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FORMATION OF FILAMENTARY CRYSTALS IN INTERMEDIATE COMBUSTION PRODUCT OF ALUMINIUM NANOPOWDER AND ITS MIXTURES WITH MOLYBDENUM AND TUNGSTEN NANOPOWDERS IN AIR

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The characteristics and phase composition of intermediate synthesis products has been studied by burning mixtures of aluminium nanopowders and molybdenum and tungsten. It was stated that under certain conditions two-level filamentary crystals were stabilized in the process of burning, the mechanism of their formation being suggested. The compact samples of composite materials on the basis of nitride-containing ceramic powders reinforced by filamentary crystals and refractory metals were obtained.

Introduction

Improving strength properties of ceramic and composite materials is a very urgent problem [1]. Its solution is made in different directions, one of which is introduction of filamentary crystals, raising resistance to ceramic decrepitation, to the initial batch. The most significant results have been achieved in application of filamentary crystals referring to nanomaterials in one of the parameters – their thickness should not exceed 100 nm [2]. Filamentary crystals of aluminium nitride are of great interest: besides their strength properties of composite materials they raise heat conductivity and improve insulating properties [3].

One of the synthesis methods of refractory ceramic materials is combustion synthesis [4, 5]. It requires lower power inputs in comparison with other industrial methods. Combustion synthesis does not involve complex equipment and restrictions in output of ceramic materials. The synthesis process is started by local batch heating, proceeding then spontaneously in thermal explosion conditions. The recently stated phenomenon of air nitrogen fixation at burning of powder metals [6] opens up fresh opportunities for synthesis of ceramic nitride-containing materials in industry. In aluminium nanopowder (NP) burning there are two stages different in temperature: low-temperature (1000...1200 °C) and high-temperature (2200...2400 °C), accompanied by relatively low temperature disturbances (within 200 °C). According to explanation suggested before [7] sharp decrease in temperature is explained by formation of aluminium nitride in gas phase with heat absorption. Decrease in temperature seems to be connected with reduction in interaction rate of aluminium with oxygen and increase in interaction rate of aluminium with nitrogen etc. The formed phases of aluminium nitrides are filamentary crystals of 1...2 mkm thick and up to 40 mkm long. Application of NP allows for production of ceramic materials with high nitride output and more dispersivity.

The purpose of the given paper is to define the conditions of filamentary crystal synthesis in composition of intermediate combustion product of molybdenum and tungsten nanopowder mixtures with aluminium nanopowder.

Technique of nanopowder production

As an object of investigation Al, W and Mo NP produced by means of electric conductor explosion in argon have been used. NP were produced at experimental-industrial equipment UDP-4G in Scientific Research Institute of Tomsk Polytechnic University.

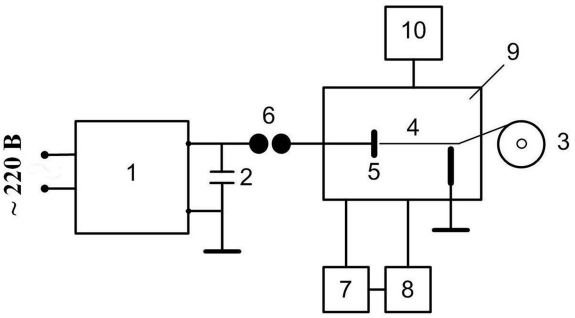

Fig. 1. *Scheme of explosive installation UDP-4G: 1) power supply; 2) capacity storage; 3) device of wire delivery; 4) blasted wire strip; 5) high-voltage electrode; 6) commutator; 7) nanopowder storage chamber; 8) fan; 9) chamber; 10) system of pumping and gas supply*

Blasted wire moves continuously by means of delivery mechanism – 3 to blasting chamber – 9. At that time there is a charge of capacity storage – 2 from power supply – 1. On reaching the spark gap by wire the explosion of wire strip – 4 occurs. Produced spray arrives at storage chamber – 7 by means of fan – 8, where NP is isolated from argon. Working voltage, supplied to conductor, is controlled by commutator – 6. Explosion frequency is nearly 1 Hz. The unit capacity for Al is 50 g/h, but for W is 300 g/h. For other metals it is in the range of 50...300 g/h.

