

INVESTIGATION OF THE EFFECT OF THERMAL POST-TREATMENT ON DENSITY AND HARDNESS OF A GREEN PART PRINTED WITH FFF TECHNOLOGY

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ABSTRACT

Additive manufacturing technologies can offer a cost-effective alternative to the production of metal parts of complex geometric shape compared to traditional production or expensive methods of melting powder coatings. In this work, the starting materials were developed by adding 75 % by volume to 316 L stainless steel powder and 25 % by volume from LDPE materials as a binder. Methods of burning and sintering were carried out in a hydrogen atmosphere at a temperature of 1387°C. The resulting metal sample was described mechanically and microstructurally. After sintering the metal samples have a powder size of ~ 7 µm, a level of 250 MPa and a nanoindentation hardness of 4.87 GPa, which are the characteristic features of burnt steel.

Keywords: fused filament fabrication, sintering, stainless steel.

INTRODUCTION

Additive manufacturing creates products based on a computerized solid-state 3D model by adding materials layer by layer [1]. The main advantages are flexibility of geometric shape to complex models, low waste material [2, 3]. The most widely used methods of metal powder as a raw material in Additive Manufacturing include selective laser melting (SLM) and electron beam melting (EBM) [4, 5]. These processes are very expensive, and they require an inert atmosphere or vacuum to prevent oxidation, as well as a lot of energy [6], and the part printed on a 3D printer must undergo processing [7]. In addition, the most widely used 3D printing methods in the world are Fused Filament Fabrication (FFF) technology [8]. In the process of FFF technology, there are small amount of waste, the principle of operation is simple, and it is possible to use several materials simultaneously [9, 10]. However, this technology allows you to use polymer composite

materials. Thanks to a lot of research, these metal polymer composite materials produce filaments (threads) with a diameter of 1.75 mm using FFF Technology [12]. One of the main limitations of a product, which is made by FFF technology using 316 L stainless steel material, is the printed volume of the product [13]. Adding a polymer as a binder to the metal raw materials when printing the product on a 3D printer with relative percentage is quite difficult. Resulting filament becomes more brittle due to the high percentage of metal powders [9].

Polypropylene (PP) and polyethylene (LDPE) polymers are used as binders. These binders ensure the flexibility of the thread, good printing quality and high product density. If the diameter of the filament is lower than the standard value (i.e. 1.75 mm), the flow rate of the molten material, as well as the thickness and width of the resulting layers, is affected, which ends with poor adhesion between the sedimentary layers or the presence of unnecessary gaps between adjacent layers. Such defects

are not eliminated during firing and are stored in the final metal part.

On the other hand, if the thread diameter is higher than the standard value, it will be difficult to transfer through the extruder. In any case, it is expected that the material will overflow, as a result of which the dimensional accuracy will decrease [14, 15]. Consequently, if polymers are not completely destroyed, the quality of the product decreases [16]. Polymers are usually destroyed by solvent or thermal separation [16, 17], and the binder removal temperature includes: heating speed, holding time, and furnace atmosphere for thermal removal of the binder [18].

Many factors lead to incomplete removal of binders, the most important of which are incorrect separation temperature, incorrect heating rate and insufficient holding time [16]. In most cases, defects are caused by rapid decomposition of the binding components. Since stainless steel powder is easily oxidized at high temperatures, a vacuum or controlled atmospheric furnace is usually used to prevent oxidation. The separation of 316 L stainless steel was carried out in a non-reactive gas (i.e. argon, nitrogen), as well as in a reducing atmosphere (i.e. hydrogen) in a furnace [19]. However, an inert gas can cause unwanted formation of a carbon product during the thermal decomposition of the binding system, which can also cause unexpected melting at high temperatures during synthesis [20]. The presence of nitrogen in the atmosphere, which leads to the deposition of chromium nitride (Cr_2N), especially in the range of 500 - 600°C, and the corrosion resistance deteriorates. To avoid air pollution, it is necessary to maintain the appropriate pressure and gas consumption [21]. When the carbon content in 316 L stainless steel exceeds 0.06 %, it leads to large defects and a decrease in corrosion resistance [22]. Consequently, due to the appearance of defects, incomplete removal of binders when removing them, internal gaps of a wide volume may appear [19]. After the process of burning and removing binders, the sinter process is performed. Sintering is the heat treatment of loose particles (i.e., the place of polymers) for the dense fusion of powders and the addition of metal powders, i.e. at a temperature of 70 - 90 % to the melting point of the metal powder [23]. During sinter, the powders are compacted and combined with contraction. Important parameters include the rate of heating and cooling, the combustion atmosphere,

