Modifying surface properties of polyamide powders for selective laser sintering

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Annotation. The purpose of this work was determination of the changes in surface properties of Polyamide-12 powder used in Selective Laser Sintering (SLS). The powders of original polyamide Duraform PA¹ (3D Systems) were investigated. Also the powders remaining around the product after the sintering process were investigated. The difference in the chemical structure of the Polyamide-12 powder surface layers has been established. The reason is the increased content of oxygen-containing groups in the surface layers. To a greater extent, this difference was revealed for powders left after sintering and intended for reuse. Aliphatic chains are subject to oxidative degradation in the surface layers of the original powder. In the powder remaining after sintering, terminal carbonyl and amine groups are subject to oxidative degradation.

Introduction

The technology of additive manufacturing in the 21st century is rapidly developing. New methods for the additive construction of products based on various physicochemical phenomena are emerging. Relatively old technologies of additive production, discovered in the last century, only strengthen their position in the hierarchy of production processes. One of such methods is the technology of selective laser sintering [1, 2]. In selective laser sintering (SLS) of polymer products, only a part of the powder layer corresponding to the product profile is subjected to laser impact. In this case, there is no need to create supports, since the product is surrounded by "green" powder, which serves as a support. It is the absence of the requirement for the presence of supports and the possibility of using thermoplastic materials that made this technology popular in the field of prototyping functional products. However, when reusing "green" powders, there are difficulties associated with the deterioration of the surface quality of the product, with an increase in roughness, especially on the vertical walls of the product [3], and sometimes with no powder in the structure of the product itself. This leads to deviations in the size of the product from the parameters of the virtual model. In addition, sometimes on the cold metal parts of the working chamber, crystalline structures form in the form of sharp thin needles and condensation of the ultrafine powder fraction, which indicates polymer sublimation processes or the presence of some amount of volatile constituents in the powder [4]. The identified problems raise questions about the impossibility of re-using the "green" powder during the next SLS cycles, which leads to its
disposal. Understanding the process of changing the properties of the powder in the future would allow the development of methods and equipment for the reuse of powder.

The aim of this work was to investigate the causes leading to changes in the surface properties of polyamide powders used in the selective laser sintering.

Main part

Selective laser sintering of polyamide powders was carried out on SLS Spro 60 HD. This setup is equipped with a continuous CO₂ laser with a power of 70 W and a wavelength of 10.6 microns. Figure 1 shows the internal view of the working chamber. The chamber has three platforms that move in the vertical direction, the right one (1) and the left one (2) are designed for storing the powder and its preheating, the central platform (3) serves as the working area of the building. The roller (4) moves the powder from the platform area (1) or (2) to the working platform and a laser scanning process is performed on the surface of the layer. Before moving the powder into the working area, the powder is heated to a temperature of 135 °C. In the working area, the temperature of the powder is maintained at 171 °C. The chamber atmosphere is pre-filled with nitrogen, in the process, the oxygen concentration is 3%.

![Figure 1. Inside view of a camera for building a SLS Spro 60 HD selective laser sintering machine. 1-right and 2-left powder storage platform, 3-working powder sinter platform, 4-powder transfer roller, 5-slide panel with infrared heaters, 6-IR sensors](image)

Warming up is performed in two ways by using the heaters, located in the pipes moving platforms, and infrared heating elements in the upper extendable panels (5). Temperature control is carried out using infrared sensors (6).

The powders of the original polyamide Duraform PA (3D Systems) (sample 1) and the powder remaining after sintering (sample 2) were investigated. The studies were conducted by X-ray photoelectron, infrared and Raman (Raman scattering) spectroscopy and electron microscopy.

To obtain X-ray photoelectron spectra (XPS), an ES-2401 spectrometer with a magnesium anode (photon energy 1253.6 eV) was used. The power of the X-ray tube was 200 W, the vacuum in the analyzer chamber was 10⁻⁶ Pa. The spectrometer was calibrated along the line Au4f₁/₂ = 84.0 eV. The value of the binding energy (Eₜₘ) C1s-electrons of carbon atoms in the aliphatic hydrocarbon chain is assumed to be 285.0 eV [5]. The accuracy of determining the position of the lines in the C1s-spectrum was 0.2 eV, the decomposition of the spectra was carried out according to the method described in [6].
IR spectra were obtained on an Excalibur Varian 3100 FT-IR spectrometer in the range of 400-6000 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\). Prepared tablets with KBr for research on transmission. The obtained spectra were normalized to the total intensity.

Raman spectra (RS) were obtained on a Horiba LabRam HR800 spectrometer using a He – Ne laser operating at a wavelength of 632.8 nm, the power consumption did not exceed 20 mW.

The surface morphology of the powders was studied using an EVO 50 Carl Zeiss AG scanning electron microscope.

**Results and discussion**

Electron microscopy (Fig. 2) showed practically identical size fractions of samples 1 and 2.

![Microphotographs of polyamide powder: a - sample 1, b - sample 2.](image)

In the IR spectroscopic study of powders, it was found that the functional groups of the powders are similar (Fig. 3) and correspond to polyamide 12 (poly (dodecanamide)) [7]. The authors of [8] for assess the quality of polyamides in the IR-spectroscopic study proposed a method for comparing the intensities of peaks of terminal amine or carbonyl groups and CH2 groups. The amine group in the studied powders is characterized by a frequency of 3304, 0 cm\(^{-1}\), carbonyl - 1639 cm\(^{-1}\), CH2 - 2920 cm\(^{-1}\). Using the approach proposed in [8], we estimated the ratios of the intensities of the bands of the terminal amine and carbonyl groups to the intensity of the band of the CH2 group. As can be seen from Table 1, the intensity ratios of the bands of the functional groups for different powders are close and their difference does not exceed 1% for amine and 3% for carbonyl groups, which indicates the proximity of the chemical structure of the powders.