Table 1. *Conditions of electric explosion and nanopowder dispersion*

Металл	U_0, kV	C, mkF	L, mkHn	l, mm	d, mm	P, Pa	W/W_s	W_a/W_s
W	13,7	2,250	0,04	60	0,200	$1{,}5\cdot10^5$	0,45	0,78
Mo	12,4	2,250	0,04	60	0,200	$1{,}5\cdot10^5$	0,61	0,61
Al	24,0	2,018	0,04	80	0,350	$1{,}5\cdot10^5$	1,45	0,38

In Table 1 the following electric parameters of NP production are presented: voltage of capacity storage U_0; capacity storage C; charging circuit inductance of the unit L; length of blasted conductor l; diameter of blasted

conductor d; argon pressure in blasting chamber P; energy density introduced into conductor, referred to metal sublimation energy W/W_s; energy density of charge arc stage referred to metal sublimation energy W_a/W_s.

Investigation techniques

Microstructure of initial nanopowders has been studied by scanning electron microscope JSM 6500 F of «Jeol» production, Japan. Experimental mixture of elecro-explosive NP were prepared by the method of dry mixing, the accuracy of component composition being ±1,5 %. The prepared samples were subjected to differential-thermal analysis (DTA) and the parameters of chemical activity for NP and the mixture under study were determined [8]: temperature of oxidation start $T_{s.o.}$, oxidation degree α, %, maximum oxidation rate V_{max}, wt. %/c and specific heat. DTA was performed by standard technique [9] (linear heating condition, air atmosphere, heating rate is 10 degree/min). Tungsten-containing samples were investigated by derivatograph Q-1500. For these samples relative specific heat $\Delta H/\Delta m$, rel.unit was defined. Molybdenum-containing samples were examined by means of thermoanalyser SDT Q 600 of Scientific-Analytical Centre of Tomsk Polytechnic University. Given equipment allows for determination of absolute specific heat ΔH, J/g. To identify phase composition of combustion intermediate products they were subjected to roentgen phase analysis (RPA) (DRON-3M). Current phases were determined with the help of JCPDS-ICDD card-file. Microstructure of the obtained cakes was studied by scanning electron microscope JSM-840 of «Jeol» production, Japan. To produce compact ceramic nitride-containing samples the method of hot isostatic pressing (environment – nitrogen, temperature – 1600 °C, compacting pressure – 460 kPa, caking time at maximum temperature – 20 min) was used. Microhardness of the produced samples was measured by microhardnessmeter PMT-3.

Properties of initial nanopowders

In Fig. 2 Al, W and Mo NP microphotography is presented. Al consists of the particles of 100 nm diameter, but there are some particles of more diameters – of the order of 200 nm. Besides, there are many particles of less diameter – 50...60 nm. The shape of particles is close to sphere; there are separate agglomerates of particles that are partially caked. Square of specific surface (in terms of BET) equals to ~12 m^2/g. W NP consists of finer spherical particles (diameter is 100 nm) and is characterised by the square of specific surface equal to 3,2 m^2/g. In contrast to Al and W NP Mo NP consists of the particles of irregular shape formed by caking of finer particles. Fragments of cakes have the size from 0,05 to 0,4 mkm. Square of specific surface (in terms of BET) amounts 5,4 m^2/g.

Experimental results and discussion

Results of DTA have shown that when heating in air NP oxidation occurs first slowly, then with increase in releasing heat, the process of oxidation passes into combustion process. Composition and parameters of chemical activity of mixtures involved are presented in Tables 2, 3.

Table 2. *Composition of NP Al and W mixtures investigated, parameters of their chemical activity*

Sample composition, wt. %		$T_{н.о.}$, °C	α, %	V_{max}, wt. %/c	$\Delta H/\Delta m$, rel. unit
Al	W				
100	0	400	45,9	0,10	2,5
90,9	9,1	380	50,3	0,10	2,9
83,3	16,7	380	58,5	0,41	3,5
71,4	28,6	380	56,2	0,05	3,3
62,5	37,5	380	53,0	0,04	3,2
55,6	44,4	380	46,8	0,04	2,9
0	100	320	24,1	0,03	1,6

From Table 2 it follows that NP mixtures start to oxidize at 380 °C. The given temperature is an intermediate one between the temperature of Al and W NP oxidation start without additives. Depending on the relation of Al – W, values of chemical activity parameters go through maximum that corresponds to the sample containing 16,7 wt. % of W NP. When iincreasing the content of W NP additive in the mixture after maximal parameters of chemical activity they decrease significantly approaching to the parameters of NP W chemical activity.

For W and Al NP mixture, containing 16,7 wt. % of W NP, three chemical activity parameters out of four are several times higher than for other compositions. This effect can be explained by the presence of superadditivity – optimal conditions for burning process (synergetic effect).

