Effect of Fullerenes Additions on Physical - Mechanical Properties of Hot-Forged Iron-Based Powder Materials

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Abstract

It is possible to expand the applications ranges of powder material products by enhancing the performance properties of these products in addition to their manufacturability and reliability together, it’s possible by materials structures modification. In this paper, the effect of fullerene (C60) additives to iron-based powder material has been studied. All samples produced by Hot-Forging (HF) powder materials technology. Green and HF density of the obtained samples calculated by volume / weight and Archimede’s principle, respectively. The effect of technological parameters on the microstructure of carbon steels’ samples was done by an ALTAMI MET-1M metallographic microscope. Tensile test executed by using of a universal testing machine UMM –5 and the microhardness (HV10) was measured by REICHERT hardness test machine. The results showed that the HF C60 steels’ samples had higher density and strength of 0.81 and 25%, respectively, with a good plasticity in comparison with graphite steels’ samples.

Keywords

hot-forging technology, fullerene (C60), iron powder, mechanical properties.

1. Introduction

Powder metallurgy methods applied to the production of parts for various purposes occur in tough competition with traditional technologies of stamping, casting, machining, rolled products. Further expansion of the range of powder metallurgy products depends on the development of effective and competitive methods to improve their operational properties. Among such techniques may be mentioned especially Hot –Forging (HF) of porous preforms which has worked well as a simple and reliable method for obtaining high density powder products [1–3]. Providing the necessary combination of manufacturability and reliability of the product together with ensuring the required properties is carried out by improving (changing) the structure of materials. Iron-based materials and parts of them are one of the main types of powder metallurgy products. In powder metallurgy, iron-carbon materials are produced by doping carbon into iron powder in the form of graphite, carbon black or cast iron powder. In [4,5], carbon powder in the form of fullerene C60 was used.
Previously it was thought that carbon had three allotropic forms: diamond, graphite and carbon. At present, the fourth allotropic form of carbon is known, the so-called fullerene, named after the American architect Richard Buckminster Fuller, who designed hemispherical architectural structures consisting of hexagons and pentagons. The C60 molecule is the most common and most stable of all fullerenes [6-8].

In metallurgy, of interest is the synthesis of fullerenes and their compounds in the structure of iron-carbon alloys. In [9], fullerene and iron powder was sintered at high temperature and pressure. As a result, a composite material was obtained, where microparticles of the superhard carbon phase were formed in the iron matrix. This material had a high wear resistance. It was shown [10] that fullerenes formed in the steel structure are synthesized during sharp quenching into diamond-like compounds. This makes it possible to increase the hardness and wear resistance of ordinary carbon steels.

The possibility of expanding the field of application of powder metallurgy methods by creating powder materials (PM) with enhanced performance properties is of paramount importance. So, the goal of this paper was studying the effect of fullerenes additives to iron-based powder materials by HF technology.

2. Experimental Procedure:

2.1 Materials:

For the preparation of samples according to the procedure described in [11], the following materials were used:

- Reduced iron powder NC100.24 (from Höganäs AB);
- Fullerene C_{60} (purity 99.5%; particle size < 10 nm; from Nano product company, Saint-Petersburg, Russia);
- Graphite powder (GK-3, composition, wt.%: ≥ 94 C; ≤ 5 ash; ≤ 1 volatile; ≤ 1 humidity; D50 = 43 μm).

2.2 Technology of Obtaining Samples:

Powder charges were carried out in a conical blender for 2 hours with ethyl alcohol as a wetting medium. Green samples were obtained by filling the die cavity with 44 ± 0.01 g of powder charges, which consisted of holder, two semi-matrices, and a lower and upper punch [12] then, powder charges had compacted by cold-pressing (CP), which was performed on a hydraulic press HPM60 model (maximum force 1000 kN) down to the abutment. The working parts of the die were made of KhVG (composition, wt.%: 0.9 – 1.05 C; 0.1 – 0.4 Si; 0.8 – 1.1 Mn; < 0.35 Ni; < 0.03 S; <0.03 P; 0.9 – 1.2 Cr; <0.3 Mo; 1.2 – 1.6 W; <0.3 Cu; bal. Fe) and Kh12M (1.45 – 1.65 C; 0.15 – 0.35 Si; 0.15 – 0.4 Mn; < 0.03 S; <0.03 P; 11.0 – 12.5 Cr; 0.4 – 0.6 Mo; 0.15 – 0.3 V; bal. Fe) steels, hardened to HRC 56-62.