the size and geometry of the product [19]. Increasing the sintering temperature and holding time leads to a decrease in porosity, which leads to an increase in density. It has been proven that the sintering temperature affects the amount of powder more than the sintering time [24]. With insufficient sintering, products with poor mechanical properties and low corrosion resistance are obtained [25]. Mechanical properties are also affected by the cooling rate. In particular, it plays an important role in preventing re-oxidation, the formation of nitrides and carbides, which affect the cooling rate and corrosion resistance from the sintering temperature to ~500°C [26].

316 L stainless steel is currently one of the most widely used materials in the field of multi-industry production.

The aim of this work is to study the quality of the sample using low-cost FFF technology with 316 L stainless steel polymer composite materials, as well as the methods of burning and sintering the printed product. A very simple binder consisting of low-density polyethylene (LDPE) was used, which eliminates the need to perform binding with a solvent. Products printed on a 3D printer were subjected to heat treatment, which allowed for binder removal and sintering.

EXPERIMENTAL

Characteristics of metal polymer composite

The raw material developed in this study as a metal powder filler consists of 316 L stainless steel powder with a carbon content of 0.018 %. Low-density LDPE polyethylene polymer was used as a binder. Metal powder was also used in polymer powder without additional processing. The raw material formula used in this study is 316 L stainless steel with a volume of 75 % and polyethylene polymer as a binder with a volume of 25 %. In the course of research on metal polymer composite raw materials, phase analysis of 316 L stainless steel powder was studied by X-ray diffraction (XRD, Rigaku MiniFlex 600, Almaty, Kazakhstan).

XRD samples were made in the range of 20° - 90° with the following characteristics: Cu K α radiation ($\lambda = 1.5408 \text{ \AA}$), step size = 0.02°, 40 KV and 15 mA, rotation speed 10° per minute and 9 minutes 31 seconds.

Metal polymer composite raw materials were analyzed by scanning electron microscopy (SEM Zeiss Crossbeam 540, Nur-Sultan, Kazakhstan). The scanning

electron microscope was used to study polymer binders and to determine the average size of microparticles. The Working energy of the Electron was 5 KV. Samples of metal polymer composite material printed on a 3D printer were taken using a scanning electron microscope, as well as samples after burning and sintering methods.

Fourier Transform Infrared Spectroscopy (FTIR) studied polyethylene polymer powder using the FTIR spectrometer (Thermo Scientific Nicole iS10, Nur-Sultan, Kazakhstan). Measured between 500 and 4000 cm^{-1} with the FTIR spectrometer.

Parameters of the model printed on a 3D printer

The filament was implemented on a single screw extruder with a diameter of 1.75 mm (FILABOT EX2, Filabot, Almaty, Kazakhstan). At a temperature of 180°C, a filament with a speed of 15 rpm was obtained. With this thread, 3D models were printed using the FFF method. Printing was carried out on a printer PrintBox3D One (Almaty, Kazakhstan). Repetier Host software and for printing G-code the following parameters are used: extruder temperature 230°C, desktop temperature 60°C, layer height 0.6 mm, filling 100 %, print speed 25 mm s^{-1} .

Description of thermogravimetric analysis

Thermogravimetric analysis (Perkin Elmer Pyris 1 TGA, Nur-Sultan, Kazakhstan) was performed on a sample printed on a 3D printer to estimate the burning temperature range. The analysis was performed in a nitrogen atmosphere (40 mL min^{-1}) with a heating rate of 0°C - 512.6°C in the temperature range of 10°C min^{-1} .

Burning and sintering characteristics

Heat treatment of samples printed on a 3D printer was carried out in a furnace (Elnik, Nur-Sultan, Kazakhstan) in a hydrogen atmosphere at 500°C for 90 minutes. Sintering was kept at a temperature of 1387°C for 180 min. The heating rate of 7°C min^{-1} was constant for both burning and sintering.

