ELECTRO SPARK DEPOSITION OF HfNbTaTiZr HIGH ENTROPY ALLOY PROCESSED IN SOLID STATE AND EXPERIMENTAL ADHESIVE TESTING

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HfNbTaTiZr high entropy alloy was deposited on a stainless steel surface by electro spark deposition (ESD) technique and investigated. The alloy was previously produced by solid state processing method and characterized, where promising results were obtained. The alloyed powder was consolidated by using spark plasma sintering technique. Electrodes were manufactured from the bulk material, with an optimized shape for better performances for the ESD process.

For the pull off test a designed and manufactured device was utilized and the results are presented. The microstructure analysis present that HfNbTaTiZr high entropy alloy coating was obtained, fissures and cracks not being present.

Keywords: high entropy alloy, adhesive testing, mechanical alloying, coatings

1. Introduction

The high entropy alloys are the main subject in different researches [1-4] due to the novelty of this high-performance alloys.

For this paper, the possibility of obtaining HfNbTaTiZr high entropy alloy coatings by electro spark deposition process was investigated. The advantage of this method is represented by the possibility of coating surfaces and repairing damaged ones, acting local at minimal costs. The electrodes design was selected after several tests, where the thickness of the electrode might impact the deposition process.

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Mechanical alloying of the HEA was previously studied [5-8] and for that matter, the time parameter was modified in order to obtain a higher alloying degree.

In order to perform the pull off test, factors as cohesive resistance of the used epoxy resin, thickness of the deposited layer, and adhesive resistance between the sample surface and the pulling device were taken into consideration.

The main goal is to obtain corrosive and wear resistant coatings, which are cost effective for aggressive environments.

2. Materials and Methods

Hf, Nb, Ta, Ti and Zr metallic powders, with very high purity, are the component elements of the desired high entropy alloy produced by mechanical alloying and consolidated. In previous papers [9, 10] the experimental procedure used in order to obtain HfNbTaTiZr high entropy alloy was discussed. After several trials [5], the milling time was increased in order to obtain a higher alloying degree. The final parameters decided for the process consist of 60 h of milling time, with 300 rot/min and BPR 10:1. As a process control agent, N-Heptane was utilized, wet milling improving the alloying efficiency.

Both metallic powder elements and final mixture were manipulated under argon atmosphere, in a glovebox, with the oxygen level under 3%.

The mechanical alloying was performed using a Planetary Ball Mill (Pulverisette 6, Frich®) with stainless steel vial and balls, under argon atmosphere.

The samples were investigated by using X-Ray Energy Dispersive Spectroscopy (XEDS) equipment and a Field Emission Scanning Electron Microscope (FE-SEM) for the chemical composition and microstructure analysis.

After the high entropy alloys was obtained by solid state processing method, it was consolidated by spark plasma sintering method with HP D25 (FCT System GmbH, Germany) equipment and high-density graphite molds. The final parameters were decided after tests and trials and the results are presented. In the spark plasma sintering process, the powder is pressed and sintered in a rapidly heated die, the temperature being controlled and uniformly throughout all the volume of the processed material under action of direct current impulses generated by a high power source [11, 12]. The HEA powder was sintered using the Spark Plasma Sintering technique and the best results were obtained for 1000ºC at 50 MPa in vacuum atmosphere.

In order to deposit HfNbTaTiZr high entropy alloy coating, the obtained bulk material was mechanically processed into electrodes, which are suitable for the electro spark deposition equipment. A final shape for the electrode was decided, to increase the deposition efficiency and also to increase the mechanical resistance.

The deposition was performed by utilizing Spark Depo Model 300 ESD, equipped with a miniature applicator. During the deposition process, protective argon atmosphere was present, to avoid the oxidation that might be present in the final coating.

For the adhesive test, a pull off test rig was designed and it is presented in Fig. 1. In order to test the adhesion of the coating, commercial epoxy resin was applied as a bonding agent between the pull off test equipment stub and the surface of the sample. According to the epoxy resin producer, it can resist to a maximum of approx. 21 MPa.

