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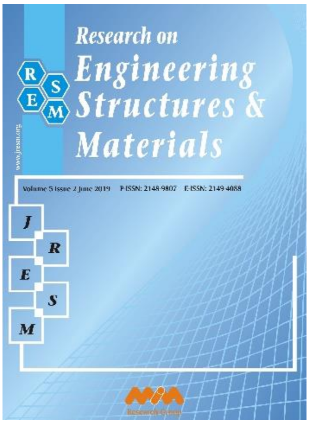

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Research Article

Microstructure, hardness and biocompatibility properties of ceramic based coatings produced by plasma spray method

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Abstract

Ceramic materials with excellent mechanical, corrosion and abrasion resistance is set in terms of features such as biomaterials. In this study, Al_2O_3, Al_2O_3-40% TiO_2, ZrO_2 - 8% Y_2O_3 and Cr_2O_3-2% TiO_2 ceramic coatings were produced by plasma spraying on AISI 316L stainless steel surface. It was aimed to investigate microstructure, hardness and biocompatibility properties of coatings. Scanning electron microscope (SEM) analysis and X-ray diffraction (XRD) phase analysis were used to determine the microstructure and phase composition properties. The biocompatibility properties of coatings have been tried to be determined by analyzing cytotoxicity and viability. The SEM images show that the ceramic coatings are connected in accordance with the substrate. The XRD analyzes show the formation of binary and ternary complex phases in the coating layers. Cr_2O_3-2% TiO_2 coating has the highest hardness in the coating layers. Biocompatibility tests reveal the most compatible and consistent results in terms of cytotoxicity were obtained with Al_2O_3-40% TiO_2 coating.

1. Introduction

Biomaterials are natural or synthetically obtainable materials which are used for prosthetic, diagnostic or therapeutic purposes and which are in contact with tissue, blood and other body fluids within the body [1, 2]. The performances of the materials used in the body are important. The performances of the materials placed inside the body can be examined from different angles. Depending on the area in which the problem is to be solved, a classification can be made at the tissue-organ level or according to the materials used [3]. Biomaterials can be used for a long time or for a short time. The most basic feature that implants should provide is that they are not allergenic or toxic. In addition, biomaterials, designs and mechanical behavior are important qualities. Ceramics are usually blends of metals formed by non-metallic elements. The interatomic bond is ionic or covalent. Ceramic materials have been used as medical materials for many years despite their fragility, porous structure, low tensile strength and low impact strength. With the recent development of new methods, ceramics are used in many different fields of biomolecules. They are widely used in dentistry as gold-porcelain crowns, silica–filled resin composites, and dentures. Due to its high wear resistance, high hardness and excellent corrosion resistance, Al_2O_3 and yttria–stabilized ZrO_2 are widely used in hip prostheses and dental industry with load carrying function [4, 5].

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Plasma spraying method is spraying of powder on the surface of the material to be coated at a plasma temperature which is ionized and can reach up to 15.000 ° C-25.000 ° C, while the diatomic gases (argon-hydrogen mixture) passing between a tungsten (cathode (-)) and a copper nozzle [6-8]. Plasma spraying is effectively and economically applied to various machine parts to reduce surface defects [9]. In this method, the complete or partial melting of the powders varies depending on their thermal properties. The controllability of the system at extremely high heating and cooling rates makes it possible to produce coatings made of metallic, non-metallic and ceramics and combinations with this method [10]. Ceramic powders are used more frequently than metallic powders in the plasma spray method due to their high chemical stability at high temperatures, excellent wear resistance and corrosion resistance [11]. Ceramic materials with high resistance to corrosive and thermal conditions, relatively low density and high hardness are preferred over polymeric and metallic materials due to their existing properties. Ceramic materials such as aluminum oxide, zirconium oxide, titanium oxide, chromium oxide, silicon oxide and yttrium oxide are widely used as surface coating materials to improve wear, erosion, cavitation and corrosion resistance of materials. Such materials are particularly needed in applications where resistance to wear and corrosion is desired [12, 13].