Determination of the hardness of the material after sintering

Nanoindentation of the initial and sintered steel plates was carried out on a NanoScan-4D nanohardness tester (NanoScan-4D, Nur-Sultan, Kazakhstan). Young's modulus and hardness were determined by the method of Oliver and Farr at a load of 10 mN.

RESULTS AND DISCUSSION

Results of the description of the metal polymer composite

As can be seen from the SEM images, 316 L stainless steel micro-particles are combined with polymer binders. However, there are few quantities of particles with the size of 6 - 7 μm . The results of raw powder of metal polymer composite with an increased magnification of SEM - 10 μm before burning are shown in Figs.1(a) and 1(b).

The presence of spherical or quasi-spherical micro-particles can be seen clearly. The average size of powders is 7 μm , where the total percentage of powders exceeding 7 μm and less than 5 μm is 5 %.

The EDX analysis is shown in Fig. 2.

The composition of 316 L stainless steel was determined as follows. The Iron (Fe) peak was 42.9 %. 7.4 % chromium (Cr) and 3.9 % nickel (Ni) were also detected. According to the chemical composition of 316 L stainless steel, 0.3 % manganese (Mn), 0.5 % molybdenum (Mo) and 0.3 % silicon (Si) were detected in the alloy. 2 θ showing the cubic structure with a center representing the randomly oriented crystalline phase of an austenite alloy Fe-Cr-Ni = 44.65°, 64.98°, 82.30°, 98.88°, and 116.31° shows sharp peaks.

The LDPE Binder was analyzed using FT-IR spectroscopy. The spectra are shown in Fig. 3. There are weak absorption peaks near the wavenumbers of 3000 cm^{-1} due to the C-H stretching vibration and peaks between the 1000 and 1500 cm^{-1} wavenumbers correspond to the C=C stretching vibration. C-H out of plane bending vibration absorption matches to the peak of 750 cm^{-1} .

It is important to consider the possibility of preparing the filament and printing FFF.

Results of thermogravimetric (TGA) analysis, burning and sintering

Thermogravimetric analysis (TGA) of the raw material was performed to remove the binders. A sample of TGA primary raw materials in the nitrogen atmosphere was studied (shown in Fig. 4(a)).

The mass loss curve of the binder and raw materials shows a single-stage degradation. This corresponds to LDPE decomposition due to random chain separation and free space formation [27, 28].

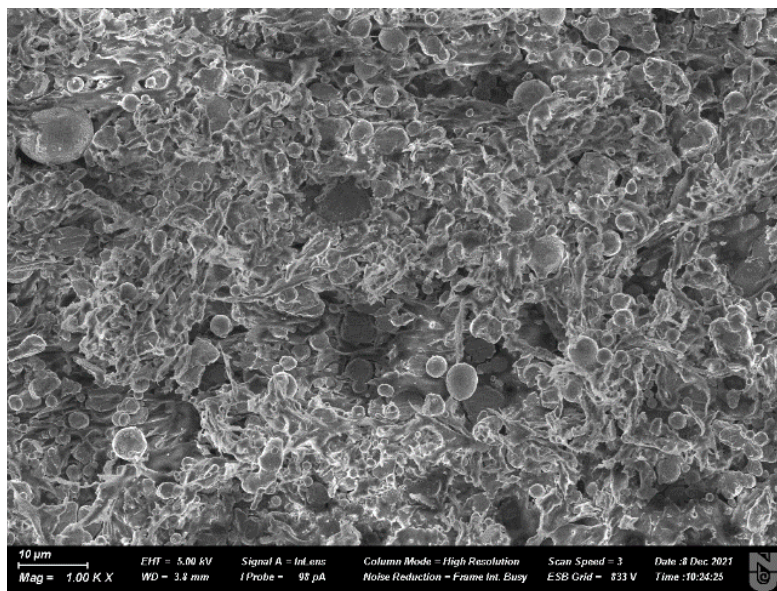


Fig. 1.(a) Image of metal polymer composite raw powder with SEM - 10 μm magnification before burning;