The adhesion test was performed according to ASTM D4541 [13] and the sample surface was prepared according to ASTM D2651 [14]. Walter+Bai Ag LFV-300 kN testing machine was used to perform the experiment.

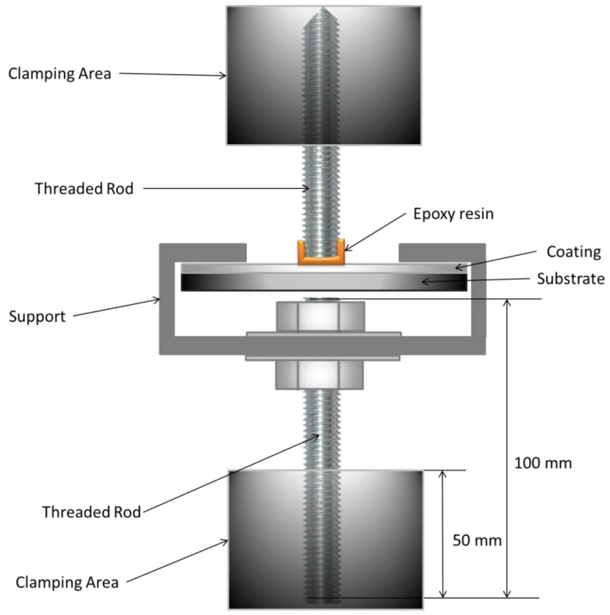

Fig 1. Schematic representation of the Pull-Off test experimental device

The device was manufactured from stainless steel parts, in order to have an increased mechanical resistance during the process and to avoid contamination the device was cleaned with high purity alcohol.

3. Results and discussions

The raw pure materials were mechanically alloyed in a planetary ball mill for a period of 450 minutes [9]. The SEM analyses and EDS analyses obtained results indicate a good alloying degree with no oxygen contamination or other impurities. The results are presented in Fig. 2.

The obtained alloying degree results in promising results and the powder can be further processed by pressing and sintering.

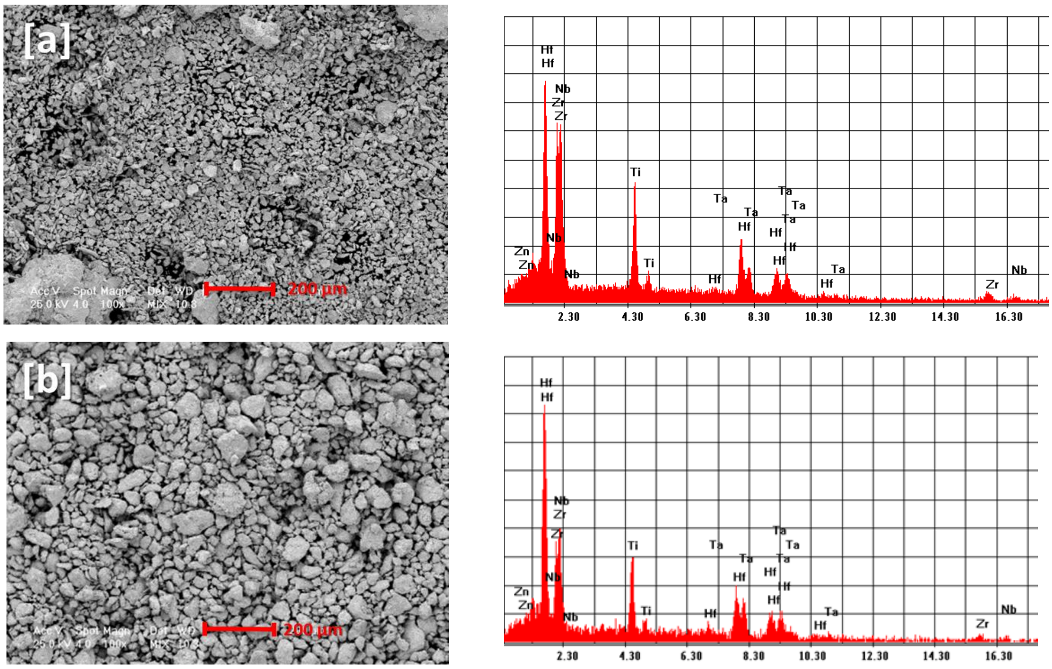

Fig. 2. a. Homogenized sample analysis of HfNbTaTiZr and b. sample analysis of HfNbTaTiZr after 450 min of milling [9]

