The Effect of Mechanical Activation of Metal Powders on Their Reactivity and Properties of Plasma-Deposited Coatings

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Abstract

The effect of the preliminary mechanical treatment of metal powders on the quality of coatings obtained by plasma deposition is investigated. Substantial improvement of the inner structure and strength properties of the coatings is demonstrated. It is stated that the specific heat effect of the interaction of mechanically treated copper powder with acetic acid increases for mechanical treatment up to 15 min, which is likely to be due to the accumulation of defects in metal volume. The chemical reactivity of the mechanically activated copper powder and of the copper powder obtained by means of the electric explosion of wires is demonstrated to correlate with interplane distances between the planes with (111) Miller indices.

INTRODUCTION

The properties of ultrafine powders (UFP) of metals [1] and ceramics [2] are substantially different from the properties of coarse powders or monoliths. This is first of all due to the excess surface energy, which distorts the equilibrium and symmetry in the distribution of forces and masses, and causes the changes of equilibrium interatomic distances, in comparison with the values for macrocrystals (normal relaxation); this also causes share deformations, changes of the atom ordering motifs on surface faces, smoothing of vertices and edges due to small angle deformations of interatomic bonds (tangential constituent) [1]. Changes of chemical bond lengths, in comparison with macrocrystal, cause the change of the reactivity of ultrafine particles: rapid oxidation, ability to get agglomerated at unusually low temperatures with self-heating [3].

One of the methods to obtain metal UFP is electric explosion of wires (EEW) [3]. This method leads not only to the grinding of metal particles but also to the conservation of non-equilibrium states in which the deformed bonds are fixed, because explosion is followed by very fast cooling of particles. However, mechanical action of solids leads to the deformations of chemical bond lengths, too [4, 5]. This means that the reactivity of solids can be changed not only by dispersing but also with the help of mechanical deformations. The decrease of metal particle size till finely dispersed state is possible with the help of surface-active agents. Because of this, in the present paper we investigate the effect of mechanical action on the reactivity of metal copper and

on the strength of plasma-deposited coatings obtained from copper UFP, and compare the reactivity of mechanically activated copper powder with that of copper UFP obtained by means of EEW.

EXPERIMENTAL

Copper powder of the PMS-A grade, State All-Union Standard 4960-75 with dendrite structure and specific surface of 0.16 m^2/g was used in the investigation. Oxygen content of the copper powder did not exceed 1 %. Mechanical treatment of the powder was performed in a centrifugal planetary mill (AGO-2) [6], in steel vials loaded with steel balls 8 mm in diameter, their total mass being 200 g for powder load mass of 10 g. In order to test the influence of ball and vial materials, as well as the effect of environment, similar treatment was carried out in copper vials with copper balls in argon, which did not lead to the observation of any substantial differences in powder properties. Mechanical treatment of copper powder was carried out for 30 s; then the mill was turned off for 2 min in order to cool the material and the balls; after cooling, the procedure was repeated till the necessary total time of mechanical treatment was reached.

In order to study structural changes that occur in copper powder, X-ray phase analysis was applied (DRON 4.0, monochromatic CuK_a radiation). Specific surface of the samples was measured using the BET procedure with thermal desorption of argon, with the internal reference. Errors of determining specific surface were not larger than 10 %. The reactivity of copper powder was determined as the heat of its interaction with acetic acid using the MKDP-2 microcalorimeter manufactured by the Institute of Petroleum Chemistry, SB RAS. The error of heat measurement did not exceed 5 %. Electron microscopic images were taken with the JSMT-20 scanning electron microscope.

Deposition was performed with the help of the electric arc plasmatron of the linear system with sectional inter-electrode insertion (IEI) [10]. Plasmatron power in the conventional mode of operation was ~50 kW. Air at the flow rate of 2 g/s was used as plasma-forming gas. The current of the plasmatron arc was 180 A, arc voltage was ~280 V. The consumption of the deposited material was 1.39 g/s. The consumption of carrier gas (air) was ~0.1 g/s. Powder was introduced by one-side injection of the powder under the nozzle section. Deposition distance (from the nozzle section to the surface) was ~200 mm. Deposition was carried out on steel plates.