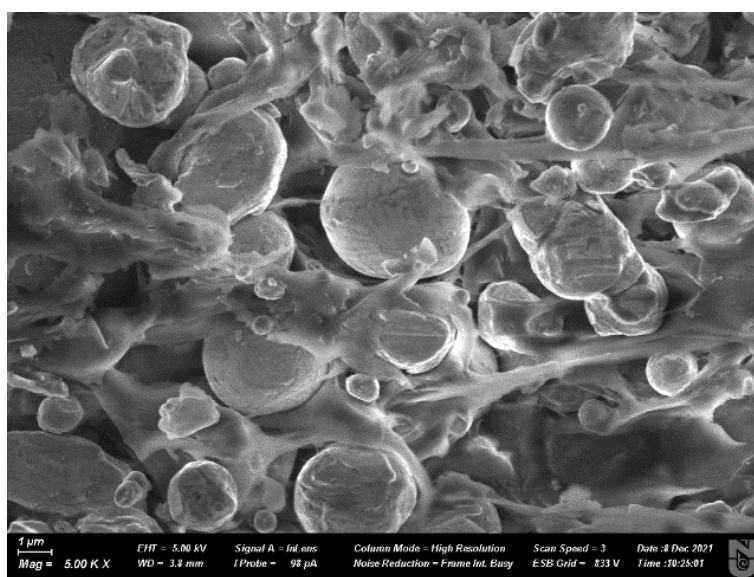


Fig. 1.(b) Image of metal polymer composite raw powder with SEM - 2 μm magnification before burning.

The decomposition temperature of pure LDPE, taken as the minimum derivative curve by weight, is 418°C, and the decomposition temperature of raw materials is 492°C. According to the literature, thermal stability increases due to the presence of metal fillers [29]. The polymer completely decomposes at 500°C, and the actual amount of steel powder calculated by measuring the residual mass percentage (R) of the TGA curves is 94.5 % and corresponds to the theoretical composition of the filler 94.2 % by mass. Thus, thermal combustion

was established at a temperature of 90°C with a heating rate of 7°C min⁻¹ for 500 minutes in a controlled oxygen-free atmosphere. Then a SEM analysis was performed to check for the presence of residual polymer in the TGA removal sample (shown in Fig. 4(b)).

This result, together with the SEM analysis, confirmed the removal of 90 % of the binder, i.e. polymers, during the final heat treatment. This was a very good result, as the use of a single binding component (LDPE) in the literature can make the burning process

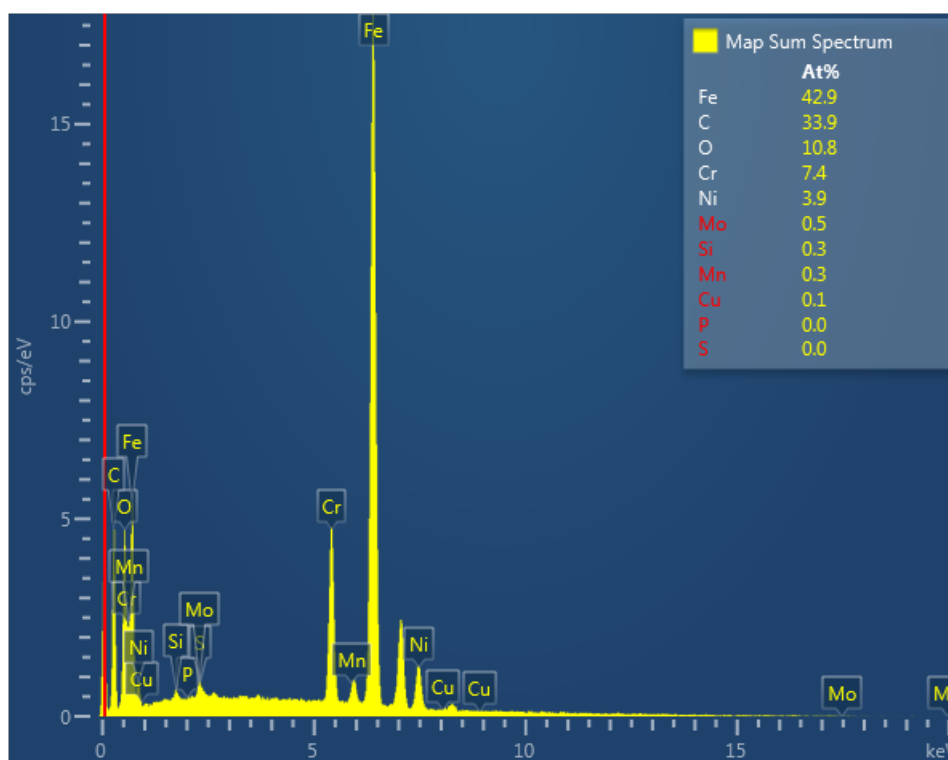
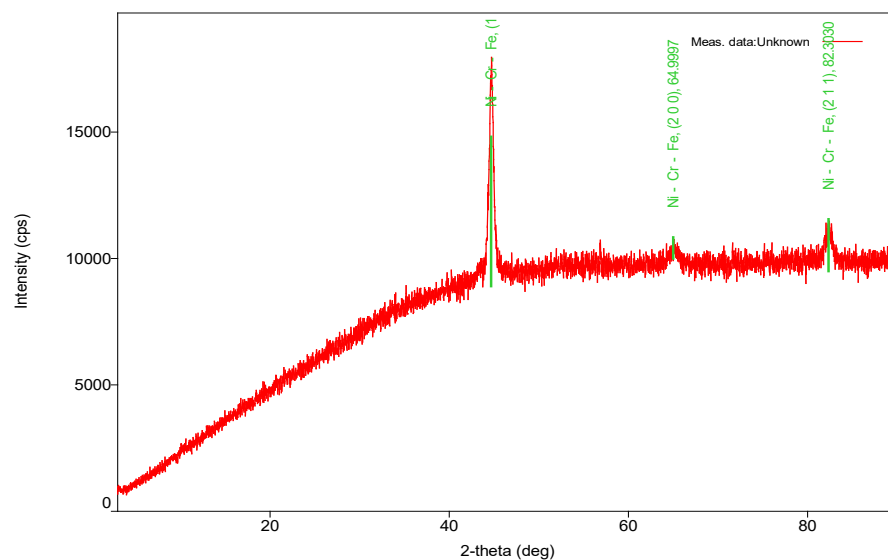


