I. ABSTRACT

1. English version abstract

The doctoral dissertation entitled "*Investigation of properties of cobalt-based alloys with high glass-forming ability developed by selective laser melting and plasma spraying*" concerns research on the development of amorphous structures in cobalt-based alloys using advanced manufacturing technologies such as selective laser melting and atmospheric plasma spraying. The aim of the research is to obtain an amorphous structure from cobalt-based alloys using these technologies, while achieving mechanical properties comparable to those of samples obtained by well-established casting methods. This aim has enabled a deeper understanding of the manufacturing of these modern alloys, which has so far been limited to casting methods such as die casting or vacuum casting and continuous casting on a wheel (melt spinning). Selective laser melting and plasma spraying offer the possibility of manufacturing more complex shapes with larger surface area or volume than those developed by casting, making them an area of research interest.

The research contained in the doctoral dissertation is organized around two main hypotheses. The first hypothesis states the possibility of obtaining an amorphous structure from a cobalt-based alloy using selective laser melting or atmospheric plasma spraying. The second hypothesis concerns the mechanical properties of the manufactured samples, which should be comparable to those manufactured using conventional manufacturing methods, namely casting. To confirm these hypotheses, the doctoral dissertation includes the following chapters: *Literature Review*, *Research Methods*, *Results*, *Discussion*, and *Conclusions*. The *Literature Review* chapter provides a comprehensive overview of the definition and types of amorphous metals, along with an overview of the technologies used to manufacture them and their applications. The *Literature Review* also provides insight into the unique properties of cobalt-based alloys and knowledge of their manufacturing, enabling the execution of the plan of experimental studies. The next chapter, *Research Methods*, describes in detail the research plan carried out as part of the doctoral dissertation. The results of these studies are collected and presented in the *Results* chapter. The analysis of the research results is included in the *Discussion* chapter, and finally, the conclusions, summary, and confirmation of the hypotheses are presented in the *Conclusions* chapter.

In the *Research Methods* chapter, based on the literature review, two cobalt-based alloys were selected and described: $Co_{47.6}Fe_{20.4}B_{21.9}Si_{5.1}Nb_5$ and $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$. The experimental part of the work includes a description of the development of reference samples by casting, and then atomization to prepare powder for selective laser melting and plasma spraying. As a result, samples such as cast plates and ribbons, gas-atomized powders, printed bulk samples, and plasma-sprayed coatings were obtained. Subsequently, analytical techniques such as digital microscopy, scanning electron microscopy, X-ray diffraction, calorimetric studies, and nanoindentation were used to assess the structure and mechanical properties of the manufactured samples.

The *Results* chapter is divided according to the alloys studied and then according to the manufacturing technologies used. The analysis of manufacturing parameters allowed for obtaining fully amorphous bulk samples and amorphous cobalt-based coatings using selective laser melting and plasma spraying techniques, respectively. The results of the experiments and the conclusions drawn from them confirmed both scientific hypotheses regarding the $Co_{47.6}Fe_{20.4}B_{21.9}Si_{5.1}Nb_5$ alloy. Samples made of $Co_{47.6}Fe_{20.4}B_{21.9}Si_{5.1}Nb_5$ using die casting, selective laser melting, and plasma spraying showed a range of values for the supercooled liquid region

from 41 to 50°C. Each of the applied manufacturing technologies with appropriately selected parameters enabled the development of fully amorphous structures, which was confirmed by the presence of a glass transition temperature on the graphs of differential scanning calorimetry tests. These results were confirmed by X-ray diffraction analysis, which did not detect evidence of crystallization; instead, an amorphous halo was recorded with a maximum for the angle at 46° 2θ (Cu Kα irradiation). Additionally, digital and electron microscopy confirmed the presence of only one phase without the presence of precipitations. Optical microscopy revealed the porosity of samples prepared using both alternative manufacturing technologies. Although porosity can affect the strength of the material and reduce the elastic modulus. Another research challenge, observed in all printed samples, was the cracking of the structure, which requires a solution in future studies. Suggestions for solving this challenge arising from this research dissertation are included in the *Conclusions* chapter. The hardness and elastic modulus of bulk samples and coatings were lower than those of cast samples; however, this difference was a maximum of 10%. The hardness of the printed samples was 14.5 GPa, the coatings 14.2 GPa; cast samples showed a hardness of 15.6 GPa. The elastic modulus for the printed samples was 200.6 GPa, and for the coatings 213.7 GPa; the cast samples had an elastic modulus of 222.8 GPa. The observed decrease in hardness and elastic modulus is attributed to differences in cooling rates between technologies and potential structural relaxation related to the heat-affected zone present in both alternative manufacturing processes but absent in casting. The literature review and experimental studies of the $Co_{47.6}Fe_{20.4}B_{21.9}Si_{5.1}Nb_5$ alloy have shown that the optimal energy density using selective laser melting is in the range of 39 to 68 J/mm³. The lower limit of energy density provides sufficient heat to melt the powder particles in order to join them. The upper limit limits the value of residual stress in the samples, which could lead to their destruction during processing. In plasma spraying experiments, the energy supplied to melt the powder in the plasma stream was also regulated to avoid overheating the substrates on which the powder particles were deposited. For this purpose, argon was used as a plasma-forming gas, which proved effective in limiting heat transfer at spraying distances between 90 and 110 mm, enabling the development of amorphous coatings. The coatings thus developed showed a favorably low abrasive wear coefficient of $2.0 \cdot 10^{-5}$ +/- $0.2 \cdot 10^{-5}$ mm³/Nm.