RESULTS AND DISCUSSION

Investigation of metal coatings obtained by plasma deposition of mechanically activated and non-activated metal powders demonstrated that preliminary mechanical activation of metal powder causes substantial increase of break-off effort and to the decrease of the porosity of these coatings. In order to understand why the structure and mechanical properties of these coatings improve, electron microscopic studies were carried out (Fig. 1). Since

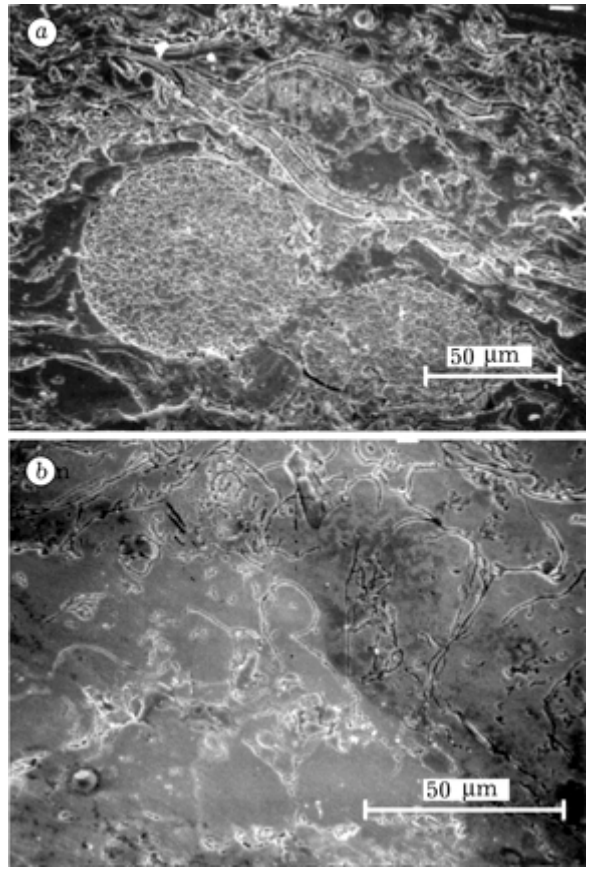

Fig. 1. Electron microscopic images of the cross section of coating obtained by plasma deposition of the initial (*a*) and mechanically treated (*b*) metal copper powder.

the conditions for the deposition of the initial powder and mechanically activated one are identical, the differences in the properties of coatings can be caused only by the changes in the properties of powder itself. This is likely to be due to the fact that mechanically treated powder possess the energy accumulated in the form of various defects; their energy is released during plasma deposition, which causes better fusion of the coatings being deposited and improvement of their adhesion and strength characteristics. Because of this, the question concerning the accumulation of energy in metal powder during its mechanical treatment is of substantial interest.

In order to study the accumulation of mechanical energy in mechanically treated copper powder, in the present work we studied heats of the interaction of mechanically treated copper powder with acetic acid. It is well known [7, 8] that metal copper reacts with acetic acid in the presence of molecular oxygen to form basic acetate of divalent copper:

$$2Cu + O_2 + 2CH_3COOH \rightarrow Cu(CH_3COO)_2 \times Cu(OH)_2$$

We demonstrated that the interaction of the mechanically treated copper powder with acetic acid purified from oxygen by bubbling argon leads to the pressure raise in the reaction volume, which is likely to be due to the reaction:

$$Cu + 2CH_3COOH \rightarrow Cu(CH_3COO)_2 + H_2\text{-}$$

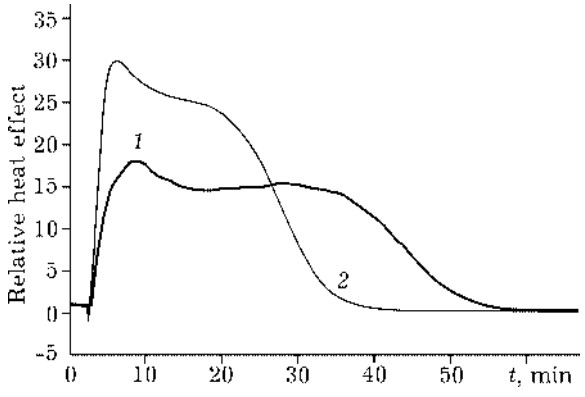

Fig. 2. The kinetics of heat effect during the interacrion of metal copper powder with acetic acid: *1* – initial powder, *2* – after mechanical treatment for 30 s.