Fig. 2. 2 θ radiography of metal polymer composite raw material powder in the range of 10 - 90°.

more important. In particular, in the initial stages, some defects may occur, such as swelling, due to stresses caused by the trapped gas that occurs as a result of the decomposition of the binder. In our case, even if the binder consists of one component, the degradation process was successfully carried out in all research samples, and the trapped gas was not detected due to the fact that the heating rate was slow enough to allow the

polymer to evaporate properly. After sintering, the steel particles seem to come into contact with each other. This is an important aspect, because the first stage of baking is the formation between two adjacent powders. Heat is considered as the driving force because it increases the vibration of atoms, and mass transport occurs mainly by surface transport mechanisms (i.e. evaporation and condensation, surface diffusion and volumetric

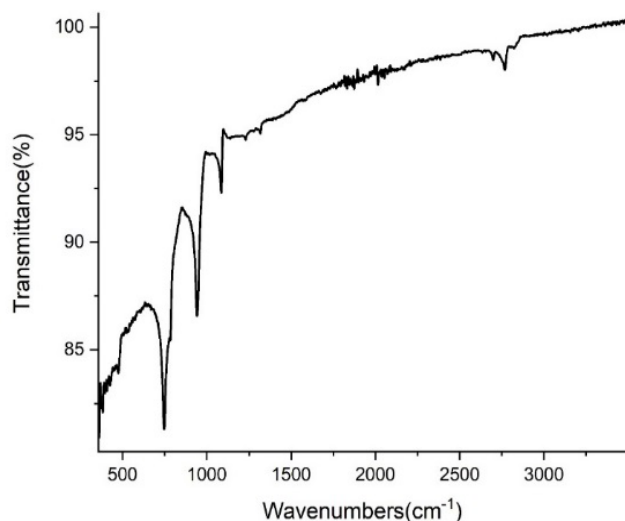


Fig. 3. FTIR spectra of LDP binder in the range of 4 cm^{-1} - 3000 cm^{-1} with a resolution of 500 cm^{-1} .

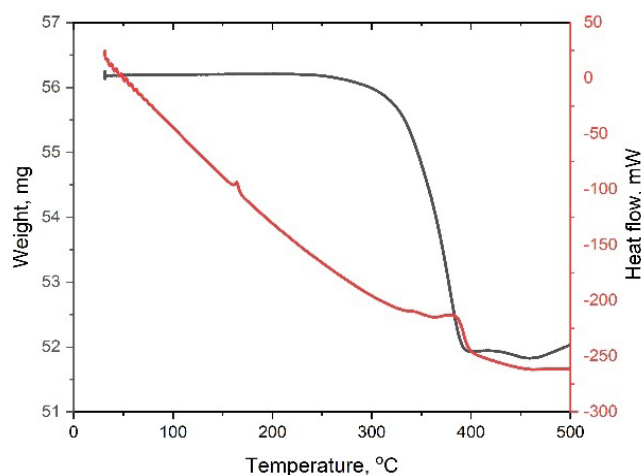


Fig. 4(a). TGA mass loss of a sample printed on a 3D printer.