In this study, Al_2O_3, Al_2O_3 - 40% TiO_2, ZrO_2 - 8% Y_2O_3 and Cr_2O_3 - 2% TiO_2 oxide coatings were produced by plasma spraying on AISI 316L stainless steel surface since they have high wear resistance and high corrosion resistance. Stainless steels are used in orthopedic applications. They have the ability to bear significant loads and withstand fatigue loading. Therefore, in this study, AISI 316L stainless steel was preferred as substrate. Microstructure and biocompatibility properties were experimentally investigated. Microstructure, microhardness and phase properties were determined by scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray diffractogram (XRD) analyzes. The microhardness change was measured from the top of the coating layer. The biocompatibility properties of coatings have been tried to be determined by cytotoxicity and viability analysis.

2. Materials and Methods

AISI 316L stainless steel was used as substrate and Al_2O_3 (Metco 105SFP), Al_2O_3 - 40% TiO_2 (Metco 131VF), ZrO_2 - 8% Y_2O_3 (Metco 204B-NS) and Cr_2O_3-2% TiO_2 (Metco 106F) were used as coating powders. A Sulzer Metco 9MB atmospheric plasma spray coating system with 80 kVA of power was used to produce the coating layer (Fig. 1). The flow rate of the argon gas used to produce the plasma beam in all coatings is 35-73 l/min. The plasma spray gun was fixed so that the spray distance was 75 mm, so that the coating powders were injected externally to the gun and parallel to the plasma flow. H_2 gas flow rate was 6.6 l/min and carrier gas ratio was set as 9-11.4 l/min. About 250 µm thick layer was produced as coating layer. For metallographic investigations, the samples were sanded by passing through coarse and fine sanding steps, respectively. The sanded samples were polished using diamond solutions and etched using a solution of HNO_3 (40 pct.) + C_2H_5OH (60 pct.). A FEI QUANTA 250 FEG scanning electron microscope (FEI Inc., OR, USA) was used to determine the chemical composition of the microstructure. X-ray diffraction (XRD) analysis was performed to determine the phases formed in the microstructure using a Bruker D8 Advance XRD system (Bruker Optik GmbH, Ettlingen, Germany).

The hardness measurement was made with SHIMADZU HMV-G21 brand microhardness device with a waiting period of 15 seconds from the top surface of the coating and a load of 200 gf (1.961 N). From each sample, 6 hardness measurements were taken from different regions. Their averages were taken and evaluated. Hardness tests were carried out according to ASTM C1327–15 standard [14].

The biocompatibility properties of coatings have been tried to be determined by cytotoxicity and viability analysis. The cytotoxicity tests of the prepared composite materials were performed by in vitro tests based on cell viability. For this aim, MTT [3- (4,5-dimethyldazol-2-yl) -2,5-diphenyl tetrazolium bromide] (Sigma, USA) test was used to measure cell viability and mitochondrial dehydrogenase activity. MCT3T3-E Mouse osteoblastic cells were used in the studies because of coating materials' potential to be used as a bone implant. In the tests, 6-well petri dishes were used, depending on the size of the samples. 200 µl cell suspension (containing ~$2x10^5$ cells) was added onto each prewetted sample placed in a well of 6-well plate; kept in the incubator for 10 min and then was gently covered with basal medium. After freshly prepared 4.5 ml of medium (without FBS) was added to each well, 0.5 ml fresh MTT reagent was added to provide 10% concentration, and they were incubated at 37°C and 5% CO_2 for 4 h. However, no sample was placed in one of the wells as a control. The formazan, insoluble dark blue complex that was formed by MTT reduced in the mitochondria, was monitored under an inverted microscope (Leica DMIL LED, Germany). Semi-quantitative data were obtained spectrophotometrically at the wavelength of 570 nm using a multi-well plate reader (Biotek, USA). The MTT tests applied to the cultures were repeated three times and the mean values of the measurements were taken according to the days.

