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Investigation of Methods for Removing Polymers of a Sample Printed with a Metal-polymer Composite Material in Additive Manufacturing

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Abstract. *The purpose of this work is to study the structure of the printed sample using a 3D printer with a compasite material with the addition of 25% polyethylene polymer as a binder to the stainless steel powder, which is 75% by volume. Based on the methods of burning and sintering, the internal structural quality of the sample was improved. At a temperature of 1387°C, the main point was the fusion of powders. It was found that during the sample burning period, the polymer remained on the surface of the largest micro-particle containedpowders with the size of 7,377 microns and removed after sintering stage. 90 percent of the polymers in the sample weredestroyed. This is a very good indicator.*

Keywords: *Fused Deposition Modeling technology, SEM analysis, XRD analysis, polyethylene polymer, stainless steel, 3D printer, burning, sintering, Additive technology, FTIR spectrum, Perkin Elmer Pyris oven, Metal polymer composite material.*

Introduction

In the process of applying additive technologies, with the using of materials science and understanding of what structure is formed in the finished product, it is possible to thoroughly study the necessary properties of the material [1, 2]. One of the most widely used technologies in Additive Manufacturing Technologies is Fused Deposition Modeling (FDM) [5, 6, 13]. The materials used in FDM technology are usually plastics, i.e. polymers. However, using this technology, it is possible to obtain a sample from the raw materials obtained by mixing stainless steel powder into a polymer. The resulting sample is obtained by burning and sintering methods, removing the polymers contained in it, and the product made of pure steel. The function of the polymer is to hold the steel powders together, that is, to bind them together. Steel powders are 316 L stainless steel powders. In this work, we used a polyethylene polymer (LDPE) as a binder [4, 12]. Using this material, the model was printed in FDM technology, i.e. on a 3D printer [3, 7, 15]. Polymers are usually destroyed by thermal combustion [7, 8], and the complete destruction of the polymerization depends on the time of heating and holding, as well as on the atmosphere. Stainless steel powders are easily oxidized at high temperatures, and a vacuum or atmospheric furnace is usually used to prevent oxidation. In the atmosphere, argon, nitrogen gases, as well as hydrogen in the regenerating atmosphere were realized [9]. After the method of burning and destroying polymers, the method of sintering is carried out [10, 11, 14]. During sintering, the powders are compacted together. The purpose of this paper is to study the methods of sintering and welding of the polymer contained sample. The sample preparedon a 3D printer using the polymer composite material made of stainless steel. The reason for the use of polyethylene polymer is the low density.

Experimental materials and methods

Characteristics of raw materials

In this study, the raw material consisted of 75 percent stainless steel powders and 25 percent polyethylene polymer. The phase analysis of specially prepared raw materials were determined by X-ray diffraction. XRD analysis were performed on the Rigaku MiniFlex device. The samples were made in the range of 2θ 3-90° with the following characteristics: CuKa with a beam of 1,5408 Å and a step of 0,02°. The sample obtained on a 3D printer was also analyzed using a scanning electron microscope to determine its characteristics before burning and after sintering. SEM analysis were carried out on the Zeiss crossbeam device. With the help of a scanning electron microscope, you can determine how many percentages of binders have been removed, as well as how close the steel powders are to each other. In the process of removing the polymer, it is necessary to take into account chemical processes, in particular, the moisture content of the polymer depending on the temperature. Infrared spectroscopy was used to detect this phenomenon. The FTIR spectrometer was performed on the Thermo Scientific Nicole is 10 instrument and measured between 500-4000 cm^{-1}.

Parameters of printing with specially prepared material in FDM technology

3D printing was done on the PrintBox3D one unit, which in FDM technology is created by printing thin layers of molten material into each other. The heating temperature of the material in the extruder was 200°C, and the temperature of the platform was 90°C degrees. It is assumed that the main parameters for 3D printing are: layer thickness, percentage of filling, printing speed, extrusion width, and the amount of material provided.

Characteristics of melting point analysis

To determine the melting point of the polymer, thermogravimetric analysis were performed on the Perkin Elmer Pyris instrument. The pre-prepared sample was carried out in a nitrogen atmosphere with a temperature range of 0°C – 766,8°C.

Characteristics of polymer destruction and convergence of steel powders

In a specially prepared Elnik oven for the purpose of removing the polymer of the sample printed on a 3D printer, when the temperature reached 500°C with the addition of 10°C every 5 minutes in a hydrogen atmosphere, the sample was kept at 500°C for 90 minutes. Caught for 90 minutes, continued the process and brought it to a temperature of 1387°C, held for 180 minutes. At a temperature of 1387°C, the steel powders converged.

