Abstract

In recent years, special attention has been paid to additive manufacturing, which include the laser powder bed fusion method (L-PBF). This technology successfully produces machine parts from commercial materials used in various industries. Almost a decade ago, the production of metallic glasses in the L-PBF technology was initiated, which until now was possible only with the use of specific methods developed for this type of materials. The main conventional techniques for producing metallic glasses include – the melt-spinning method and copper mold casting.

The key to obtaining metallic glasses is achieving a high cooling rate by cooling from the melt. The critical cooling rate, enabling the formation of an amorphous structure, is a variable value and depends on the chemical composition of the alloy. The melt-spinning technology produces ribbons with a thickness of about 20 μm, achieving cooling rates of 10^4-10^6 K/s. This method is mainly used for metallic glasses with a low glass-forming ability (GFA) due to the higher than critical cooling rates obtained, enabling the formation of an amorphous structure. The term "glass-forming ability" refers to the ability of an alloy to form an amorphous structure from the liquid phase upon cooling. The measure of the glass-forming ability is usually the cooling rate or the minimum cross-sectional dimension of the element for which only the amorphous structure was obtained. Therefore, the values of the GFA are the thickness of the ribbons produced in the melt-spinning method and the thickness of the plates or the diameter of the rods obtained by casting into copper molds. In the copper mold casting method, rods of more than 1 mm diameter are usually produced, achieving cooling rates not exceeding 10^3 K/s. Alloys this technology produces have the high glass-forming ability and are called bulk metallic glass (BMG). So far, a rod with a critical diameter of 18 mm has been produced for iron-based metallic glasses. In the laser powder bed fusion technology, cooling rates of 10^3-10^8 K/s are obtained, which are determined by the size of the melt pool, depending on the supplied laser power and scanning speed. The wide range of cooling rates obtained in the L-PBF technology enables the production of metallic glasses, which, combined with the freedom of shape of the parts produced in this method, resulting from the layered nature of the process, is an advantage over conventional techniques, preferred for this group of materials.

The main aim of this doctoral dissertation is to determine the processability of two iron-based metallic glasses with different glass-forming abilities in the laser powder bed fusion technology and to determine the effect of selected L-PBF process parameters on the microstructure, defects formation and hardness. As a result of the literature analysis, two alloys

with different chemical compositions were selected. The $Fe_{79}Zr_6Si_{14}Cu_1$ alloy, with a low glass-forming ability, so far produced in the form of ribbons, is characterized by properties characteristic of soft magnetic materials. It is used for inductor cores, linear actuators and sensors. In turn, the $Fe_{45}Cr_{15}Mo_{14}C_{15}B_6Y_2Ni_3$ alloy achieves high strength properties and hardness. Due to its much higher ability to form an amorphous structure, this alloy allows the production of rods with a diameter of 3 mm using conventional technologies.

The thesis presents a method of selecting the parameters of the L-PBF process for both types of metallic glasses according to the defect minimization criterion. The produced alloy samples were subjected to microstructure studies using light microscopy (LM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). These tests allowed the identification of the remaining phases and defects in the form of pores and cracks.

In the microstructure of the $Fe_{79}Zr_6Si_{14}Cu_1$ alloy produced in the L-PBF process, crystalline phases were found, mainly the α-Fe(Si) solid solution and the $Fe_{23}Zr_6$ intermetallic phase. In addition, an increase in the proportion of the $Fe_{23}Zr_6$ phase was observed as the volumetric laser energy density increased due to the increase in laser power. The TEM tests, however, showed the presence of an amorphous structure in the characteristic zone near the beads fusion line. In this zone, in the amorphous phase matrix, a nanometric α-Fe(Si) solid solution precipitations were identified. Two porosity types were observed in the produced samples - technological and metallurgical. The technological porosity was characterized by an extensive shape and the presence of powder particles inside the pores, which was caused by insufficient melting of the powder layer and previous layers due to too low values of the supplied laser beam energy. This kind of porosity was eliminated by increasing the volumetric energy density by increasing the laser power and reducing the scanning speed. The metallurgical porosity was characterized by spherical gas pores, the share of which did not exceed 1%. The presence of residual stresses induced during the process was revealed by the appearance of microcracks three weeks after the end of the sample production process. The nature of the cracks was indicative of cold cracking and was related to thermal stresses generated during the process due to volumetric shrinkage and linear thermal expansion.

In the case of the second $Fe_{45}Cr_{15}Mo_{14}C_{15}B_6Y_2Ni_3$ alloy, produced by the L-PBF method, it was possible to produce an amorphous structure in a wide range of laser power (80-160 W). At low laser powers, 80-120 W range, and 333-500 mm/s scanning speeds, an amorphous structure with porosity ranging from 2.78% to 8.55% was obtained. The increase in laser power to 160 W and 180 W and the increase in the scanning speed to 700-1000 mm/s resulted in a decrease in porosity, reaching a minimum of 1.26%. The limit values of laser power and scanning speed, for which a fully amorphous structure was obtained, were 160 W and 1000 mm/s, respectively. Further increasing the power and lowering the scanning speed resulted in the crystallization of the $(Fe, Cr)_{23}(C, B)_6$ phase. The primary type of porosity occurring in this type of material was gaseous porosity. In addition, during the L-PBF process, hot microcracks were formed, which propagated in the direction of the bead formation. The nature of the cracks indicated liquation cracks associated with local melting and thermal stresses created during the process.

Hardness measurements were carried out for both alloys produced in the L-PBF technology. For the $Fe_{79}Zr_6Si_{14}Cu_1$ alloy, the highest hardness (953 HV1) was achieved for the laser power of 120 W and the scanning speed of 900 mm/s. Regarding the $Fe_{45}Cr_{15}Mo_{14}C_{15}B_6Y_2Ni_3$ alloy, the produced samples were for low laser power (80-120 W) and low scanning speed (333-500 mm/s) characterized by hardness of 1105-1196 HV1. In turn, the samples produced with laser powers of 160 and 180 W had a hardness of 1141-1196 HV1, and re-melting increased the hardness, reaching a maximum value of 1279 HV1.

Based on the conducted research and the obtained results, conclusions were formulated regarding the processability of iron-based metallic glasses in laser powder bed fusion technology. The glass-forming ability was found to be crucial in obtaining the amorphous structure. In the case of alloys with a low GFA processed in the L-PBF technology, partial crystallization occurs due to the achieved cooling rates lower than the critical cooling rate that guarantees the formation of an amorphous structure. On the other hand, alloys with high glass-forming ability in a wide range of laser power and scanning speed allow for achieving an amorphous structure. Both in the case of the alloy with low and high GFA, the increase in laser power and the reduction in the scanning speed lead to a reduction in porosity, which is one of the criteria for the material's applicability in the L-PBF technology. Manufacturing metallic glasses in laser powder bed fusion technology is a significant technological challenge due to their low plasticity in ambient temperature. During processing, thermal stresses occur, leading to micro-cracks formation. The dissertation confirmed the possibility of obtaining amorphous structures for metallic glasses in the L-PBF technology. Nevertheless, to reduce or eliminate cracks, it is necessary to undertake further research on the reduction of thermal stresses by heating the built plate or selective heating with an additional laser beam and post-processing heat treatment.