It is well established that copper stays after hydrogen in the electrochemical row, so it cannot reduce protons to hydrogen in reactions with acids. However, it is also known [2] that the equations of classical thermodynamics are only to a limited extent applicable to mechanochemical reactions. For example, some reactions with positive change of the free energy DG proceed under mechanochemical treatment; thus, the possibility for the interaction of mechanically activated copper with carbon dioxide was demonstrated in [2]:

$$2Cu + CO_2 \rightarrow 2CuO + C$$

For this process, DG = +140 kcal/mol. Thermodynamic calculation of the free energy for the reaction of metal copper with water gives DG = +118 kcal/mol, while for the reaction with hydrochloric or sulphuric acid it is DG = +20 kcal/mol, which is much lower than the change of free energy in the reaction of copper with carbon dioxide. So, the interaction between mechanically activated copper and acetic acid accompanied by hydrogen evolution is quite possible. Besides, it was demonstrated in [2] that the negative shift of the electrode potential of copper reaches 100 mV at macroscopic deformation, even for bulk metal copper samples. The authors of [10] discovered the increase of negative shifts of the equilibrium potential of copper electrodes with lattice distortions arising under mechanical action.

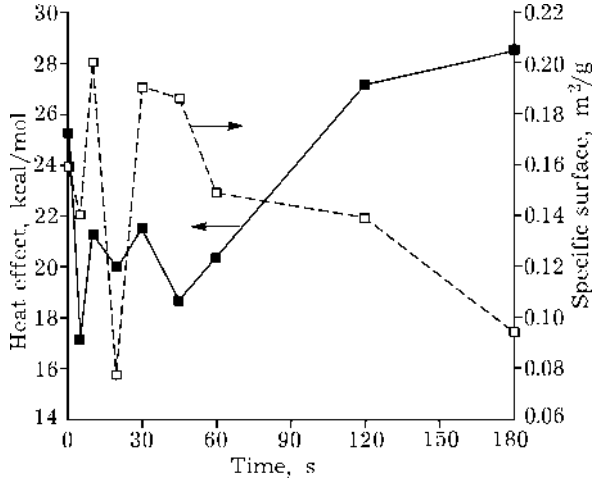

Fig. 3. Changes of specific surface and heat effects of the interaction of acetic acid with mechanically activated metal copper powder depending on the time of mechanical treatment.

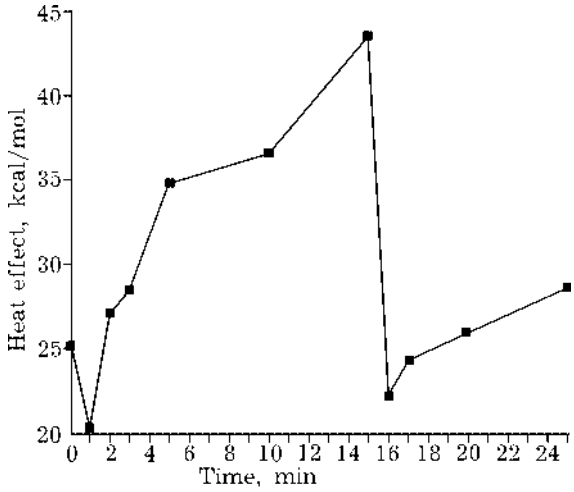

Fig. 4. Changes of the heat effects of acetic acid interaction with mechanically activated copper powder depending on the time of mechanical treatment.

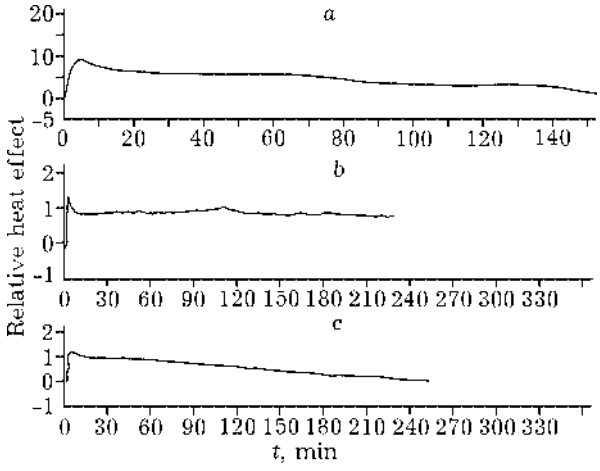

Fig. 5. The kinetics of heat effect during the acetic acid interacrion with metal copper powder mechanically treated for 3 (*a*), 15 (*b*) and 16 min (*c*).

Since it is rather difficult to prevent copper powder from oxidation by the oxygen of the air, besides the above-mentioned processes the interaction of copper oxides with acetic acid is also possible:

$$CuO + 2CH_3COOH \rightarrow Cu(CH_3COO)_2 + H_2O$$

$$Cu_2O + 4CH_3COOH + 1/2O_2 \rightarrow 2Cu(CH_3COO)_2 + 2H_2O$$

Because of this, we also investigated the heats of the interaction of mechanically activated copper oxides with acetic acid.