Redox was carried out in a hydrogen atmosphere in a specially designed Elnik furnace to remove the binder, ie polymer, of the product printed on a 3D printer. We used it to protect the product from oxidation and contamination in a hydrogen-reducing atmosphere. When the burning method reached 500°C, increasing the temperature by 10°C every minute, the product was held at 500°C for 90 minutes. The purpose of holding the product for 90 minutes is to evenly remove the polymers, and the paraffin, polypropylene and stearic acid in the polymer are gradually destroyed. After 90 minutes, the process was continued and the temperature was increased to 10°C per minute to 1387°C and kept for 180 minutes. At a temperature of 1387°C for 31 minutes, 316 L of stainless steel powder comes together. The burning and sintering stages are shown in figure 1 below.

Results and discussion

Results of raw material description

As a result of SEM, steel powders are combined with polymer. The size of steel powders is most often almost 3 microns (shown in figure 2). Most of the powders are spherical. The volume of the largest powders of steel powder is 7,377 microns, and the volume of the smallest powders is 699,5 nm. In the XRD analysis, the structure of the arrangement of atoms was determined. At first, the polymer peak was not fully visible, and then the polymer peak was detected

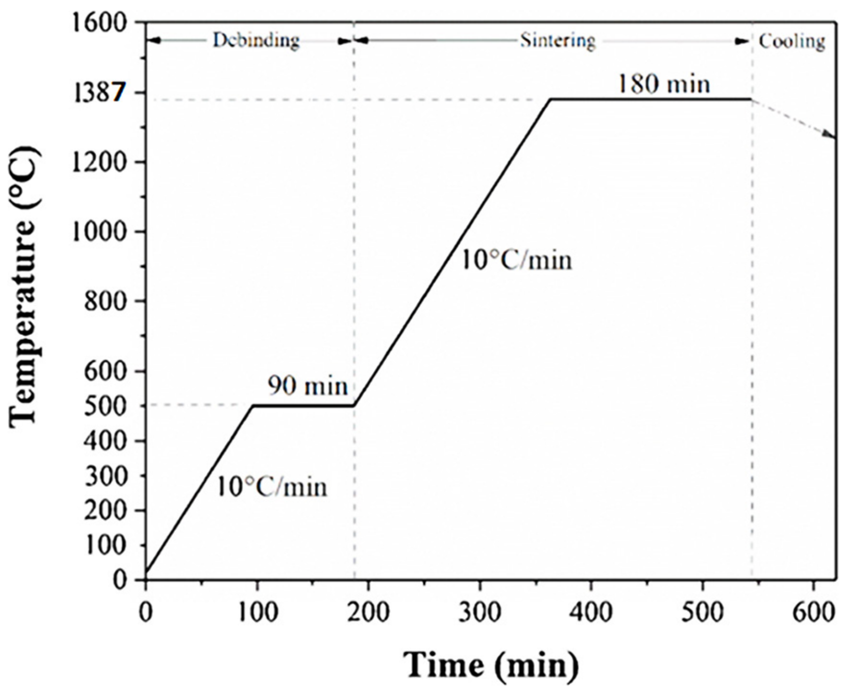

Figure 1 – Burning and sintering process

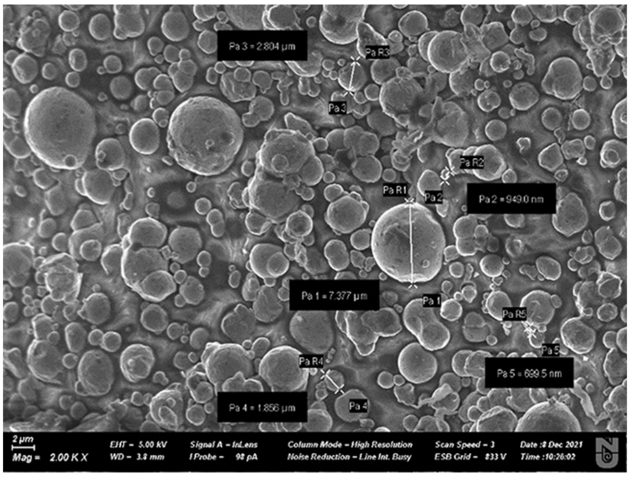

Figure 2 – Polymer mixing with steel powder

when the 0.02° pile was lowered (shown in figure 3). 2θ of the austenitic alloy Fe-Cr-Ni = 44.65°, 64.98°, 82.30°, 98.88°, and 116.31° was detected in sharp peaks. The percentage of chemical elements is as follows: Fe – 42,9%, C – 33,9%, O – 10,8%, Cr – 7,4%, Ni – 3,9%, Mo – 0,5%, Si – 0,3%, Mn – 0,3%, Cu – 0,1%. LDPE binders were investigated by FT-IR method. As can be seen from the spectra (shown in figure 4), the presence of moisture was observed at a peak of 3000 cm^{-1} due to the tensile vibration of the polymer. This increases the chances of creating a template.