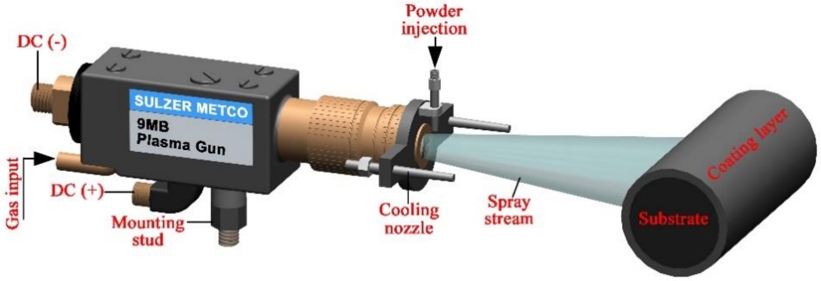


Fig. 1 Principle diagram of plasma spray coating process

3. Results and Discussion

The macro images of Al_2O_3, Al_2O_3-40% TiO_2, ZrO_2-8% Y_2O_3 and Cr_2O_3 - 2% TiO_2 ceramic based coating samples produced on AISI 316L stainless steel are given in Fig. 2. All surfaces of the samples were coated. In the samples produced, color change occurred according to the content of the coating material. It is also noted that the coating layers are smooth.

SEM images of ceramic coatings produced by plasma spray process are shown in Fig. 3. The SEM images exhibit splat by splat lamellar structure formation in all of the coatings with the presence of partially melted regions and some un-melted particles in ceramic coatings. The coating layer is connected to the bottom material as compatible. This is a positive result of the strength of the coatings against mechanical forces. The porosity in the coating layers came to fruition. Although this is negative for mechanical properties, it is considered to be favorable in terms of biocompatibility. Pore formation is inevitable in studies carried out in the literature [15, 16]. Porosity is caused by the lack of insufficient surface wetting of the melted particles striking rough substrate surface [17]. The distribution of the elements forming the coating layer in the main matrix also affects both the mechanical and physical properties. While homogeneous distribution affects the characteristics positively, heterogeneous distribution affects negatively. In order to determine the distribution of the elements, SEM-MAP analysis of the Cr_2O_3-2% TiO_2.coating given in Fig. 4 was performed. According to the analysis, the elements Ti and O were distributed relatively homogeneously in the main element of Cr. This indicates that the features will be the same all over the coating.

