Characteristics of Nano-dispersed Powder by Electric Explosion of Conductors

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Abstract   The phenomenon of electrical explosion of conductors is considered in the context of the changes in the energy and structural states of the metal at the stages of energy delivery and relaxation of the primary products of EEC. It is shown that these changes are related to the forced interaction of an intense energy flux with matter and to the subsequent spontaneous relaxation processes. The characteristics of nano-sized metal powders are also discussed. The preferential gas media during EEC is Ar+H_2. An increase in e/e_s (in the range of values studied) leads to a reduction in the metal content. For reactive powders obtained with high metal content, it is necessary to separate the SFAP fractions, which settled on the negative electrode of the electric filter.

Keywords : Electrical explosion, Nano-sized metallic powder, Pulsed electric discharge, Passivation

1. Introduction

The electrical explosion of a conductor (EEC) is a type of the action of intense energy fluxes or energy of high power density ($J_p = 10^8 - 10^9$ W/cm³a) on metals[1]. At present, it is thought that early in an EEC the Joule heating of the conductor is accompanied by its rather slow linear expansion (normally, at a rate of $(1-3) \cdot 10^2$ cm/s)[2]. During the electrical explosion as such, the exploded conductor expands with a rate of $(1-5) \cdot 10^5$ cm/s, producing perturbations in the surroundings. These perturbations initiate a so-called head or primary shock wave. The maximum temperature of the metal during the explosion stage is determined by the rate of energy delivery and by the energy released in the conductor, and its value may vary over a rather wide range: from 1 eV at a characteristic time of energy delivery $\tau < 1$ μs to 10 eV at $\tau < 0.1$ μs. The present notions of the changes in the physical state of an electrically exploded metal rely on the consideration of phenomena which can be treated as quasi-equilibrium or equilibrium, such as bulk boiling, formation of structural irregularities and magneto-hydrodynamic instabilities, and other. Approaches like

this are not sufficiently justified to analyze EEC, while being the subject of wide speculation in the literature[2-5].

The basis for a conceptually new approach is the experimental data that are difficult to explain within the framework of the present notions of EEC. Even in the early EEC studies, based on the measurements of the energy and resistance of wires, it was found that as a pulsed current passes through a tungsten or iron wire, abnormally intense electron emission occurs from the undestroyed wire, such that the emission current density can be 100 times greater than the saturation current density for these metals[6]. Subsequently, the phenomenon of explosive emission was discovered which is characterized by an explosion-like increase in plasma conductivity[7]. The nonequilibrium character of the processes occurring in an electrically exploded conductor is testified by the fact that as energy comparable only with the heat of sublimation of a conductor is delivered to the latter, 30−40% of the conductor material are in the ionized state. Later experiments with Co wires[8] have demonstrated that the energy of the infrared radiation related directly to the explosion as such is approximately 100 times greater than the thermal radiation energy at a tempera-

ture to which the metal would be heated, providing the whole of the input energy was expended in this process. The radiation in the visible and UV spectra that was observed during the explosion as such also possesses the properties of luminescence, which, as supposed[8], can be excited due to the fast dispersion of the liquid metal and the occurrence of an electric field. Thus, the considerable content of ionized matter and the anomalies observed in the radiation spectrum during an EEC call for an alternative method for considering the relevant processes.

2. Energy delivery processes

We suggest that the entire process of EEC be subdivided into two stages:

(1) a forced process occurring from the onset of the action of current to the loss of conductivity by the conductor and

(2) a spontaneous process occurring from the loss of conductivity by the conductor to the complete cooling of the end products of the EEC.

We shall consider only the electrically matched (infinite no-current interval) explosion of a metal conductor in an inert gas (Fig. 1). At the first stage, the energy delivery with a high power density results in nonequilibrium processes: energy is dissipated through all possible channels, including ones that are unfavorable in energy terms under equilibrium conditions. In other words, in accordance with the Le Chatelier-Brown principle, in a conductor exposed to some external action (energy delivery) there occur some processes counteracting with the external action.

Formally, the problem under consideration corresponds to the case of a deep vessel in which several holes are made at different heights from the bottom,

so that the liquid supply and outflow are associated, respectively, with energy delivery and dissipation. As the rate of energy delivery (liquid supply) is increased, more and more channels of energy dissipation (upper holes) become operative. The channels of energy dissipation in a conductor are its heating in the condensed state, melting, evaporation, ionization, etc. It should particularly be noted that under nonequilibrium conditions the formation of a new surface with disrupted chemical bonds (clusterization of a metal) is of considerable importance. The energy capacity of this process increases with decreasing cluster size. The most rapid increase in energy capacity is observed if the cluster diameter is less than 10 nm[10]. The ionization processes resulting from nonequilibrium energy supply into a conductor show the highest energy capacity. Thus, for aluminum, the latent heat of melting is 10.8 kJ/mol, the heat of sublimation is 327 kJ/mol, and the first ionization potential is 577.6 kJ/mol. Under the conditions of EEC, no equilibrium is attained between the processes, implying that the material exists simultaneously in different energy states. The power density distribution in the conductor seems to be nonuniform in character, being thus responsible for the dispersion of the EEC primary products. Increasing the rate of energy delivery to the conductor (or increasing the power density) increases the degree to which the products of energy dissipation are nonequilibrium.