One can see in Fig. 2 presenting the heat effects of the interaction of acetic acid with the initial metal copper and the sample mechanically activated for 30 s that the time of this reaction decreases.

Figure 3 shows the dependencies of the changes of specific surface and heat effects of

TABLE 1

Characteristics of copper powder mechanically treated in AGO-2

Time of mechanical treatment, s	Heat effect, kcal/mol	Reaction time, min	Transformation degree, %	Specific surface, m^2/g
0	25.2	60	40.2	0.16
5	17.1	42	56.9	0.14
10	21.3	55	50.3	0.20
20	20.0	35	52.5	0.08
30	21.5	45	49.8	0.19
45	18.7	37	57.5	0.19
60	20.3	50	47.9	0.15
120	27.1	63	38.5	0.14
180	28.5	155	29.0	0.09
300	34.7	160	33.3	
600	36.6	340	13.9	
900	43.5	2400	100.0	
960	22.1	215	8.4	
1020	24.2	135	19.2	
1200	25.8	190	11.7	
1500	28.6	180	35.6	

TABLE 2

Characteristics of Cu_2O and CuO mechanically treated in AGO-2

Time of mechanical treatment, s	Heat effect, kcal/mol	Transformation degree, %	Specific surface, m^2/g
		Cu_2O	
0	16.4	72.3	0.37
30	14.8	87.1	2.5
60	13.3	94.3	4.9
120	15.2	97.6	6.5
180	9.2	98.5	2.4
		CuO	
0	10.6	40.9	0.20
30	8.5	94.7	1.4
60	9.1	98.6	1.9
120	8.9	99.2	2.2
180	5.1	99.2	3.3

interaction of metal copper powder with acetic acid *versus* the time of copper powder mechanical treatment. It follows from these data that the heat effect of the interaction of mechanically activated copper powder with acetic acid correlates with the specific surface of the powder for mechanical treatment up to 60 s; for longer mechanical treatment, specific surface decreases but the heat effect increases.

Figure 4 shows the dependence of heat effects of the interaction of metal copper powder with acetic acid versus time of mechanical treatment; a monotonous increase of the heat effect up to 43 kcal/mol is observed versus the time of mechanical treatment up to 15 min, power input by the balls being 55 W/g (40 g); for 16 min of mechanical treatment, the heat effect drops down to 22 kcal/mol; further it again starts to increase.

Figure 2 shows the kinetics of heat evolution in the interaction of initial copper powder with acetic acid; Fig. 5 (curve *1*) shows the same for the powder activated for 3 min. One can see that the time of reaction has increased nearly by a factor of 3. An increase of copper powder mechanical activation time to 15 min gives the longest reaction time (~40 h) and the highest completeness of the reaction (see Fig. 5, curve *2*, and Table 1). Mechanical activation of copper powder for 16 min leads to the decrease of reaction time to 260 min and to a 25 % completeness (see Fig. 5, curve *3*). These data are

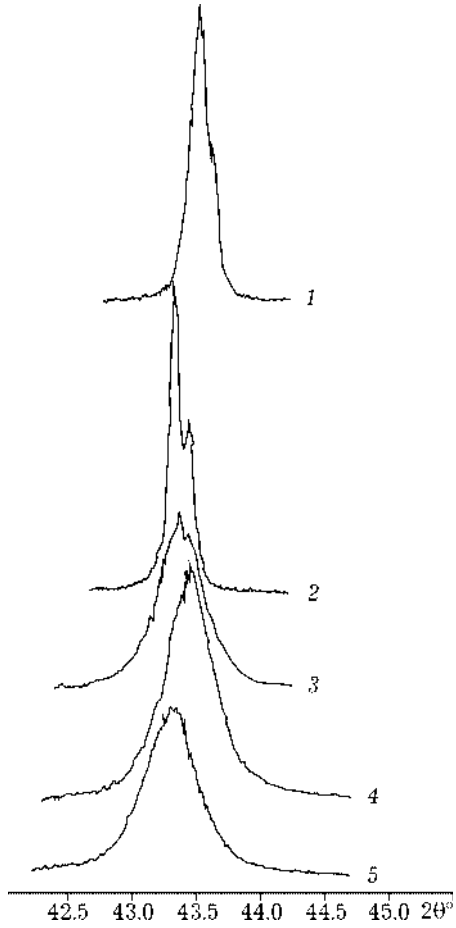

Fig. 6. X-ray diffraction patterns of metal copper powder: *1* – initial powder; *2* – copper metal powder obtained by electric explosion of wires; *3–5* – copper metal powder after mechanical activation for 15 (*3*), 18 (*4*), and 25 min (*5*).

the evidence that the volume of copper particles activated mechanically for 15 min is fully saturated with defects, so they exhibit the highest reactivity. After mechanical activation for 16 min, 75 % of the volume is deactivated.