From Table 3 it follows that Mo NP additive results in monotone decrease in temperature of mixture oxidation start: from 450 °C for Al NP without additions up

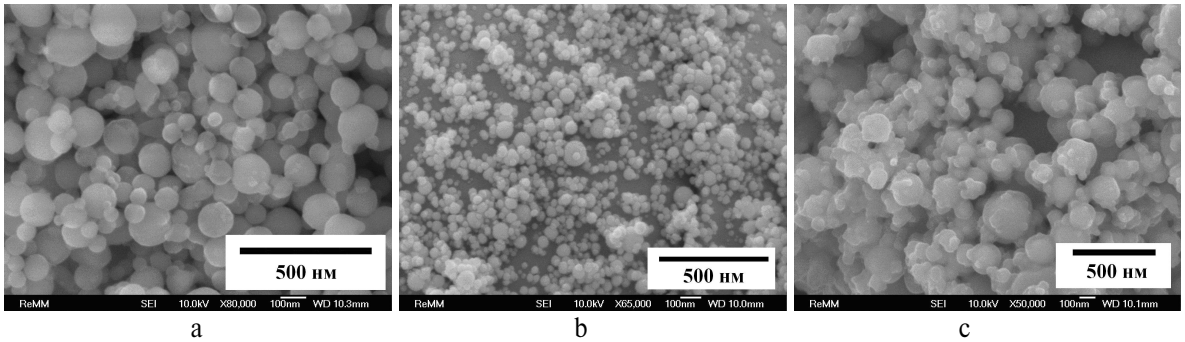

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Fig. 2. *Microphotography of initial NP: a) Al, b) W, c) Mo*

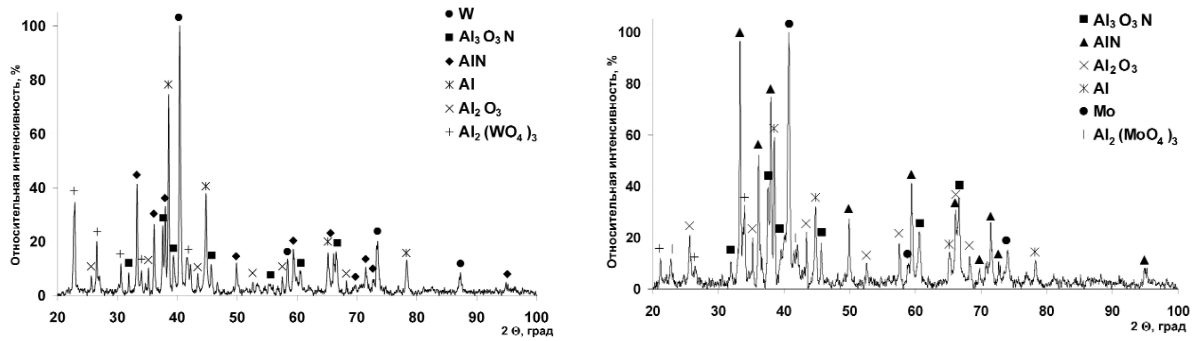

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Fig. 3. *X-ray photograph of Al NP intermediate mixture combustion products with NP of a) W (16,7 wtc. %); б) Mo (28,6 wt. %)*

to 350 °C for Mo NP without additions. Other parameters of mixture chemical activity change in non-monotone way: maximum oxidation rate decreases with raise of Mo NP content. When heating to 1200 °C the degree of NP mixture oxidability is lower than Al NP without additives and passes through the minimum (20,3 %) for the sample containing 28,6 wt. % of Mo NP. As for the value of specific heat, it is less for the mixtures than for Al NP without additives: in general, specific heat decreases with increasing Mo NP addition.

Table 3. *Composition of Al and Mo NP mixtures involved and parameters of their chemical activity*

Sample composition, wt. %		$T_{н.о.}$, °C	α, %	V_{max}, wt. %/c	ΔH, J/g
Al	Mo				
100	0	450	63,8	0,130	4995
90,9	9,1	400	52,5	0,130	4265
83,3	16,7	380	42,8	0,080	4612
71,4	28,6	370	20,3	0,020	4020
62,5	37,5	360	50,7	0,012	3775
55,6	44,4	355	50,1	0,010	3827
20	80	350	42,4	0,010	2938
0	100	350	42,3	0,007	3299

To examine intermediate combustion products in the mixtures involved they were burnt in air. The burning process was ceased by crushing hot mixture between two large plates, in this way providing heat removal and discontinuance of air access. The cakes obtained were disaggregated and bolted with 63 mkm size of mesh. According to X-ray pictures (Fig. 3) composition of combustion intermediate products in the mixtures involved includes: aluminium nitrides (of cubic and hexagonal crystal phases), aluminium alpha-oxide, spinel and underburnt metals.