The thermal current power density, if it is comparatively low, is equal to the product of the conductivity by the squared electric field strength (Joule-Lentz law)[10]. According to this law, at any stage of an EEC, energy must be transferred to the crystal lattice due to the interaction of electrons and core ions. During rapid energy delivery, part of the energy goes into disrupting chemical bonds, ionization, etc., and the energy converted to heat is thus smaller than that determined by the Joule-Lentz law:

$$\Delta H < \gamma E^2,$$

where γ is the conductivity of the metal and E is the electric field strength.

The onset of the dispersion of an exploded conductor seems to be associated with thermal fluctuations in the conductor bulk. As the temperature in the conduction channel reaches a maximum, given by

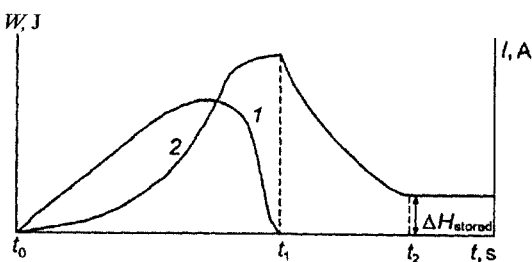$$T_{max} = (|I^2 \cdot R \cdot t|/(\alpha \cdot S)) + T_0,$$

Fig. 1. Time variation of the current (1) and energy of a conductor (2) due to the passage of an electric current (t_0 – t_1) and due to the energy dissipation in the electrical explosion products (t_1 – t_2).

where I is the current, R is the resistance of the conduction channel; α is the coefficient of heat transfer from the wall of the conduction channel, S is the area of the heat-releasing surface, T is the conductor temperature beyond the conduction channel, and t is time, quasi-equilibrium is established, which is determined by the electrical resistance.

With increasing power density, the conductor is destroyed due to the passage of a current pulse with a short risetime ($\tau \leq 1$ µs). It is supposed that if the power density I_p is high, conduction channels with fluctuating distribution and lifetime appear in the metal[11]. An increase in temperature in a conduction channel leads to an increase in electrical resistance and, hence, to a decrease in current and the formation of a conduction channel in the adjacent region of the metal. The fluctuations of conduction channels cause the increasing temperature to level off in the bulk of the metal until its continuity is disrupted.

3. Relaxation processes

The end products of an EEC, nanopowders (NP's), are metastable solid-gas systems. Consequently, the relaxation of the EEC products that occurs at the stage of their cooling is incomplete and part of the energy is "frozen" (stored) as surface energy, energy of internal defects, and energy of charge states[12]. The nonequilibrium processes that occur in cooling and the conservation of the stored energy by the metal also violate the Joule-Lentz law even if the EEC is completed and its products are stabilized. Thus, in a physical sense, the nonequilibrium in an electrical explosion is a violation of the Joule-Lentz law both in energy delivery to the metal and in cooling of the EEC products.

The direct correlation between the rate of energy delivery to a conductor - a kinetic parameter - and the degree of dispersion of the EEC products points to the fact that the nonequilibrium failure of an exploded conductor is a more complicated process than mere boiling. The electric current action integral (energy delivered to a conductor, W) is insufficient to analyze both the EEC and the explosion end products for different rates of energy delivery. With the same value of the action integral, the end products of dispersion of the conductor will differ at least in specific surface area and in particle size distribution function. According to experimental data, increasing the rate of electric energy delivery to a conductor or the relative input
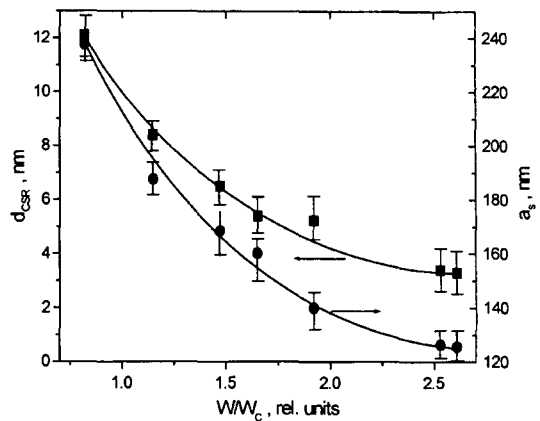

Fig. 2. The surface-mean diameter of the particles, a, and the diameter of the coherent scattering regions in the particles, d_{CSR}, as functions of the relative energy delivered to the conductor, W/W_C, for Al wires electrically exploded in Ar.

energy W/W_C (where W_C is the energy of sublimation of the exploded conductor) increases the degree of dispersion of the end products; the surface-mean diameter of the particles asymptotically approaches the diameter of the coherent scattering regions in the particles (Fig. 2).

