EFFECTS OF PROCESSING PARAMETERS ON THE CHARACTERISTICS OF EXFOLIATED GRAPHITE AND MATERIALS COMPACTED FROM IT

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A study has been made on how the process parameters in making exfoliated graphite (grain-size composition of the GAK-2 natural graphite, concentrations of sulfuric acid and (NH₄)₂S₂O₈ oxidizer, and heat treatment mode) influence the bulk density of powder and the compressive strength of compacted materials made from it. The compressive strength of pressed exfoliated graphite is determined not only by the degree of structure loosening in the initial graphite (specific surface or bulk density) but also by the physicochemical state of the surface, which is affected by the thermochemical treatment conditions.

Keywords: exfoliated graphite, granulometric composition, bulk density, heat treatment, pressing, strength.

INTRODUCTION

Exfoliated graphite (EG) is produced by thermochemical treatment of natural graphite and is an initial material for a wide class of industrial products: seal for thermal power plant, sliding electrical contacts, and components of chemical plant [1-3]. Recently, there have been extended experiments on the technology for forming EG from the viewpoint of minimizing the material and energy losses and of raising the ecological cleanliness of the process. Most are concerned with optimizing the stages of making materials on the basis of EG: intercalation [4-6], heat treatment [7, 8], compacting [9, 10], and alloying [11-13]. As a rule, the basic parameters in making EG relate to the stage of forming the intercalation graphite (IG), together with the bulk density of the EG powder, and parameters concerning the pressability. Not much is known about the dependence of the strength parameters of EG materials on the above parameters [10, 13], particularly how the parameters in making the EG affect the mechanical characteristics of items made from it.

The structure and properties of an EG-based materials resemble those of many materials made by powder metallurgy methods in that they are formed directly during the pressing or rolling and are dependent to a significant extent on the properties of the EG powder itself. Certainly, one characteristic that influences the final properties of the pressed material is the specific surface of the powder, which in turn is correlated with the bulk density \( \gamma \) [6]. That specific surface may attain 45-50 m²/g, while the bulk density is 1.5-2.0 g/dm³ [8].

The bulk density is dependent on several production parameters. It has been shown [4] that the bulk density decreases in the graphite – H₂SO₄ – oxidizer system as the sizes of the initial graphite particles increase and as the amount of oxidizer rises under otherwise equal conditions (the oxidizer may be K₂Cr₂O₇ or (NH₄)₂S₂O₈). In the graphite – H₂SO₄ – K₂Cr₂O₇ system, the bulk density is dependent on the degree of intercalation, but that is not so in the graphite – H₂SO₄ – (NH₄)₂S₂O₈ one. It has been found [6] that the bulk density under otherwise equal conditions is also related to the chemical nature of the intercalant, and it has been shown [8] that \( \gamma \) falls monotonically as the heat treatment temperature for the intercalated graphite rises. It has been established [12] that the bulk density of EG falls monotonically to a certain level and then begins to rise gradually as the amount of oxidizer increases in graphite – H₂SO₄ – oxidizer systems. It was found there that varying the ratios of graphite and sulfuric acid with fixed amounts of
oxidizer does not influence $\gamma$ over the range 2-10 kg $\text{H}_2\text{SO}_4$ per 1 kg of graphite. Optimum conditions were determined for making EG to provide minimal bulk density: sulfuric concentration not less than 93%, amount of oxidizer 7 g-eq per 1 kg of graphite, reaction time 10 min, and heat treatment temperature for the intercalated graphite not less than 850°C. At the same time, in [9] it was shown that the morphology and amount of defects of the EG particles, which are dependent on the heat treatment temperature, substantially influence the pressability. The best treatment temperature from the viewpoint of the ability of the EG powder for pressing has been found to lie in the range 700-1000°C. It has been concluded [10] that the physicomechanical characteristics of pressed EG materials are substantially dependent on the forming methods and apparent density of the material, while in [13] it has been shown that the higher the EG bulk density, the lower the mechanical strength of materials pressed from it (in that case, regulating $\gamma$ with the fixed heat treatment temperature was done by changing the amount of oxidizer in the graphite – $\text{H}_2\text{SO}_4$ – oxidizer system).

We have examined the effects of oxidation parameters in the treatment of the natural graphite and of energy factors in the heat treatment of intercalated graphite on the bulk density of the EG thus obtained and on the mechanical strength of materials formed from it.

**Materials and Methods**

We used GAK-2 natural graphite from the Zavall deposit in the Ukraine as raw material for making EG. The intercalation compounds were made in the graphite – $\text{H}_2\text{SO}_4$ – (NH$_4$)$_2$S$_2$O$_8$ system by the [8] method. We used ammonium persulfate as oxidizer because of its lack of residue and slight contamination of the EG [6]. The maximum sulfuric acid concentration was 93.64%, and the concentration was varied by diluting the acid with distilled water. When we examined the effects of the acid concentration, and also in other cases with a fixed concentration of the oxidizer, we used standard ratios for the masses of graphite, sulfuric acid, and oxidizer as given in [12]. When we changed the amount of oxidizer per kg of graphite, the amount of sulfuric acid was kept constant and constituted 2 kg per 1 kg of graphite. The initial temperature of the oxidizing mixture in all researches was 20°C, and the reaction time was 30 min. The graphite intercalation compounds were washed to pH 6-7 of tap water and dried at 100°C to a water content less than 1%. The heat treatment of the IG was under static conditions in a silica reactor in an electric oven. In examining the concentration and temperature dependence of the bulk density, we used specimens of equal mass. We examine the effects of the heat treatment factors such as the heating rate at a fixed temperature for the reactor wall by varying the mass of the IG specimens. We produced conditions which in all cases had the mass of the specimen and the volume of the graphite much less than the mass and volume of the reactor, so one could neglect the scale factor. The quartz reactor in the shaft oven previously brought to the set temperature was supplied with the specimen of IG powder of mass $m_h$. The temperature change and the heating rate were monitored with a thermocouple placed at the center of the specimen. To examine the effects of the bulk density (specific surface) on the strength, the exfoliated graphite was also made by heating standard oxidized graphite and crushing in liquid EG made in the standard way. When the EG powder was made by gradual heating as above, the temperature of the oven was raised gradually from 200 to 600°C taking 30 min for each 100 deg. To prepare the EG powder in liquid, it was stirred in distilled water for 1, 5, and 10 min, after which the bulk density was changed. The product was dried to constant mass. The bulk densities of the IG and EG powders were determined in accordance with GOST 14922-77. The grain-size compositions for the initial graphite and the IG were determined by grading with laboratory sieves. The strength of cylindrical specimens shaped from the EG with height and diameter 20 mm was examined with a 2167R-50 equipment employing uniaxial compression with simultaneous strain diagram recording [14]. The densities of the shaped specimens whose properties were examined were $\rho_s = 0.6$-1.0 g/cm$^3$. That density allowed us to rule out any effect from structural anisotropy [10]. To determine the strength, we measured $\sigma_{10}$, the compressive stress for 10% deformation. The measurement error was 3%.

**Results and Discussion**

Table 1 gives the grain-size compositions of the initial GAK-2 graphite and intercalation compounds made from it under standard conditions [12]. More than half of the initial graphite particles have sizes in the range 100-200 $\mu$m. Intercalation increases the mean size. The bulk density is reduced by more than a factor 2. Subsequent heat treatment of each IG fraction showed a reduction in the bulk density of the EG, but it was observed that there was an