In Fig. 2.a, a homogenized SEM analysis is presented. It can be observed that the particles have different shape and sizes and in figure and the sample is not homogeneous. After mechanical alloying, the microstructure presented in Fig. 2.b revealed a homogenous powder, with particles of relatively same dimensions. During repeatedly welding and de-welding process during mechanical alloying process, the particle become light grey and presented the tendency of agglomeration. From the EDS analyses of the obtained alloy it can be observed a relatively homogenous material and the presence of all the compositional elements.

The solid sample after SPS consolidation was cut and machined in order to obtain Electro Spark Deposition electrodes with which stainless steel coupons were coated for further testing. The electrode shape was decided after several tests, in order to obtain a good mechanical resistance and it is presented in Fig. 3.

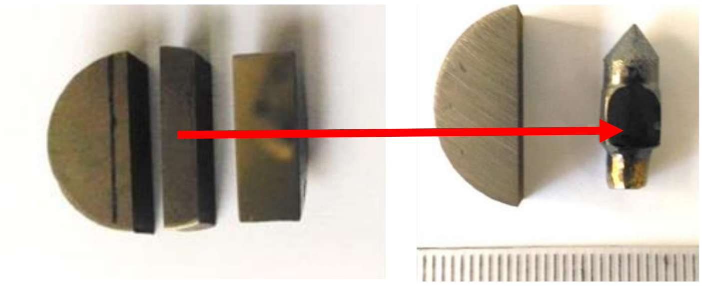

Fig.3. Electrode of HfNbTaTiZr HEA cut and machined for ESD process

The stainless steel substrates were sandblasted and cleaned with alcohol, removing the impurities. Deposition parameters for the electro spark deposition process are presented in the following table. The coating was performed under argon flow to avoid the formation of oxides during deposition.

Table 1

Deposition parameters for the electro spark deposition technique

Deposition material	Substrate	Capacitance	Voltage	Frequency	Atmosphere
HEA HfNbTaTiZr	Stainless Steel	40μF	100 V	260Hz	Argon (3 l/min)

In Fig. 4, are presented the stainless steel coupons during the deposition process. The first is the unprepared sample, the second is sandblasted and decontaminated with alcohol and the 3rd is the deposited sample.

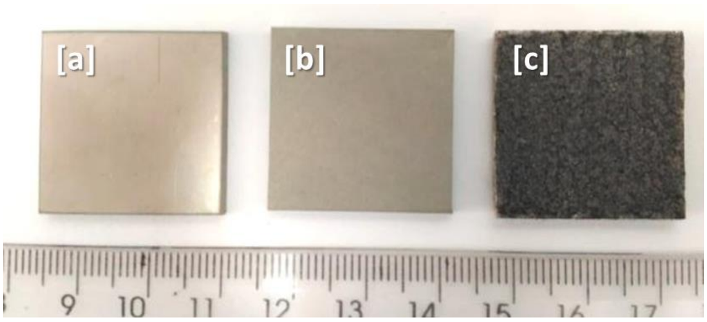

Fig.4. a. Stainless steel substrate, b. Sandblasted and cleaned substrate
c. Coated substrate with HfNbTaTiZr HEA

On the right side is presented a microscopy of a cross section of the deposited layer. It can be seen that the roughness of the substrate affects the uniformity of the deposited layer. The analyses results are presented in Fig. 5.