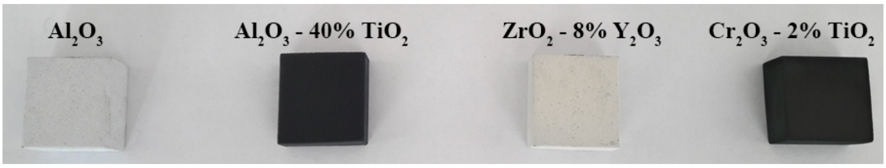
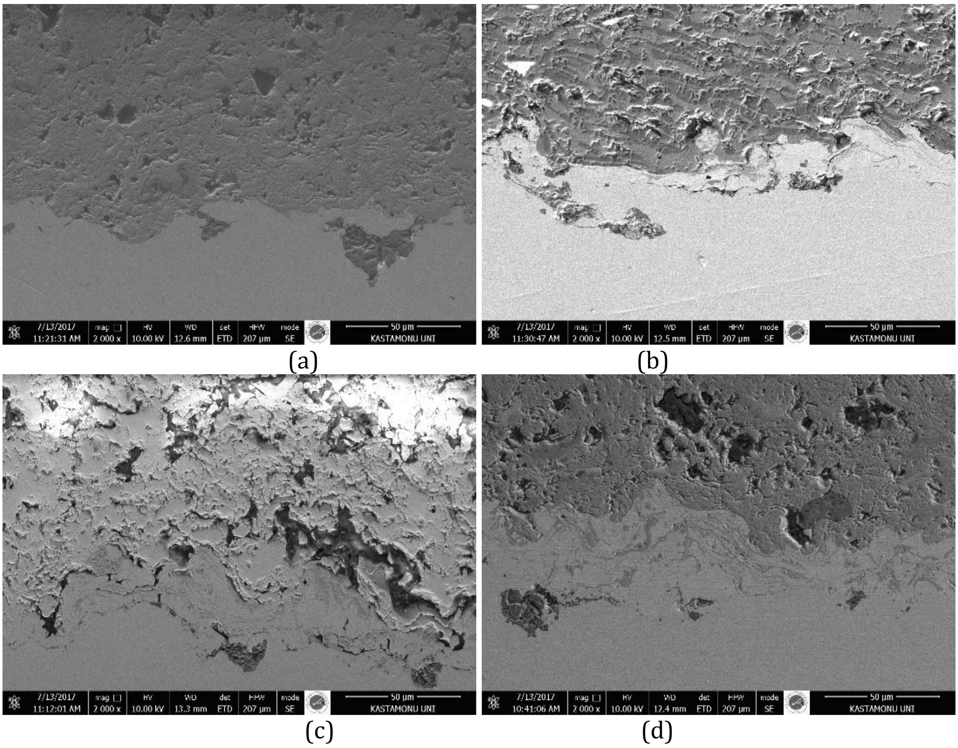


Fig. 2 The macro images of ceramic based coatings



(a) (b) (c) (d)

Fig. 3 (a) Al_2O_3 (b) Al_2O_3 - 40% TiO_2, (c) ZrO_2 - 8% Y_2O_3 and (d) Cr_2O_3 - 2% TiO_2.

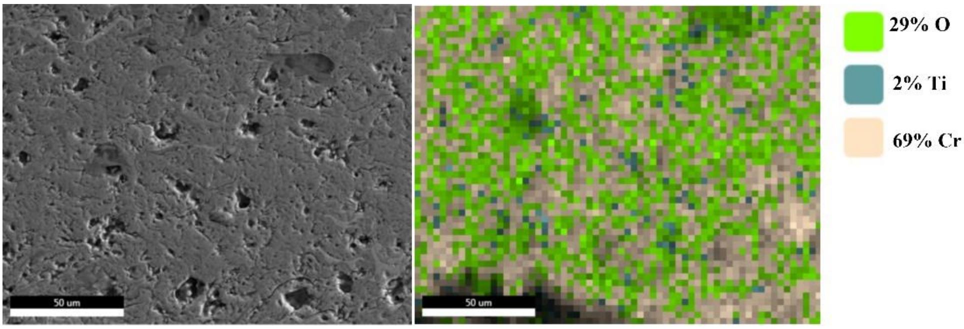
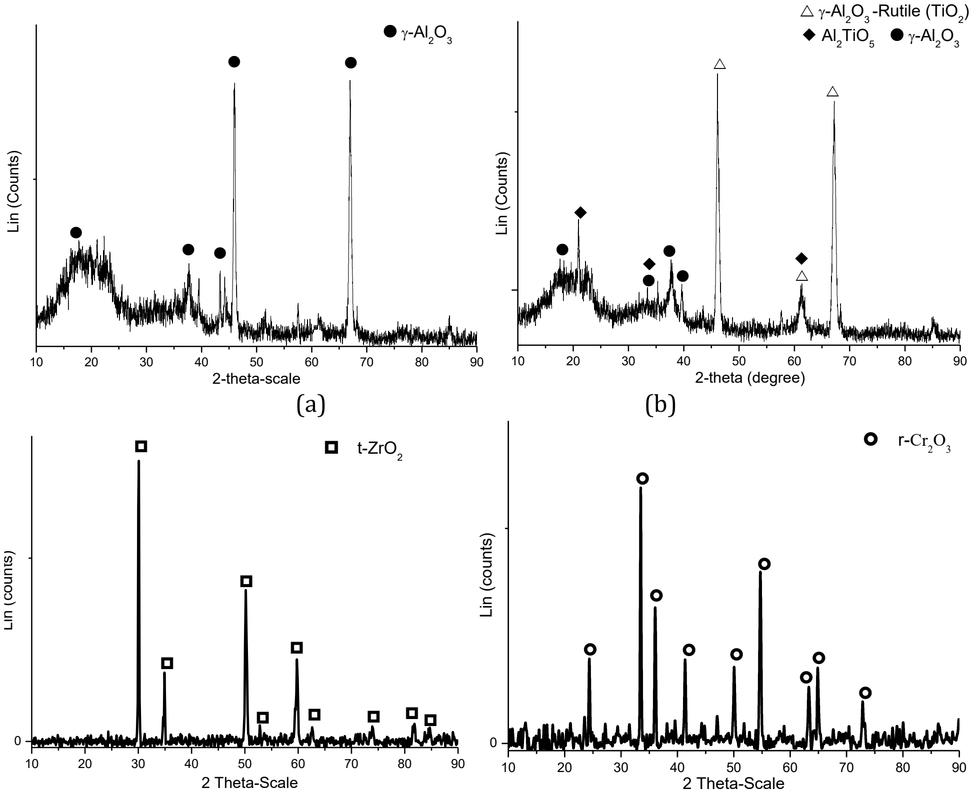


