GASLESS COMBUSTION OF MIXTURES OF METAL POWDERS

II. EFFECT OF MIXTURE COMPOSITION ON THE COMBUSTION RATE AND THE PHASE COMPOSITION OF THE PRODUCTS

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UDC 536.46 +541.412 +621.762.242

Intermetallic compounds are used in producing catalysts; in producing heat-resistant, superconducting, magnetic, and cutting materials; and in alloying steels and alloys. An extremely simple and economical method has recently been developed for producing these compounds; this is the method of "self-propagating high-temperature fusion" or "combustion-regime fusion" [1, 2]. The influence of various factors (the porosity of the briquets, the dispersion of the components, and the degree of dilution) on the combustion regime and rate has been studied [3, 4].

Here we report data on the influence of the concentration of the original reactants in a mixture of different metal powders on the phase composition of the products and on the combustion rate. This information is very important for developing an optimum technology for producing intermetallic compounds and materials based on such compounds by means of self-propagating high-temperature fusion.

For the experiments we used mixtures of powdered aluminum (type ASD-1 or ASD-4) and powdered nickel (fine-grained type PNK-2), from which we pressed cylindrical samples 1 cm in diameter and 1.5-2 cm long with an initial porosity of 40%. The combustion rate was determined by the method of [3, 4]. The composition of the combustion products was studied by x-ray diffraction, x-ray spectral, and metallographic methods. The composition of the gases adsorbed on the powder particles was determined through a mass-spectrographic analysis (through the use of an IPDO-1 omegatron partial-pressure gauge and an RMO-4s omegatron tube). The mass spectra were recorded under linear-heating conditions (the rate of change of the temperature was 7-10 deg/min) over the temperature range 20-600°C for the powders of the separate components and over the range 20-550°C for the powders of the mixtures.

Figure 1 shows the combustion rate as a function of the mixture composition. At the composition Ni−13.5 wt. % Al (the stoichiometry of the Ni_3Al phase), the combustion rate begins to increase with increasing aluminum content in the initial mixture. The rate reaches a maximum for the composition Ni−31.5 wt. % Al (the stoichiometry of the compound NiAl). As the aluminum concentration is raised further, to 58 wt. % (the stoichiometry of the compound $NiAl_3$), the combustion rate decreases. Compositions near the compound NiAl undergo combustion in the steady-state regime, while the mixtures near Ni_3Al and $NiAl_3$ undergo combustion in the pulsating regime (in some cases, these samples do not undergo combustion completely). For all the mixtures the combustion rate is higher, the smaller the size of the particles in the mixture.

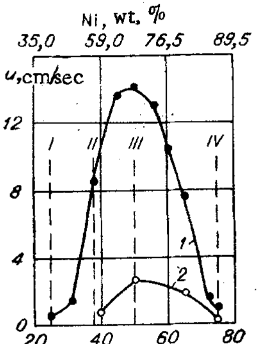

Fig. 1. Combustion rate as a function of the mixture composition. 1) Mixture of Ni (type PNK-2, fine grained) and Al (ASD-4); 2) mixture of Ni (PNÉ, 63 μ) and Al (ASD-1). I) $NiAl_3$; II) Ni_2Al_3; III) NiAl; IV) Ni_3Al.

Data on the composition of the combustion products are given in Table 1 and Fig. 2; this figure shows intensity curves of the radiation by the nickel in the combustion products. Shown for comparison in Fig. 3a is the structure of the orig-

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Tomsk. Translated from Fizika Goreniya i Vzryva, Vol. 11, No. 5, pp. 734-738, September-October, 1975. Original article submitted October 17, 1974.