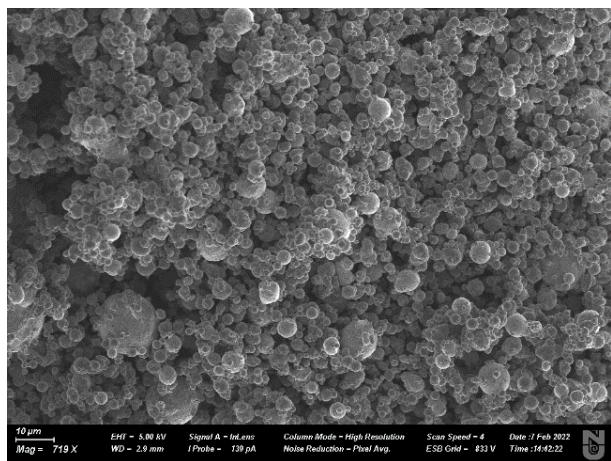


Fig. 4(b). Removal of the sample binder with an increase of SEM - $10\text{ }\mu\text{m}$.

diffusion) [30]. Atoms move from the surface of the particles to the point of contact of the particles. If the powders are not in good contact, this process will fail.

Morphology, phase analysis and mechanical properties of samples printed from a 3D printer

Shrinkage is the result of the destruction of pores in the green body, being the driving force of volumetric transport mechanisms [31]. In particular, plastic flow, viscous flow, boundary diffusion and volumetric diffusion occur [32].

The shrinkage was not isotropic because it was 11 % in the X and Y direction and 15 % in the Z direction, the literature mentions a linear shrinkage (x direction) of about 14 % for the volume fraction [33]. Since our samples dropped only 5 % in the x direction, it should be assumed that some porosity remained.

After sintering, no visible defects were observed (for example, surface cracks or swelling). We have determined the presence of an austenitic crystalline phase of the Fe-Cr-Ni alloy, which confirms that there are no chemical and phase changes in the entire process.

Metallographic analysis of the surface of the treated sample revealed a well-compacted austenite granule structure. The normal average size of equal-axis powders is $7 \pm 3\text{ }\mu\text{m}$. The microstructure is characteristic of austenitic steel, the sintering temperature of the house is higher than the recrystallization temperature, which allows the powder to grow, in addition, the uncontrolled cooling process is very slow ($1 - 2^\circ\text{C min}^{-1}$), and the cooling of the powder growth continues. Reaches the recrystallization temperature. When analyzing the image, some intergranular porosity is observed. The porosity obtained as a result of the analysis of the image of 316 L stainless steel was 7 %. According to these results, the density after sintering is in the range of 91 - 93 %, which is usually compared with samples obtained by MIM [34].

The shape and the type of porosity can provide information that determines it. If the porosity is not spherical, then this process is the porosity resulting from FFF printing, and if it is spherical, it is associated with heat treatment, i.e. burning [4, 11, 35].

In our case, it is expected that this may be due to defects obtained during 3D printing and affect the resulting mechanical properties. For example, in tensile strength and micro-hardness, the average point is 252 MPa and

the average tensile strength is 520 MPa. In particular, the low fluidity and maximum tensile strength should be due to the high sintering temperature (which leads to a large number of pellets) and the presence of porosity. Porous materials can be considered as two-phase composites, in which pores act as a zero-strength dispersed phase. The size of the pores, their geometric shape, their location in space, and their mechanical reaction are affected.

When shooting a sample of 316 L stainless steel under a SEM microscope at a degree of 2 μ m after sintering, defects were formed due to the presence of 2 - 4 % binders (places marked in red in Fig. 5).

This achievement is very good.

The result of the stiffness of the material after sintering

Nanoindentation is a contact nanomechanical testing technique which involves pressing a rigid tip of a known shape and material into a material under the study of a gradually increasing load, followed by its removal and measurement of the dependence of the tip displacement on the applied load [36].