Fig.4 SEM-MAP analysis of Cr_2O_3-2%TiO_2 coating

Fig. 5 shows the XRD analyzes of the coatings. Phases seen in coatings represent powders before coating. Besides this, it is formed in ternary phases in addition to binary phases. For the Al_2O_3 coating, while the α-Al_2O_3 phase was present in the powder material, the phase γ-Al_2O_3 was detected in the coating layer. During the spraying process, the conversion from α-Al_2O_3 to γ-Al_2O_3 occurred in a crystal structure [18-20]. In the specimens coated by Al_2O_3-40%TiO_2 contents, XRD data give Al_2TiO_5, and γ-Al_2O_3-TiO_2 phases beside γ-Al_2O_3 phase. Due to very small size of the particles, the contact area among them were very large and during plasma spraying this large area caused the formation of Al_2TiO_5 reaction phase whose thermal expansion coefficient was too small and therefore it was desired for the applications where thermal resistance was needed [21-24]. For the ZrO_2 - 8% Y_2O_3 coating, tetragonal (t) ZrO_2 phase is formed in the microstructure. This phase is a metastable phase. This is an expected situation, given the work done in relation to ZrO_2-Y_2O_3 [25]. No phase other than this phase has been formed. The XRD analysis of Cr_2O_3 - 2% TiO_2 coating revealed that the strong diffraction peaks detected were related to Cr_2O_3 phase (rhombohedral crystal system). No phase related to TiO_2 was detected. 2% TiO_2 is used in the starting powder which is quite less and difficult to be detected comprehensively by XRD analysis [26, 27].



(a) (b)

(c) (d)

Fig. 5 XRD analyses: (a) Al_2O_3 (b) Al_2O_3 - 40% TiO_2, (c) ZrO_2 - 8% Y_2O_3 and (d) Cr_2O_3 - 2% TiO_2.