Melting point analysis results of the description

During this analysis, polymer melting and mass loss were determined. We also analyzed weight changes, heat flow changes, temperature changes, and no exothermic process. The decomposition process begins at a temperature of 0°C. Endothermic process temperature difference 166,4°C, 394,4°C. Also, the thermal endothermic process is 166,7°C, 396,8°C, 471,2°C, 514,6°C, 766,8°C [12]. 160-200°C thermal effect, and 354-410°C this process increases. As a result, according to this analysis, 9,7% lost weight. This melting point was one of the parameters we needed during a certain sample production period.

Results of burning and sintering methods

As it turned out in literary studies, the polymer is not completely removed from the sample. Our indicators correspond to this. The longer the burning time, the more the polymer is destroyed. If the size of the steel powder was the same as 3 microns, the percentage of polymer loss would be up to 3%. At present, it can be seen that the polymer residues on the surface of 7,377 micron powders have not been completely removed after sintering at 1387°C. But when the sample is held for a long time, due to the gases released from the polymer, pores are formed between the steel powders in the sample. Such defects are difficult to eliminate with temperature. The polymer is 90 percent removed. As shown in figure 5, the 90 percent of polymers are removed. 10

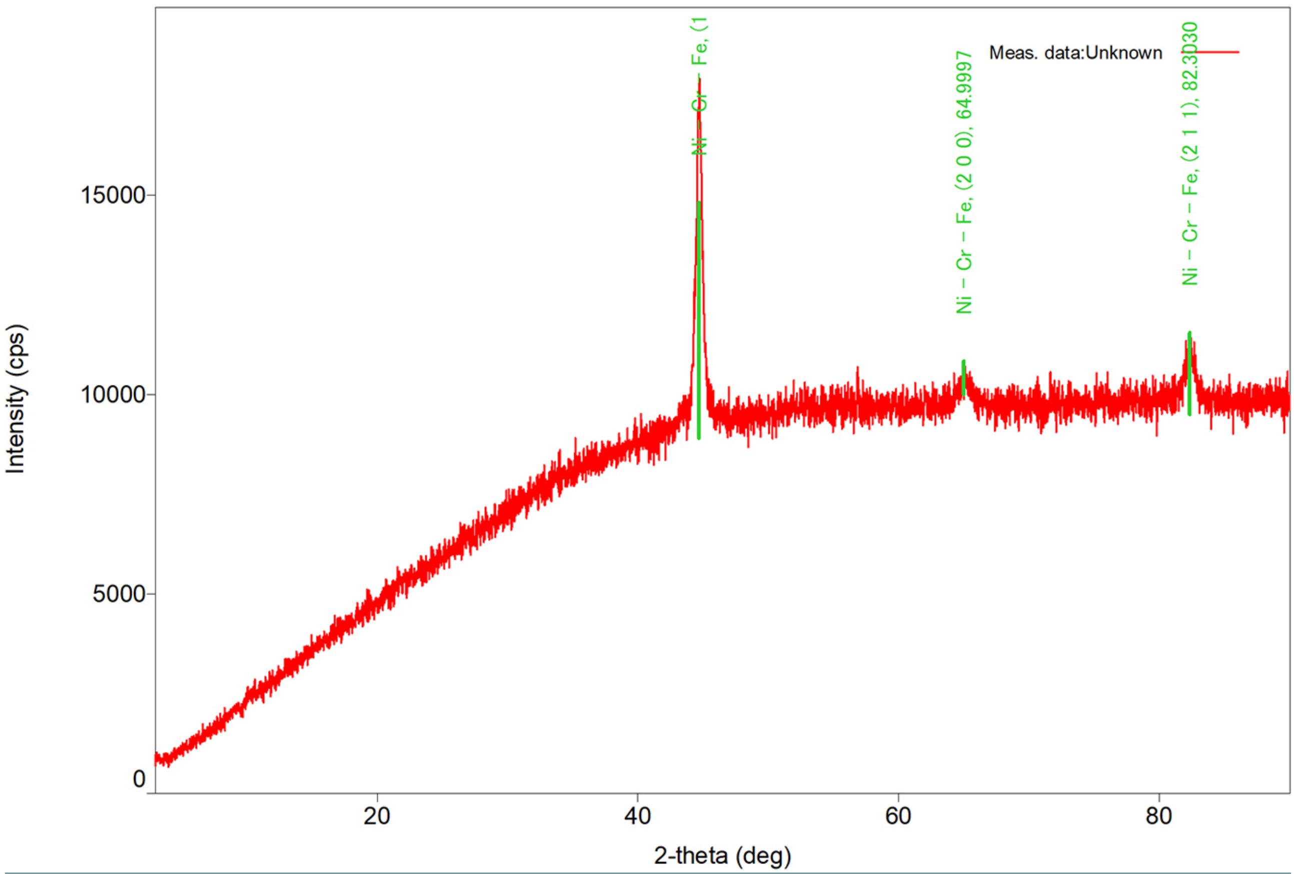

Figure 3 – 2θ radiography of raw materials in the range of 10-90°

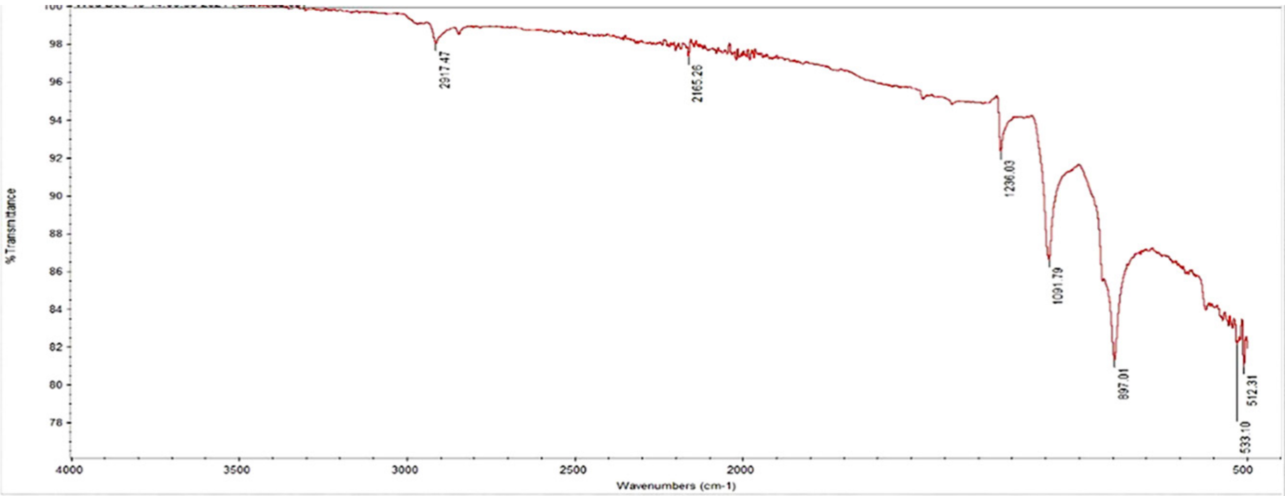