Experiments have shown that for a fixed relative energy delivered to a copper conductor in air (W/Wc = 1.5) the degree of dispersion of the end products increases with increasing J_p. The formation of the end products of an EEC is accompanied by coalescence, sintering, and aggregation of primary clusters. These processes give birth to coarse particles and result in a larger spread in particle size.

From the above discussion it follows that the interaction of a high energy flux with a metal (EEC), causing the latter to disperse, is a nonequilibrium process of energy dissipation in the metal, which results in the formation of discrete structures - primary products. According to the results of dissolution calorimetry, the energy stored in Al powders obtained under certain EEC conditions is 40–60 kJ/mol, which is greater than the standard heat of melting for aluminum (Table 1).

4. Characteristics

In non-passivated superfine aluminum powders (SFAP) obtained in (Ar+10 vol.% H_2) medium with e/e_s between 1.10 and 2.12 (Table 2), the content of

Table 1 Energy stored in electrical-explosion-produced powders. Results of dissolution calorimetry

Sample (process gas)	S_s (m^2/g)	Enthalpy of formation of Al_2O_3 (kJ/mol)	Enthalpy of dissolution (kJ/mol)
Al NP (hydrogen)	7.4	1728.4±6.0	590.3±8.0
Al NP (argon)	6.4	1729.7±2.1	578.4±7.4
ASD-4 (standard)	0.8	1667.7±5.0	510.8±8.3

Table 2 Characteristics for SFAP obtained with EEC and passivated by air

Gas media by EEC	Voltage by EEC (U) (kV)	e/e_s (a.u.)	$[Al^\circ]$ (mass %)	S_{sp} (m^2/g)	a_s (nm)	$[Al_2O_3]^a$ (mass %)	Calculated thickness of oxide layer[b], nm
	30	1.82	88.0±1.4	10.8±0.3	210	19.0	5.0
	28	1.71	87.9±0.3	9.9±0.3	220	19.1	5.4
Ar+10 vol. % N_2	26	1.62	88.1±1.1	9.9±0.9	220	18.9	5.4
	24	1.45	88.5±0.9	9.3±0.3	240	18.4	5.6
	22	1.30	90.9±0.8	8.8±0.25	250	16.1	4.9
	20	1.13	90.0±0.6	6.7±0.2	330	17.0	6.9
	18	0.92	91.0±0.7	7.7±0.25	290	16.0	5.6
Ar+10 vol.% H_2	–	1.10-2.12	90.2-93.6	7.7-15.8	140-290	1.1-3.7	0.2-1.7
Ar	–	1.52-2.25	86.3-89.1	18.5-13.8	120-160	8.4-8.8	1.5-2.1
Micron sized industrial Al powder	–		98.5±0.1	0.8±0.02	10000	1.0	13.6

$^a[Al_2O_3] = 100\% - [Al^\circ]$ [adsorbed gases].
^{b}calculated by the amount of absorbed gas by BET / size and the number of particles.

metallic aluminum was 91–99.5 mass %. The content of metallic (non-oxidized) aluminum determined by the standard volumetric method under the volume of liberated hydrogen during interaction of aluminum powder with aqueous 5% NaOH solution. During the passivation by air, the metal content exponentially decreased in a period of 6 days, and the quantity of aluminum stabilized at a level between 90.2 and 93.6 % (see Table 2). The production atmosphere(gas media) contains small amount of impurities. These oxygen, hydroxide and carbonate impurities effect on the purity of the final products of EEC dominantly.