The micro hardness values of the substrate and coating layers are given in Fig. 6. Hardness values are taken from six different regions. The coating was also taken from six different regions from the layers and taken from the upper surface of the coatings. Evaluation was made by taking the average of the values received. While the hardness of the substrate is 215 $HV_{0.2}$, the hardness values of the Al_2O_3, Al_2O_3 - 40% TiO_2, ZrO_2 - 8% Y_2O_3 and Cr_2O_3 - 2% TiO_2 coating layers are 905 $HV_{0.2}$, 760 $HV_{0.2}$, 950 $HV_{0.2}$ and 1215 $HV_{0.2}$, respectively, which are 3.5-5.6 times higher than the substrate. The hardness of the Al_2O_3-40% TiO_2 coating layer was lower than the TiO_2-free Al_2O_3 coating. Al_2O_3 material is known to be harder than TiO_2 material. In the coating of Al_2O_3-40% TiO_2, TiO_2 has a toughening role [28]. Cr_2O_3 - 2% TiO_2 coating has the highest hardness value among ceramic coating layers. This measured value is compatible with the literature [26]. These increases in hardness are due to the natural hardness of the ceramic materials. During this hardness measurement, no cracks were formed in the ceramic coatings.

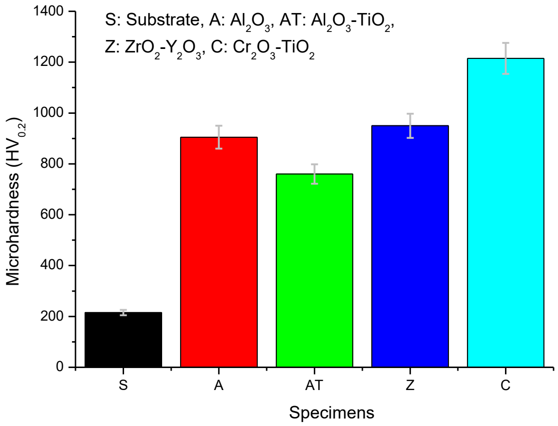
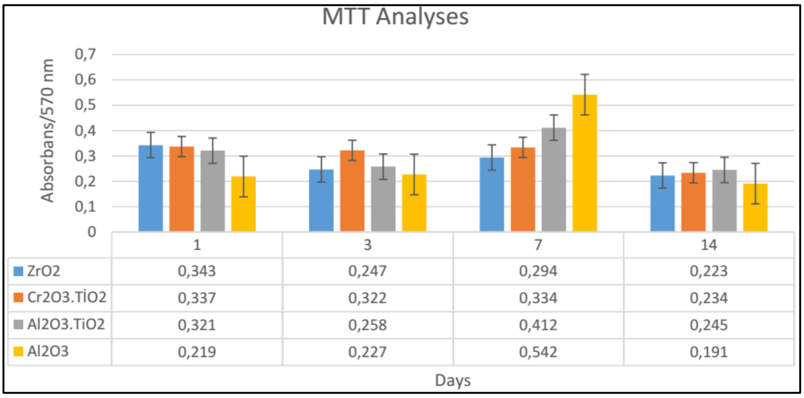


Fig. 6 Micro hardness values of the substrate and coating layers

In biocompatibility analysis, it was observed that cell viability did not change much in all ceramic coatings and the highest absorbance value was obtained on the 7th day. In addition, although it is clear that biocompatibility due to cell viability shows similar values for all coatings, the most compatible and consistent results in terms of cytotoxicity were obtained in the coating of aluminum oxide-titania. Change of absorbance values measured at 570 nm wavelength of ceramic coatings according to culture time is given in Fig. 7. According to semi-quantitative analyzes, cell viability in the alloy with the zirconium oxide coating was generally maintained in 14 days of continued cell culture, but at the 14th day a 35% reduction was determined. This change in chromoxide-titanium oxide coating was calculated as 31%, in aluminum oxide-titanium oxide coating as 24% and in aluminum oxide coating as 13%.



	1	3	7	14
🟦 ZrO2	0,343	0,247	0,294	0,223
🟧 Cr2O3.TiO2	0,337	0,322	0,334	0,234
⬜ Al2O3.TiO2	0,321	0,258	0,412	0,245
🟨 Al2O3	0,219	0,227	0,542	0,191

Fig. 7 Change of absorbance values measured at 570 nm wavelength of ceramic coatings according to culture time.