Figure 4 – FT-IR polymer spectra

percent is covered with a thin thickness on the surface of steel powders. This means that the steel powders can be combined with each other due to the small percentage of polymer during sintering process. Since the sizes of steel powders vary, gaps, i.e. lumps, remain during the sintering period.

The size of the pores affects to the geometric size of the sample, as well as the mechanical reaction.

The residual polymer effect, as mentioned above, was shown in the yellow circle in Figure 6. A good indicator is the presence of 10 percent polymer in the sample.

Conclusions

In this work, the production of a sample was provided by additive injecting of thepolymer into a steel powder, and the removal of the polymer contained in the resulting sample and the fusion of steel powders by sintering at a temperature close to the melting point. One of the factors influencing the quality of the resulting sample is the lack of single sized steel powders, 10 percent polymer residue, and the speed of burining, sintering. It was found that during the melting period, paraffin, polypropylene and stearic acid are simultaneously destroyed by the polymer structure at 500°C. The largest steel powder in the SEM analysis was 7,377 microns. At a temperature of 1387°C, polymer residues on the surface of powders with a degree of 7,377 microns were not completely destroyed. If steel powders have the same size as 3 microns, the polymer has a probability of destruction of up to 3 percent. It has been studied that the appearance of stainless steel can be made with complex patterns and simple technologies.