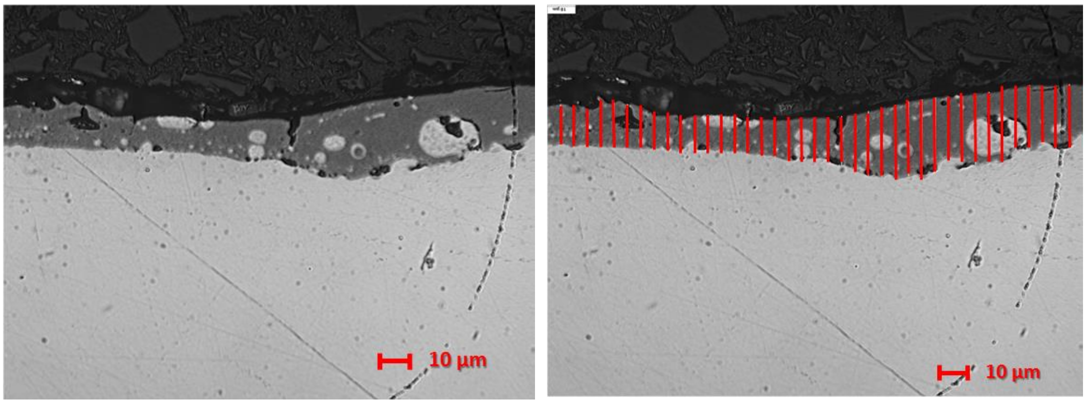

Fig. 5. Microscopic analyses for the cross section of the ESD coating

For the present case, successive passes were made, changing the direction of deposition after each pass obtaining the final average thickness around 18 microns. Further attempts will be performed in order to obtain a more uniform and crack-free layer.

After the coating of HfNbTaTiZr was produced, the sample was tested by performing a pull off test. Pictures from before and after the test are presented in Fig. 6.

Fig.6. The sample performance during the pull off test

For optimum results, the epoxy resin used for the testing was applied 24 h previously. At a maximum load applied of 1.56 MPa, the epoxy resin failed and detached from the sample. No exfoliation of the coating has been observed.

The results are correlated with the load chart obtained during the test, presented in Fig. 7.

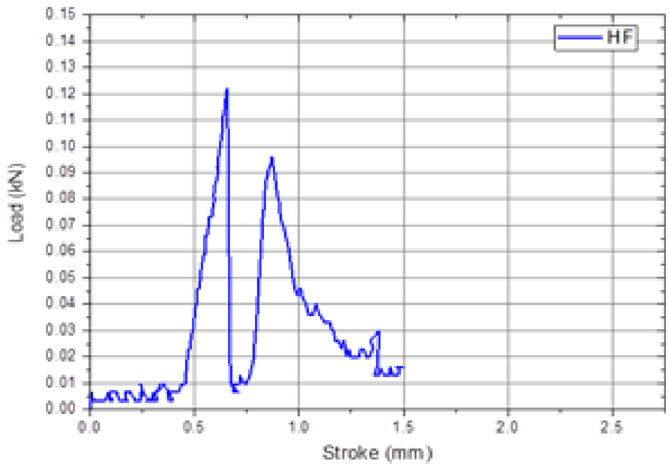

Fig.7. Load chart obtained during the pull off test for the HfNbTaTiZr coating

From the load chart can be observed the moment when the epoxy resin yields, which is when the maximum load is applied. The elastic behavior and the failure point for the resin are also present. According to the adhesion test, no adhesive or cohesive failures occurred, the adhesion between the deposited layer and the substrate being stronger than that of the epoxy resin.

4. Conclusions

The HfNbTaTiZr high entropy alloy was produced by solid-state processing technique and the results are presented. Due to the alloying and homogenization degree obtained, the powder was further processed.

Spark plasma sintering process was used in order to consolidate the samples so a high resistance electrode can be obtained.

The samples were cut and machined into electrodes for the electro spark deposition technique, with and improved design for increased mechanical resistance.

The HfNbTaTiZr high entropy alloy coating, produced by ESD processing was obtained and analyzed and the results are promising but further testing will be performed in order to obtain a coating with less defects. The coated was adhesion tested, by using an experimental pull off test rig, designed for this purpose. The results show good performance, where no exfoliation is present.

Future work will be focused on mechanical testing of the obtained coating through other methods and testing the obtained coated sample in aggressive media, due to the corrosive resistance characteristics of the high entropy alloy component elements.

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