material characteristics or their influence on the mechanical properties of the alloy is insignificant.

### 4. Conclusions

1. The macrokinetics, structure, and properties of the SHS materials based on TiC–40% Ni-alloy with nanosized additives of ZrO$_2$, Al$_2$O$_3$, W, WC, WC–Co, NbC, Si$_3$N$_4$, and microcrystalline ZrO$_2$ (<20 μm) have been studied.

2. Addition of nanosized powders results in the decrease in the combustion temperature and velocity and considerable (6–8)-fold modification of the SHS material structure.

3. When added to the green mixture, the ZrO$_2$ and NbC nanosized powders have a positive effect on all mechanical properties of the alloy. The crack resistance is rather positively influenced by the W and WC nanodispersed powders, whereas the WC–Co additive exerts a noticeable effect on the alloy strength. Introduction of the Al$_2$O$_3$ and Si$_3$N$_4$ nanodispersed powders into the green mixture negatively affects all mechanical properties of the alloy. Despite the structure-modifying effect produced by micropowder ZrO$_2$ (<20 μm), its addition does not entail enhancement of the physicochemical characteristics, on the contrary, the alloy crack resistance is even decreased.

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### Table 5

The physicochemical properties of the alloy based on TiC–40% Ni-alloy

| Electrode material                  | The mean particle size (μm) | $\rho$ (g/cm$^3$) | $\sigma$$_{\text{bend}}$ (MPa) | $K_{ic}$ (MPa m$^{1/2}$) | HV (kg/mm$^2$) |
|-------------------------------------|-----------------------------|------------------|-------------------------------|-----------------------|---------------|
| TiC–40% Ni-alloy                    | 3.00                        | 5.94             | 699                           | 9.5                   | 1404          |
| TiC–40% Ni-alloy + ZrO$_2$          | 0.52                        | 5.88             | 767                           | 10.6                  | 1722          |
| TiC–40% Ni-alloy + ZrO$_2$ (<20 μm) | 1.27                        | 5.78             | 678                           | 8.0                   | 1364          |
| TiC–40% Ni-alloy + Al$_2$O$_3$       | 1.14                        | 5.77             | 344                           | 8.0                   | 1098          |
| TiC–40% Ni-alloy + W                | 2.83                        | 6.17             | 501                           | 13.2                  | 1306          |
| TiC–40% Ni-alloy + WC               | 2.12                        | 6.56             | 689                           | 11.3                  | 1286          |
| TiC–40% Ni-alloy + WC–Co            | 1.70                        | 5.99             | 517                           | 9.1                   | 1513          |
| TiC–40% Ni-alloy + NbC              | 1.00                        | 5.86             | 710                           | 9.8                   | 1557          |
| TiC–40% Ni-alloy + Si$_3$N$_4$       | 0.89                        | 6.09             | 564                           | 7.9                   | 1343          |
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