Table 1. The intensity attitude of the bands of the functional groups of polyamide powders according to IR spectroscopy.

| Sample | \(-\text{NH/CH}_2\) | \(-\text{CO/CH}_2\) |
|--------|----------------|----------------|
| 1      | 0,971          | 1,10           |
| 2      | 0,967          | 1,11           |
The study of RS-spectroscopy powders also revealed the similarity of the spectra of all the studied powders (Fig. 4) and their correspondence to the chemical structure of poly (dodecanamide) [7].

It should be noted that both IR and RS - spectroscopy in these studies provide almost volumetric characteristics of powders. XPS is a surface research method, the analysis depth of which does not exceed 10 nm [9]. Studies conducted by the XPS method showed a difference in the chemical composition of the surface of the powders (Table 2, Figure 4). As follows from the chemical formula of polyamide 12, the ratio of C: O: N elements (at.%) should be 86: 7: 7. However, an excess of the amount of oxygen in the surface layers of all samples was found, which follows from the O / N ratio (Table 2). The range of content of elements in the surface layers of powders with parallel surveys of different samples (of which there were at least three) of the same sample indicates the presence of powder in the sample with different chemical composition of the surface.

Table 2. The content of elements in the surface layers of polyamide powders (the range is indicated for parallel surveys).

| Sample | Elements, at.% |  |  |  |
|--------|----------------|---|---|---|
|        | C   | O   | N  | O/N |
| 1      | 81-90 | 7-12 | 3-7 | 2.3-1.7 |
| 2      | 82-84 | 10-12 | 5-7 | 2.0-1.7 |
According to [5], the N1s- and O1s-spectra of polyamide 12 are represented by single lines with binding energy ($E_{be}$) 399.8 eV and 531.3 eV, corresponding to nitrogen and oxygen atoms in the amide group (CO) NH. In the C1s spectrum there are four lines with $E_{be}$ 285.0 eV, 285.3 eV, 285.9 eV and 288.0 eV, corresponding to carbon atoms: in the aliphatic chain, in the $\alpha$-position to the amide group, in connection with the amide nitrogen groups and carbon in the amide group itself, respectively. The relative intensities of (I) lines in the C1s spectrum are 75: 8: 8: 8.

Our study on sample 1 found that the C1s- spectrum is represented by three $E_{be}$ lines at 285.0 eV, 285.9 eV and 288.0 eV (Fig. 5a). The lines with $E_{be}$ 285.0 eV and 285.3 eV are not allowed, as close as possible. The relative intensities of the lines in the C1s spectrum 74: 19: 8. The increase in the second line I and the appearance in the O1s spectrum of the line with $E_{be}$ 533.2 eV indicates the presence of functional groups containing a C – O bond in the surface layers of the polyamide [5].

The appearance of such groups can be explained by the oxidative destruction of the main chain of
the polyamide. Even at low (room) temperatures, aliphatic polymer chains are prone to oxidative aging [10]. The study of the powder remaining after sintering (sample 2) revealed that the range of the content of elements during parallel surveys decreased, with an overall increase in the amount of oxygen (Table 2). New lines appeared in the spectrum of B N1s- with $E_{be}$ 398.0 eV, 400.8 eV and 402.8 eV (Fig. 5b). The first line can be attributed to the terminal amino group. The appearance of lines with $E_{be}$ of 400.8 eV and 402.8 eV can be associated with the processes of thermo-oxidative destruction of terminal amino groups during hydrolysis ($E_{be} = 531.5$ eV in the O1s- spectrum for OH- ions [11]) and in their interaction with air oxygen. It is possible that the terminal carbonyl groups are also subject to thermal oxidation, as evidenced by the appearance in the O1s- spectrum of a line with $E_{be} = 532.4$ eV, corresponding to an isolated C=O bond [5]. The ability of aliphatic polyamides to react by terminal carbonyl and amino groups is known [8]. Most likely, layers of powder bordering the contour of the obtained part are subject to thermal oxidation (sintering temperature of polyamide powders is 183 °C). This is indicated by the characteristic redistribution of the line intensities in the N1s- and O1s- spectra in parallel surveys only for sample 2. It is not excluded that the main thermal oxidation occurs after contact of the powders with the atmosphere.

Conclusions

The difference in the chemical structure of the surface layers of polyamide powders used in selective laser sintering, which consists in an increased content of oxygen-containing groups in the surface layers, is established. This difference is revealed for powders left after sintering and intended for reuse. In the surface layers of the original polyamide powder, aliphatic chains are mainly subject to oxidative degradation, while in the powder remaining after sintering, carbonyl and amine end groups are subject to oxidative degradation. When recycling powders, additionally appeared polar functional groups of the surface layers can initiate coagulation of the particles. This leads to the formation of large-sized particles, which degrades the quality of the surface of the finished product. To avoid deterioration of part surfaces when using "green" (secondary) powder in subsequent cycles, it may be necessary to remove the powder adjacent to the part contour from the process, or create conditions that exclude thermal oxidative destruction of the powder outside the part field. Another alternative is to restore the "green" powder to its original state.

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