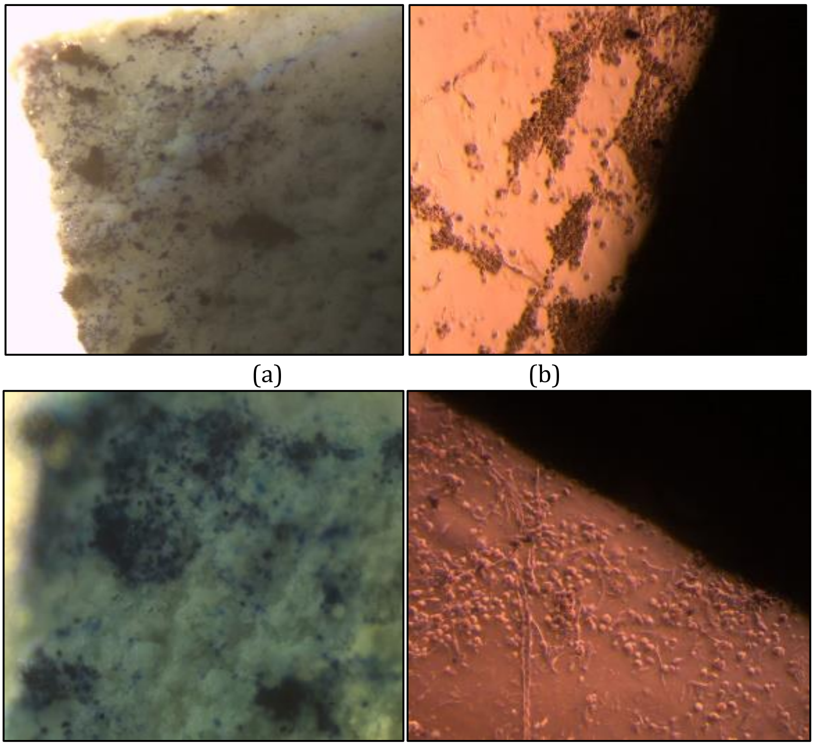

(a) (b)
(c) (d)

Figure 8. Formation of formazan crystals as a result of MTT analysis: (a) Al_2O_3 (b) Al_2O_3-40% TiO_2, (c) ZrO_2-8% Y_2O_3 and (d) Cr_2O_3-2% TiO_2.

Formazan crystals formed by MTT reagent reduction are shown in Fig. 8. It has been observed that formazan crystals are formed on the surface of composite structures and in micropores. In addition, because of the weak bonding with the material surfaces cells had been separated from the materials, and formazan crystals were formed in the vicinity of these scattered cells on the plate surface [29].

4. Conclusion

In this study, Al_2O_3, Al_2O_3 - 40% TiO_2, ZrO_2 - 8% Y_2O_3 and Cr_2O_3 - 2% TiO_2 oxide coatings were produced by plasma spraying on AISI 316L stainless steel surface. The conclusions drawn from this study are given below:

- The SEM images showed that the coating layers were mechanically bonded to the substrate, had a slightly porous structure, and generally the coating layers had lamella formation.
- The γ-Al_2O_3, Al_2TiO_5, γ-Al_2O_3-TiO_2, t-ZrO_2 and r-Cr_2O_3 phases were determined by the XRD analysis of the coating layers.
- The hardness of the coatings varied between 760-1215 $HV_{0.2}$ and there was a 3.5-5.6-fold increase compared to the substrate. The highest hardness was obtained in Cr_2O_3 - 2% TiO_2 coatings.
- Although it is clear that biocompatibility depends on cell viability, similar results are obtained in all coatings, but the most compatible and consistent results in terms of cytotoxicity were obtained with Al_2O_3-40% TiO_2 coating.

5. Acknowledgements

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