Hot-forging green samples was executed by using the method developed at the Platov South Russian State Polytechnic University (PSRSPU) [13]. So, the forging applied work which was used here, is approximately, equal to 342 MJ/m^3, which had calculated by using the following equation:

\[
\text{work}_{HFS} = w_f [kg] \times 9.8 \left[ \frac{m}{s^2} \right] \times H_f [m] \times \rho_k [g/cm^3] / w_{HFS} [g] \times MJ/m^3;
\]

Where:
- \( w_f \) : the work done by forging the preheated samples; \( w_f \) : weight of falling-mass, it was 100 kg; \( H_f \) : the height of the falling-mass dropped from, here, was 1.95 m; \( \rho_k \) : theoretical density of carbon steel, which is approximately, 7.88 g/cm^3; \( w_{HFS} \) : dry weight of hot-forged sample.
The die for HF was similar to the die for CP of samples (Fig. 1.) But has a slightly larger size. Working parts of the HF die were made of steel 5KhNM (composition, wt. %: 0.5 – 0.6 C; 0.1 – 0.4 Si; 0.5 – 0.8 Mn; 1.4 – 1.8 Ni; < 0.03 S; < 0.03 P; 0.5 – 0.8 Cr; 0.15 – 0.3 Mo; < 0.3 Cu; bal. Fe) with hardness HRC 45 - 48. Heating of green samples before the HF was carried out in a chamber electric furnace with silicate heaters. Green samples were laid in a container of heat-resistant steel 10Kh23N18 (composition, wt. %: < 0.1 C; < 1.0 Si; < 2.0 Mn; 17.0 – 20.0 Ni; < 0.02 S; < 0.035 P; 22.0 – 25.0 Cr; < 0.2 Ti; < 0.3 Cu; bal. Fe), placed in the working space of the furnace and purged with protective gas - dissociated ammonia. Extraction of heated sample from the furnace was after 10 minutes. Then, the heated sample was placed in a HF die then a seal was applied and lefted to cool in air. Thus, HF technology (Table 1) of powder material includes: preparation of powder charges; formation of green samples after CP with porosity of 14-18%

(400 - 490 MPa); hot-forging with 342 MJ/m³ at a heating temperature of 1100 °C to a residual porosity of 0.55-2.7%. Finally, prepare samples for studying physical-mechanical properties.

![Figure 1. Die of green and forged samples 1-holder , 2-semi-matrix, 3- upper punch, 4-insert (lower punch).](image)

| Powder Charge | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|---------------|----|----|----|----|----|----|----|----|----|----|
| NC100.24, wt. %| 99.8 | 99.6 | 99.4 | 99.2 | 99.0 | 99.8 | 99.6 | 99.4 | 99.2 | 99.0 |
| Coo, wt. %    | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 0  | 0  | 0  | 0  | 0  |
| GK-3, wt. %   | 0  | 0  | 0  | 0  | 0  | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |

3. Methodology of Investigation of Physical-Mechanical Properties:
Green and HF density of steel powder samples were determined by volume / weight and Archimedes' principle, respectively. Weighing was carried out on an analytical balance of the type WA-35 with an accuracy of up to 0.0001 g. The error in determining the density was 0.8%.
A metallographic microscope was used by ALTAMI MET-1M to study the effect of technological parameters on the microstructure of carbon steels of samples obtained after HF. For this, microsections were made with the test surface d = 5 mm (Fig. 2 a). The etching modes of microsections were chosen experimentally. Etching was carried out in a 3% solution of HNO3 in ethanol, as well as Marble reagent.
Testing of powder materials produced to determine the strength properties and hardness. The main criterion for evaluating the strength properties of powder materials is tensile strength. To study the mechanical properties of the steels, Gagarin tensile specimens of forged samples (Fig.2a and b) were machined with the working part diameter $d_0 = 5\text{mm}$ and the gage length $l_0 = 25\text{mm}$. The ultimate tensile strength (UTS, MPa) as determined by using a universal testing machine UMM - 5 according to GOST 1497-84.

The microhardness (HV10) of the structural components of the HF samples was determined according to GOST 9450-76 with the use hardness test machine (REICHERT, Austria).

![Figure 2.](image)

Figure 2. Represents (a) microstructures’ studying sections which prepared from; b) hot-forged Gagarin tensile test samples after fracture.

4. Results and Discussion:

4.1. Density

The density of produced carbon steels materials decreased with increasing carbon content (Fig.3a and b). After CP, density of green samples with graphite carbon type were higher than those with fullerene (C60) due to bigger density of graphite, 2.2670 g.cm$^{-3}$ than for C60, 1.5651 g cm$^{-3}$ [14]. Conversely, the porosity of cold pressed samples decreased with increasing density of carbonaceous additive. The porosity decreased from 16 % and 16.9 % (highest porosity values after CP) for samples with graphite and fullerene, respectively to 1.3 % with graphite, 0.6 % with fullerene (lowest porosity values after HF). So, samples of fullerene steels after HF had higher densities (lower porosities) about 0.81% than HF graphite samples. The higher density of the samples with fullerene is due to the smaller size of the initial fullerene particles, as well as the greater diffusion mobility of carbon atoms in the fullerene composition [14]. Also, with increasing C60 additives (decreasing of relative density) the volume change increased significantly in comparison with graphite powder content of HF steels samples because of relatively low density of C60.