Completely passivated superfine particles obtained in Ar-based gas media had a shape close to spherical, and a smooth surface of oxide (Fig. 3). The calculated thickness of the oxide layer (1.5–2.1 nm, Table 2) agreed with the experimental one (1.8 nm, Fig. 3). It should be noted that the characteristics of passivated powders are strongly dependent on the production conditions employed. These characteristics are given in Table 2. The samples of SFAP were obtained using different values of e/e_s. The area of specific surface increases for SFAP with increasing e/e_s, but the content of metal is reduced in the passivated powders. The calculated content of oxides is high for this series of powders (more than 16 mass %).
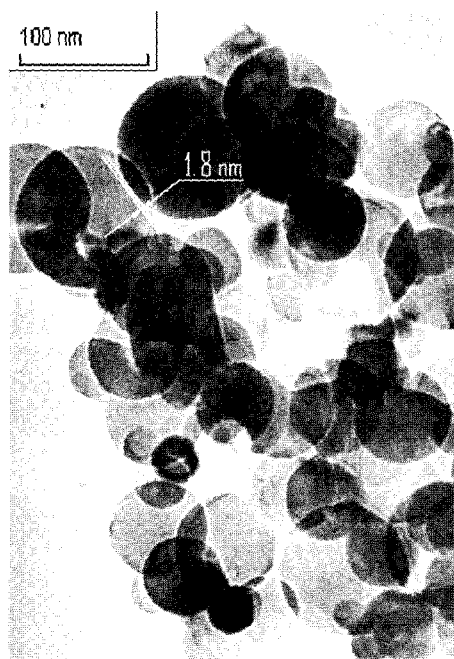
Fig. 3. Tem images of SFAP passivated by air

The obtained superfine particles, which were charged during EEC, were divided in the electric filter inside the EEC machine before collection. The charge of a particle can be determined by thermo-

Table 3 Enthalpy of Al_2O_3 formation[a] (Δf_f^{298}) and specific surface area[b] (S_{sp}) for separate fractions of electric explosive SFAP, obtained in H_2 media and divided into separate fractions by the electric filter before passivation

Type of powder	S_{sp}, m²/g	$\Delta H_f^{298}(Al_2O_3)$, kJ/mole
Mixed fractions of SFAP	7.4	1728.4±6.0
SFAP collected from positively charged electrode	5.4	1804.1±6.0
SFAP collected from negatively charged electrode	6.1	1737.5±6.0
Neutral fraction of SFAP	9.0	1595.2±5.5
Micron sized industrial Al powder[c]	0.8	1667.7±5.0

[a]Measured by bomb calorimetry.
[b]Determined by BET method.
[c]Spherical particles.

emission and ionization under electric field conditions. The stabilization of charge structures contribute to: (1) a high rate of cooling of products and (2) presence of electromagnetic fields at EEC[13]. Mixtures of fractions or separate fractions of aluminum particles coagulated and were collected in the steel container after EEC. Taking it into account that the explosion process is conducted under the gas (Ar) pressure $P = 2.5$ atm. and SFAP has a very low apparent density (~0.1 g/cm³), we assume that the presence of impurities in Ar gas media such as hydroxide(or carbonate and nitrate, conformed to XPS measurement) adsorbed on the particle surface prevents inter-particle contact during the first few hours after production and prevents sintering.

SFAP particles remaining on the electrodes of the electric filter after EEC possess low electrical conductivity, non-characteristic of metals. The migration of SFAP particles onto the electrodes of the filter is due to the electrostatic charges they possess, which are formed directly during EEC. The reactivity of the three different fractions of SFAP (i.e. the fractions from the positive and negative electrodes, and that which bypasses the electrodes altogether) were obtained using bomb calorimetry (Table 3). Bomb calorimetry is one of the standard methods for obtaining chemical reactivity in such energetic materials as SFAP[14]. The fraction of powder which passed through the electrodes of the electric filter showed the highest dispersion ($S_{sp} = 9.0$ m²/g), but an enthalpy of Al_2O_3 formation smallest amongst the three fractions (and lower than standard see Table 3). SFAP collected from the negatively-charged electrodes possessed the lowest dispersion ($S_{sp} = 5.4$ m²/g), while having a value of Δf_f^{298} (Al_2O_3) higher than standard, the difference being ~137 kJ/mole, i.e. this fraction had higher metal content, but also a lower value of a_s.

5. Conclusions

1) The new available experimental data suggest that in an electrically exploded conductor nonthermal channels of energy dissipation are operative. It is proposed to use the departure (decrease) of the energy converted to heat from that determined by the Joule-Lentz law as a criterion for the degree of nonequilibrium of the processes of energy delivery with high power density ($\div 10^8 - 10^9$ W/cm³).

2) The fact that some portion of the energy delivered to an electrically exploded conductor is stored by the end products of dispersion of the conductor metal supports the suggestion that the electrical energy converted to heat throughout the explosion process is much smaller than that determined by the Joule-Lentz law.

3) The stability of electric explosive SFAP during their passivation is determined by their production conditions. Regimes of electrical explosion should be selected for the purpose of obtaining powders with the highest metal content. The preferential gas media during EEC is Ar+H_2. An increase in e/e_s (in the range of values studied) leads to a reduction in the metal content. For reactive powders obtained with high metal content, it is necessary to separate the SFAP fractions, which settled on the negative electrode of the electric filter.

Acknowledgements

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