Using this technique the hardness value H is determined by the following relation:

$$H = \frac{P_{max}}{A_c}, \quad (1)$$

where P_{max} is the maximum applied load in mN and A_c is the contact area in nm². A_c was defined as a function of the indentation contact depth, calculated by the formulae:

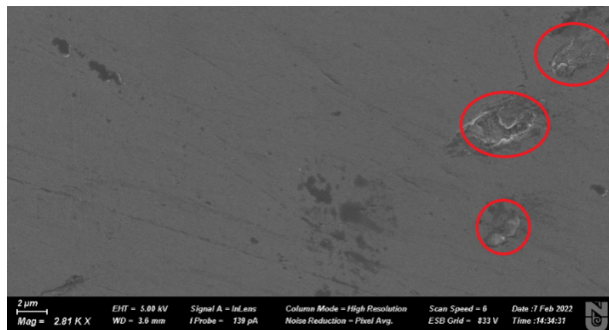


Fig. 5. 316L stainless steel sample SEM - 2 μ m drop after sintering.

$$A_c = 24.49 h_c^2$$

$$h_c = h_{max} - \epsilon \frac{P_{max}}{S}, \quad (2)$$

where h_c is the contact indentation depth in nm, h_{max} is the maximum contact indentation depth in nm, ϵ is a constant depending on the geometry of the indenter ($\epsilon = 0.75$ for the Berkovich indenter) and S is the contact stiffness.

The modulus of elasticity E of the test specimen was calculated from the contact stiffness at the initial moment after the load was removed, $S = \frac{dP}{dh}$, i.e. from the slope of the unloading curve at its beginning. Based on the indentation results, the Elastic Modulus value was obtained from the relationship:

$$E = S \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A_c}} \quad (3)$$

The results of measuring the hardness and elastic modulus of 316 steel samples before and after sintering by the nanoindentation method are shown in Table 1.

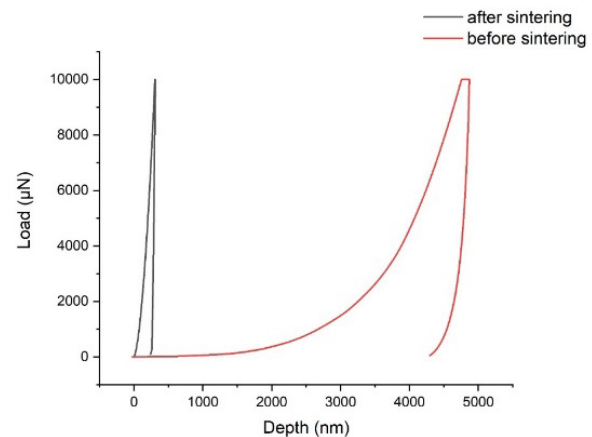


Fig. 6. Load-displacement curves of initial and sintered 316 steel plates.

Table 1. The results of the hardness of the material.

Sample	Hardness H, GPa	Nanoindentation Elastic Modulus E, GPa
Before sintering	0.63	11.67
After sintering	4.87	150

CONCLUSIONS

In this work, a single-component binder (LDPE) and 316 L stainless steel powder-based filament with a high loading percentage of 4 to 1 were obtained. With this filament 3D printer, the product was removed and the binders, i.e. the LDPE polymer, were removed by burning the resulting product, and studies were also carried out on the welding method and determination of hardness.

The main property was considered to be the ability to evaporate the modified polymer at a low thermal velocity of $7^{\circ}\text{C min}^{-1}$ during combustion and maintain its shape without surface defects. The sample was sintered at a temperature of 1387°C for 180 minutes to seal and eliminate defects. In sintered samples, a density of 93 % was recorded. Phase analysis revealed only the presence of an austenitic phase, which confirms that subsequent treatment in a hydrogen reduction atmosphere protected samples from oxidation and other contamination.

The analysis of the microstructure shows a well-compacted granular structure of austenite with a constant size of $45 \pm 5 \mu\text{m}$, and the elemental composition remained unchanged during heat treatment. The results of mechanical tests on the hardness of the surface of a metal-polymer part showed an increase in hardness after sintering by 12 %. In the future FFF method can be developed as new prospect for the production of stainless steel bars.

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