One of the important factors influencing on the strength of iron-based powder materials is the density. Higher densities (7.7 - 7.8 g/cm$^3$) can be obtained by powder forging technology among many others techniques. Higher densities lead to high physical-mechanical properties of iron-based powder parts [15].
Figure 3. represents the effect of a) carbon additives’ type and content on green and HF density; b) relative density on volume change of hot-forged steels’ samples.

4.2. Mechanical Properties

In the case after HF (Fig.4) the strength of samples with fullerene 25% more than samples with graphite. Relative elongation of samples with fullerene higher than with graphite. The reduction in area is proportional to elongation.

Figure 4. Mechanical properties of powder steels in as-forged condition versus carbon content.

As this study work compared with other works, table 2 showed that the mechanical properties of hot-forged powder carbon steels have been demonstrated and the effective rule of fullerene (C_{60}) additions in improving the UTS of steel samples. In work [16] it was found significant transformation of ferrite to martensite and austenite of compacted samples with fullerene and nanotubes additions. So, the higher strength of steel samples with fullerene additions almost came from these transformations.
Table 2. represents the comparison of mechanical properties of different production processes.

| Materials | Producing Conditions | Produced Samples | Density, g/cm³ | UTS, MPa | Elongation, % | Reference |
|-----------|----------------------|------------------|---------------|---------|--------------|-----------|
| Astaloy   | Samples were pressed at 600 MPa and sintered at temperatures of 1140 °C, and cooled at 40 K min⁻¹. | Astaloy Mo+0.5%G | 7.27 | 460 | 1.8 | [18] |
|          | Sample was compacted under 600 MPa and sintered in 1120 °C for 30 min. then sized at 200 °C (the better procedure) | Astaloy Mo+1.0%G | 7.14 | 555 | 1.1 |          |
| CrL+0.5%G | All samples compacted under 400 - 490 MPa and hot-forged after heating at 1100 °C for 10 min. and leaved to cool in air. | NC100.24 +0.4%G | 7.72 | 430 | 4.84 |          |
|          | All samples compacted under 400 - 490 MPa and hot-forged after heating at 1100 °C for 10 min. and leaved to cool in air. | NC100.24 +0.6%G | 7.69 | 465 | 3.81 |          |
|          | All samples compacted under 400 - 490 MPa and hot-forged after heating at 1100 °C for 10 min. and leaved to cool in air. | NC100.24 +0.6%F | 7.75 | 543 | 5.6 | This study |
|          | All samples compacted under 400 - 490 MPa and hot-forged after heating at 1100 °C for 10 min. and leaved to cool in air. | NC100.24 +1.0%F | 7.71 | 590 | 4.4 |          |

4.3. Microstructural Properties:

The structures of the samples with the addition of fullerene and graphite have no significant differences. They are a combination of areas of ferrite, sorbite, troostite and
Figure 5. Structures of carbon as-forged powder steels, x400. a) 0.4% fullerene; b) 0.4 graphite; c) 0.6 % fullerene; d) 0.6% graphite; e) 0.8% fullerene; f) 0.8 % graphite; g) 1.0 % fullerene and h) 0.2 % graphite.

With an increase in the carbon content, the number of sites and the area occupied by eutectoid structures increases. In Table 3, the results of measurements of microhardness of steel samples in the state after HF are presented.

Table 3. Microhardness of the structural components of as-forged steel samples with fullerene and graphite additives, individually.

| Carbon Additives | Microhardness, MPa |
|------------------|--------------------|
|                  |                    |

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It was noted that the microhardness phases of fullerene steels samples (ferrite, perlite, sorbit, troostite and bainite) increased effectively in a range from 200 to 1000 MPa more than those with graphite. The samples of the surface rolling material with 0.8 wt. % carbon have the highest surface hardness (340 HV0.1)[20]. In work [21] were a hot-compacted modified chromium-molybdenum steels’ samples by fullerenes and carbon nanotubes additions showed higher ultimate tensile strength and microhardness (HV) but with a lower plasticity than unmodified samples.

5. Conclusions:
1-Hot forging powder materials technology had effective role in improving mechanical properties of steels’ samples.
2-The addition of fullerene (C60) to iron-based powder materials contributes to an increase in the strength characteristics of samples (higher density 0.81% and higher strength 25% than for graphite steels’ samples with a good plasticity).
3-There are no significant differences between the structures of the samples with fullerene and graphite additions but the first one had higher microhardness (HV10) than the samples with graphite.
4-Higher strength of steel samples with fullerene additions came from martensitic and austenitic transformations.

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