TABLE 1

Weight percent of Al in original mixture with Ni	Combustion regime	Phase composition of combustion products according to		Comments
		x-ray diffraction analysis	x-ray spectral analysis	
13,5 (Ni_3Al)	Pulsating	Ni_3Al	$Ni_3Al+NiAl++Ni$	Basic product Ni_3Al
15	»	Ni_3Al	$Ni_3Al+NiAl$	
20	Steady state	$Ni_3Al+NiAl$	$Ni_3Al+NiAl$	
23,5	»	NiAl	—	
31,5 (NiAl)	»	NiAl	NiAl	
36	»	NiAl	—	
42,5 (Ni_2Al_3)	»	Ni_2Al_3+NiAl	Ni_2Al_3+NiAl	Basic product Ni_2Al_3
50	Pulsating	—	$Ni_2Al_3+NiAl_3$	
58	»	$NiAl_3+Ni_2Al_3$	$NiAl_3+Ni_2Al_3$	

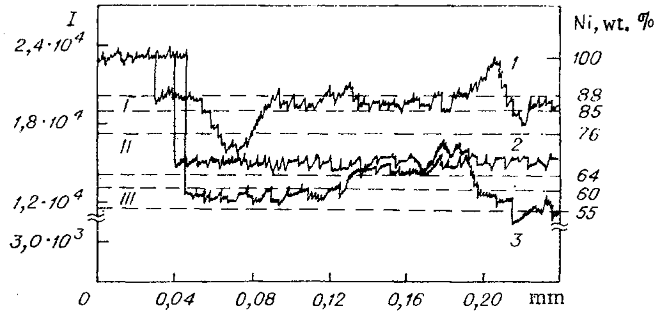

Fig. 2. Emission spectrum of nickel NiK_α in the combustion products. Fine-grained type PNK-2 Ni, type ASD-4 Al. I) Ni_3Al; II) NiAl: III) Ni_2Al_3.

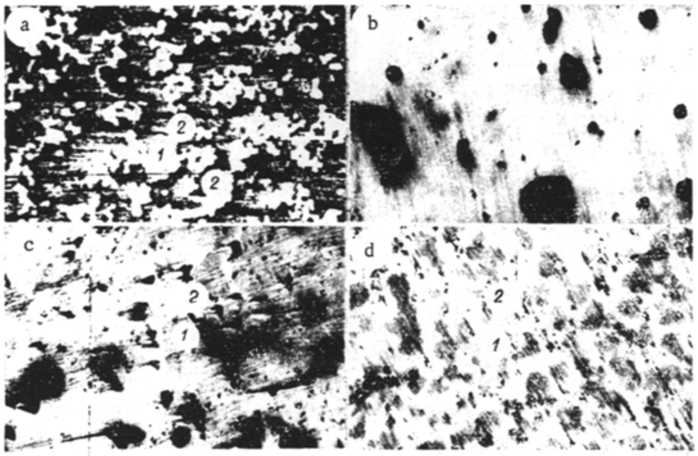

Fig. 3. Photomicrographs of surfaces. a: Original material. 1) Ni; 2) Al (150 ×). b: Ni−13.5 wt. % Al sample after combustion (500 ×). c: Ni−42.5 wt. % Al after combustion. 1) Ni_2Al_3; 2) NiAl (500 ×). d: Ni−58 wt. % Al after combustion. 1) $NiAl_3$; 2) Ni_2Al_3 (500 ×).

inal sample (the bright particles are nickel particles, surrounded by aluminum). The single-phase intermetallic compounds are synthesized in the combustion of the mixtures with compositions corresponding to the homogeneous region of the nickel monoaluminide (curve 2 in Fig. 2; Ni−31.5 wt. % Al) [6]. Polyphase combustion products form for the other compositions. For example, in the combustion of the composition Ni−13.5 wt. % Al (the stoichiometry of Ni_3Al), it is primarily the Ni_3Al phase (cubic lattice, $a = 3.550$ Å)

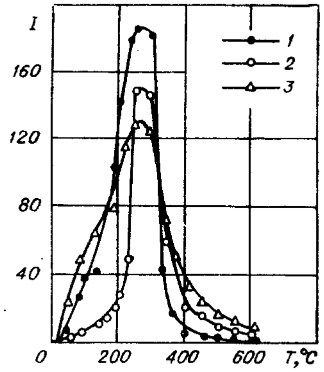

Fig. 4. Mass spectrogram obtained during heating of nickel powder.