According to the results of electron microscopy in burning of the investigated mixtures in air the two-level filamentary crystals stabilize in intermediate products: onto the crystals of 0,1...0,5 mkm thick in perpendicular direction the crystals of less thickness of less than 0,1 mkm (Fig. 4) are settled. Such hierarchical structure is likely to be formed within two high-temperature cycles: temperature increase and condensation of crystals of more thickness, but heating to less temperature with aluminium nitride condensation from gas phase causes the formation of filamentary crystals which are thinner, but less resistive to heat.

At high temperatures (more than 2000 °C) the following reactions are possible:

$$4Al_{(г)}+3O_{2\,(г)}\rightarrow 2Al_2O_{3\,(ж)}, \quad (1)$$

$$2Al_2O_{3\,(ж)}+8Al_{(г)}\rightarrow 6Al_2O_{(г)}, \quad (2)$$

$$6Al_2O_{(г)}+6N_{2\,(г)}\rightarrow 12AlN_{(г)}+3O_{2\,(г)}. \quad (3)$$

According to thermodynamic calculations [7] the reaction (1) is exothermic, but reaction (3) is strongly endothermic. The reaction (2) occurs with weak heat effect; therefore the result of reaction (1-3) is cooling fi-

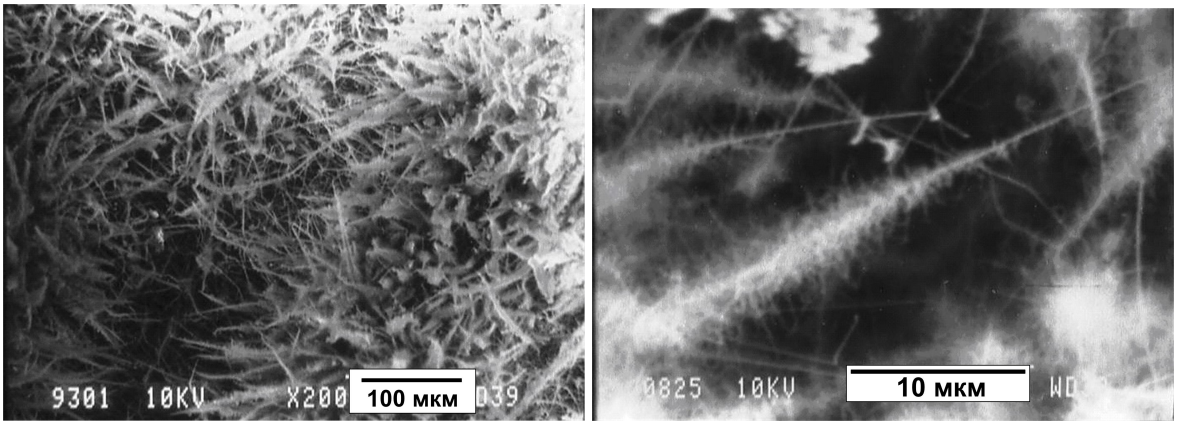

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Fig. 4. *Microphotography of intermediate combustion products of Al NP mixtures with a) W (16,7 wt. %); б) Mo (28,6 wt. %)*

nal products produced by the reaction (3), i. e. gaseous aluminium nitride. Cooling leads to AlN condensation in the form of filamentary crystals.

Grinded intermediate combustion products containing two-stage filamentary crystals were exposed to hot isostatic pressing, diameter of the produced samples being 14 мм, thickness being 5 mm. Apparent density of the pressed samples amounted ~3 g/sm^3. After polishing the samples reinforced by filamentary crystals their microhardness was measured: for tungsten-containing sample it was 12914 MPa, for molybdenum-containing one it was 11300 MPa.

Conclusions

1. Nanopowder mixture composition and conditions of combustion synthesis of filamentary crystals in intermediate combustion products were determined. It was stated that when burnt aluminium and tungsten nanopowder mixtures (16,7±0,25 wt. %) in air two-level filamentary crystals stabilizes in intermediate products: finer crystals were settled on the filaments of more thickness in perpendicular direction.
2. The mechanism of filamentary crystal formation of aluminium nitrides in burning of aluminium nanopowders at high temperature condition. Stabilization of aluminium nitrides occurs at endothermal reaction of aluminium suboxide interaction with molecular nitrogen.
3. Compact samples of composite materials reinforced by nitride-containing ceramic powders, containing filamentary crystals of aluminium nitrides and refractory metals: microhardness of tungsten-containing sample amounted 12914 MPa, molybdenum-containing one was 11300 MPa.

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