Unlike the case of mechanically activated metal copper powders, the heats of interaction of the initial and mechanically activated copper oxides CuO and Cu_2O with acetic acid do not exceed 16 kcal/mol (Table 2) and decrease with increasing time of mechanical treatment, though specific surface and transformation degree increase unlike the case of metal powder (see Table 1).

The separation of the powder mechanically activated for 15 min into the coarse and fine fractions demonstrated that the interaction of the coarse fraction with acetic acid results in the release of ~60 kcal/mol while the fine fraction gives ~30 kcal/mol, which is the evidence that the energy is accumulated mainly in coarse fractions.

The investigation of mechanically activated metal copper powder by means of X-ray phase analysis demonstrated that the coherent length decreases monotonously with mechanical treatment time from 160 nm (initial powder) to 25 nm (mechanically activated for 25 min) (see Table 1), though, as one can see in Fig. 4, specific heat of the reaction of mechanically activated copper powder with acetic acid increases monotonously only till mechanical activation tine of 15 min. Because of this, in order to reveal the reasons of the chemical reactivity of mechanically activated copper powder and copper powder obtained by electric explosion of wires, let us consider the results of X-ray phase analysis in more detail.

It follows from Fig. 6 that, in comparison with the powder metal copper sample (curve *1*), metal copper powder activated for 15 min (curve *2*) and metal copper powder obtained by electric explosion of wires (curve *3*) exhibit larger distances between the planes with (111) Miller indices. Mechanical activation of metal copper powder for 18 min (see Fig. 6, curve *4*) makes this interplanar distance the same as that in the initial copper, which explains the drop of the reactivity of metal copper powder in case of mechanical activation lasting for more than 15 min (see Fig. 4). Further mechanical activation till 25 min (see Fig. 6, curve *5*) again causes an increase of this interplanar distance and to the increase of the reactivity of this sample (see Fig. 4).

CONCLUSIONS

So, in the present study we (1) discovered the effect of preliminary mechanical treatment of metal powders on the quality of the coatings obtained by plasma deposition; (2) observed an increase of the specific heat effect of the interaction of mechanically treated copper powder with acetic acid for the time of mechanical treatment up to 15 min, which is likely to be due to the accumulation of defects in metal volume; (3) discovered the relaxation of defect accumulation in metal volume during mechanical treatment of metal copper powder during mechanical treatment for longer than 15 min; (4) demonstrated that the reactivity of mechanically activated metal copper powder and the metal copper powder obtained by the electric explosion of wires correlates with interplanar distances between the planes with (111) Miller indices.

REFERENCES

1 I. D. Morokhov, V. I. Petinov, L. I. Trusov, V. F. Petrunin, *UFN*, 133, 4 (1981) 653.
2 G. Heinicke, Tribochemistry, Akademie-Verlag, Berlin, 1984.
3 G. V. Ivanov, N. A. Yavorovsky, Yu. A. Kotov *et al.*, *DAN SSSR*, 275, 4 (1984) 873.
4 V. A. Poluboyarov, O. V. Andryushkova, E. G. Avvakumov *et al.*, *Sib. khim. zhurn.*, 1 (1993) 119.
5 V. A. Poluboyarov, O. V. Andryushkova, E. G. Avvakumov *et al.*, *FTPRPI*, 1 (1993) 93.
6 Pat. 975068 RF, 1982.
7 Vysokoenergeticheskiye protsessy obrabotki materialov, Nauka, Novosibirsk, 2000.
8 R. Ripan, I. Chetyanu, Neorganicheskaya khimiya, Mir, Moscow, 1972, p. 692.
9 E. E. Sirotkina, N. S. Kobotaeva, N. V. Svarovskaya, Materialy Vseros. konf. "Fizikokhimiya ul'tradispersnykh sistem", Ekaterinburg, October 9–13, 2000, Moscow, 2000, p. 51.
10 E. M. Gutman, Mekhanokhimiya metallov i zashchita ot korrozii, Metallurgiya, Moscow, 1974.