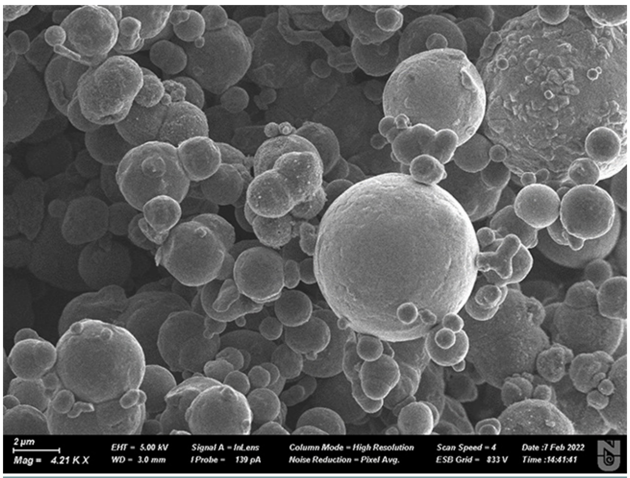

Figure 5 – SEM analysis after Polymer removal

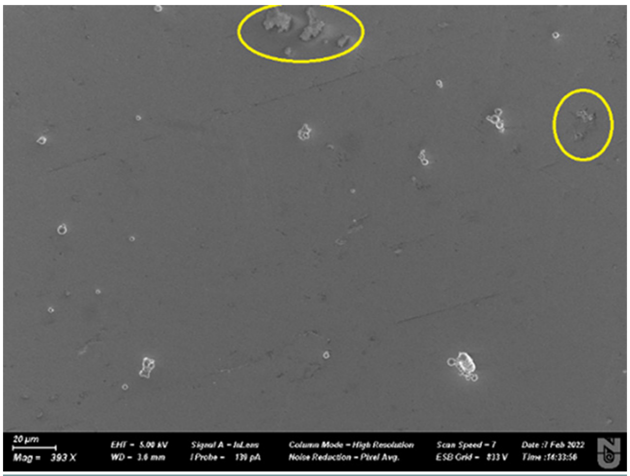

Figure 6 – SEM analysis after sintering

Acknowledgments

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Аддитивті өндірісінде металл полимерлі композиттік материалдарымен басып шығарылған үлгілердің полимерін жою әдістерін зерттеу

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Аңдатпа. *Бұл жұмыстың мақсаты көлемі бойынша 75 пайызды құрайтын тот баспайтын болат ұнтағына, байланыстырушы ретінде 25% полиэтилен полимері қосылған композиттік материалын 3D принтерде қолданып, басып шығарылған үлгінің құрылымы зерттеу болып есептеледі. Үлгінің құрамындағы байланыстырғыштарды жою әдістері ұсынылды. Күйдіру және пісіру әдістері негізінде үлгінің ішкі құрылымдық сапасы жақсарды. 1387°С температурасында ұнтақтарды біріктірудің негізгі нүктесі болды. Үлгіні күйдіру барысында полимер, ең үлкен өлшемді 7,377 мкм болатын болат ұнтақтардың бетінде қалып, пісіру кезеңінен кейін жойылғаны анықталды. Үлгідегі полимерлердің 90 пайызы жойылды. Бұл өте жақсы көрсеткіш.*

Кілт сөздер: *балқытылған тұндыру моделі, СЭМ талдау, рентгендік талдау, полиэтилен полимері, тот баспайтын болат, 3D принтер, күйдіру, пісіру, аддитивті технология, FTIR спектр, Perkin Elmer Pyris пеші, металлополимерлі композициялық материал.*

Исследование методов удаления полимеров образца, напечатанного металлополимерным композитным материалом в аддитивном производстве

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Аннотация. *Целью данной работы является исследование структуры образца, напечатанного на 3D-принтере с использованием композитного материала с добавлением 25% полимера полиэтилена в качестве связующего в порошок из нержавеющей стали, который составляет 75% по объему. На основе методов выжигания и спекания улучшилось внутреннее структурное качество образца. Температура 1387°C стала основной точкой соединения порошков. При обжиге образца было установлено, что полимер оставался на поверхности стальных порошков с максимальным размером 7,377 мкм и удалялся после спекания. 90% полимеров в образце были удалены, что является очень хорошим показателем.*

Ключевые слова: *моделирование методом наплавления, анализ СЭМ, рентгеноструктурный анализ, полиэтиленовый полимер, нержавеющая сталь, 3D принтер, выжигание, спекание, аддитивная технология, FTIR-спектр, печь Perkin Elmer Pyris, металлополимерный композиционный материал.*

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