The analysis of the second alloy revealed significant problems with crystallization in most samples. The cast plate showed significant crystallization, leading to an additional casting process to obtain a fully amorphous reference sample. For this purpose, melt spinning was used, which allowed to manufacture a fully amorphous ribbon with a thickness of about 50 µm. X-ray diffraction and differential scanning calorimetry confirmed the amorphous state of the ribbon, while scanning electron microscopy imaging did not show any crystalline phases or the presence of impurities. The hardness of the ribbon was 15.1 GPa, and the elastic modulus was 190.1 GPa. To obtain bulk samples from $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$ powder using the selective laser melting process, the energy density had to be precisely controlled. Experiments have shown that the best results were obtained in a narrow range from 41 to 50 J/mm³. Despite these limitations, the samples exhibited severe cracking problems caused by high stresses during the rapid solidification of the weld pool. Scanning electron microscope (SEM) observations, confirmed by Rietveld analysis, showed the presence of crystallization in the printed samples at the level of approximately 50% volume. The crystals formed nano- and micro-precipitates inside the amorphous matrix, which was observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Diffraction patterns obtained using the mentioned analysis confirmed the presence of both an amorphous phase and crystalline phases, including Co_5Si_2B and TaB_2. The presence of crystallization at this level led to a significant increase in the hardness of the material, amounting to 18 GPa. This increase in hardness was attributed to the hardening of the amorphous material through mechanisms including solid solution hardening by nanocrystallization or interactions between phases boundaries (amorphous and crystalline) boundaries. The elastic modulus of the coatings was 10% higher than in the case of the ribbon reference and was 225.4 GPa.

The coating developed using plasma spraying from $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$ showed almost complete crystallization with a residual content of the amorphous phase and a problem with high porosity. However, a positive effect on the reduction of porosity by approximately 3 percentage points (from 11.2% to 8.5%) was observed by reducing the spraying distance from 110 to 90 mm. The obtained coating showed good wear resistance, with a wear rate of approximately $1.9 \cdot 10^{-5}$ +/- $0.20 \cdot 10^{-5}$ mm^3/Nm. The hardness of the coating was approximately 14.0 GPa – 7% lower than in the case of the rolled ribbon reference. The decrease in hardness is typical for crystallized alloys compared to their amorphous state. The elastic modulus was similar to that in the case of the ribbon and was 198.2 GPa. The high crystallization of the coatings was attributed to the low glass- forming ability of the $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$ alloy, which was the result of insufficient homogenization of the alloy during its development from pure elements and then atomization of the powder. As in the case of other forms of the $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$ alloy, the presence of the TaB_2 phase was observed in the powder; this phase was characterized by irregular shapes of precipitates of various sizes. The presence of this phase was attributed to the lack of sufficient remelting of the pure chemical element, namely tantalum, the melting point of which reaches 3000°C. The insufficiently homogenized liquid phase of the alloy during casting led to a reduction in the glass-forming ability of the $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$ alloy and, in the case of most manufacturing technologies (except for those with very high cooling rates), resulted in significant crystallization of the samples.

The doctoral dissertation successfully confirmed the hypotheses regarding $Co_{47.6}Fe_{20.4}B_{21.9}Si_{5.1}Nb_5$ alloy. This alloy showed a high ability to produce an amorphous structure, enabling pioneering research on the use of cobalt-based alloys with an amorphous structure using selective laser melting and plasma spraying. In addition, studies of the second alloy $Co_{42}B_{26.5}Fe_{20}Ta_{5.5}Si_5Cu_1$, which in the doctoral dissertation was partially amorphous and partially crystalline, contributed to a deeper understanding of the group of alloys with a composite structure and their behavior during manufacturing. The achievements documented in this doctoral dissertation represent a significant advance in the field of mechanical sciences, which have also been published to make the findings available to a wider scientific community. This dissertation makes a significant contribution to expanding knowledge in the field of amorphous metals and their composites and the use of selective laser melting and plasma spraying technologies, confirming research hypotheses and providing insight into the behavior of cobalt- based alloys under various manufacturing conditions. The work sets a promising path for future research on the development of cobalt-based amorphous metals using innovative technologies such as selective laser melting and plasma spraying.