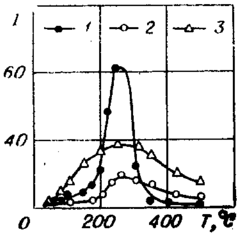

Fig. 5. Mass spectrogram obtained during heating of annealed powdered mixture Ni−31.5 wt. % Al. 1) CO_2; 2) CO; 3) H_2O.

which forms, according to the x-ray diffraction analysis. However, the x-ray spectral analysis (curve 1 in Fig. 2) shows that the Ni_3Al is accompanied by NiAl and by nickel which is not reacted. According to the metallographic data (Fig. 3b), the combustion products have a homogeneous structure and consist primarily of the Ni_3Al phase.

In the combustion of the composition Ni−42.5 wt. % Al (stoichiometry of Ni_2Al_3), the product consists of a mixture of the Ni_2Al_3 and NiAl phases (curve 3 in Fig. 2). We see two phases which are quite different in color: the grayish-blue Ni_2Al_3 phase and the bright, narrow NiAl veins (Fig. 3c). The combustion product of the composition Ni−58 wt. % Al (the stoichiometry of $NiAl_3$) is a two-phase product and consists of a mixture of the phases $NiAl_3$ and Ni_2Al_3, according to data from the x-ray spectral, diffraction, and metallographic analysis (Fig. 3d).

The phase composition of the combustion products depends on the size of the reactant particles. For example, the combustion products of the composition Ni−31.5 wt. % Al (the stoichiometry of NiAl), a mixture of aluminum and nickel powders with a particle size of 50-63 μ, is a two-phase product, consisting of NiAl and Ni_2Al_3. We know that impurities adsorbed on the surfaces of powder particles affect the reaction kinetics. We therefore studied the influence of an annealing, which cleans the surface, on the combustion rate and composition of the evolved gases.

When the nickel powder (fine-grained type PNK-2) in the state furnished was heated, we observed three peaks in the m/e distribution, corresponding to masses of 44 (CO_2, Fig. 4, curve 1), 28 (CO, Fig. 4, curve 2), and 18 (H_2O, Fig. 4, curve 3). When we annealed the type ASD-1 aluminum powder, we observed only a single peak, corresponding to a mass of 18 (H_2O). Much more water is adsorbed on the nickel powder than on the aluminum powder. These data agree with the results of a mass-spectrometric analysis of the principal carbonate of nickel [7]. The evolution of CO_2 was verified with the help of the qualitative reaction

$$CO_2 + Ba(OH)_2 \rightarrow BaCO_3\downarrow + H_2O.$$

Analysis of the mass spectrogram reveals that the heating of the composition Ni−31.5 wt. % Al results in the evolution of the same gaseous products as are observed during the annealing of the pure powders. At 550°C, an intense exothermic reaction begins in the mixture of nickel and aluminum powders (the temperature rises very rapidly to 1200-1300°C), due to the formation of intermetallic compounds [8]. Although there is an accompanying increase in gas evolution, there is no change in the composition of the products.

To determine how the gases adsorbed on the particles affect the combustion rate, we carried out a step-by-step annealing of nickel powder in a vacuum of 10^{-3} torr (T = 200°C, t = 2 h; T = 300°C, t = 3h; T = 400°C, t = 3 h; T = 500°C, t = 2 h; T = 600°C, t = 1 h). An annealing of this type reduces the amount of adsorbed gas. All three peaks shrink considerably (Fig. 5). Immediately after the annealing of the powders or the mixture of powders, we prepared the samples and burned them in the bomb. The combustion rate of the composition Ni−31.5 wt. % Al formed from powders prepared by the procedure outlined above or from a mixture of powders annealed in a vacuum of 10^{-3} torr at 400°C for 5 h is 10.5 ±0.5 cm/sec. The combustion rate of this composition prepared from a mixture of powders in the state furnished is 9.5 ± 0.5 cm/sec.

Accordingly, heat treatment of the powders in vacuum increases the combustion rate slightly.

The authors thank V. L. Shcherinskii, A. V. Lepinskikh, and L. V. Sholokhova for participating in these experiments.

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