INVESTIGATIONS ON COATING OF DIES FOR ADVANCED SQUEEZE CASTING PROCESS

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Abstract

Premature failure of dies is a critical problem of manufacturers in hot-working processes, e.g. metal die casting, hot extrusion and/or thixoextrusion of aluminium/magnesium or steel. Typically, die material has to be resistant to heat cycling or corrosion environment, to plastic deformation and wear, especially when exposed to high temperature during continuous working cycle. The resistance of dies could be increased by the modification of their surfaces, i.e. by the application of an adequate coating. An improvement of the resistance of H11 steel substrate will be presented and discussed. Here, the coatings will be realized through both by High Velocity Oxy-Fuel coating spray method and by plasma spray method. Firstly, the measurement of the residual stress will be carried out on the un-coated and coated substrate. Secondly, morphological analysis by optical and scanning electron microscopy will be performed on the powders used for the coating and on the coated materials. Such investigations aim finding the most favourable conditions, as concern the materials to be employed for the deposition and the more appropriate deposition techniques, in order to achieve improved properties for the dies which can be used in innovative casting techniques, i.e. squeeze casting and/or some related modified processes.

Keywords: Al-based alloys, deposition methods, morphological analysis, residual stress measurment

1 Introduction

Degradation of hot working components is directly correlated to the design, materials employed for the manufacturing as well as the operation history. High reactivity of steel with Al and its alloys as a consequence of the high solubility of Al in α-Fe and of Fe in liquid Al has a strong effect on the dies lifetime. As a result of the repeated contact of the die surface and the casting alloy dies are continuously exposed to erosion and corrosion. Due to different degradation mechanisms attributed to wear, as well as to corrosion- or thermo mechanical fatigue during service, a gradual failure of the die surfaces occurs, reducing the castings quality and the dies duration. The tool materials used for hot-working dies should be resistant to wear, heat cycling and thermal fatigue, plastic deformation and corrosion. In addition, they have to present high hardness, yield strength, creep resistance and toughness at high temperatures. In order to minimize or to avoid the die surface from any negative effects, the dies have to be produced employing an appropriate alloy or by modifying their surfaces through some suitable treatments. Many technological solutions are available today: some of them are related to nitriding

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processes, physical vapour deposition (PVD) or chemical vapour deposition (CVD) [1, 2], atmosphere plasma jet metallization (APS), etc. For many years gas nitriding has been one of the most successful techniques of surface treating of aluminium extrusion dies. Some of these processes, e.g. CVD, have a restriction due to possible distortion that can arise in parts treated by high temperature CVD. Therefore, steel tools are not commonly treated by CVD. Plasma nitriding is a conventional thermochemical method: by enriching the material surface with nitrogen, increased surface hardness has been obtained. Recently, PVD coatings, and the combination of plasma nitriding and PVD (duplex process) have been also developed for protection of the extrusion dies, but are severely restricted by the size of the application cell. Another way used for the protection of steel tooling is constituted by hard chrome plating, an effective system for improving wear resistance. However the use of hexavalent chromium [3, 4] generates environmentally problems, making the process less attractive.

High-velocity oxy fuel (HVOF) process has attracted much attention for coating realization, due to its ability of creating coatings with lower porosity, higher hardness, superior bond strength and less decarburization compared to many of the other thermal spraying methods [5, 6]. A well-established hard chrome replacement for mechanical components in automotive and aerospace industry is represented by HVOF method, but the application of this process to tooling materials has been limited [7]. Within this method, the abrasive wear resistance strongly increases by the addition of tungsten carbide into the metallic matrix [8-10].

Residual stress in the coating can vary with the coating thickness, substrate temperature, deposition parameters and cooling effect. Generally, residual stresses increase with increasing thickness and temperature of the coating during the deposition process. There are many stress determination methods, usually grouped as destructive and non-destructive. X-Ray diffraction stress measurement can be an useful tool for failure analysis and also for process development studies. Quantifying the residual stresses present in a component, which may either accelerate or arrest fatigue or stress corrosion cracking, is frequently crucial to understanding the cause of failure [11-15].

In the present paper our attention will be focalized on the study of the behaviour of some laboratory samples made of H11 steel coated on the surface which can be used as die material for advanced squeeze casting process. The goal is to set up, for this purpose, the suitable powder to be used as coating material and the most appropriate deposition techniques to be adopted. Indication on the effect of the coating treatment on the substrate will be assessing by evaluating the residual stress of the substrate steel prior and after coating. Morphological analysis, evaluation of the adhesion of the coating layer to the substrate, the microhardness measurement and the surface roughness will complete the study.

2 Experimental material(s) and methods

H11 (0.3% C 1.1% Si, 0.3% Mn, 5.2% Cr, 1.2% Mo, 0.3% Ni, 0.01% Co, 0.1 Cu, 0.36% V, 0.017% P, 0.004%) as a special high-alloy tool steel, belonging to the hot-work chromium tool-steel group, has been coated with the aim of using it as die material for advanced squeeze casting process.

Four types of powders, provided by Sulzer Metco Company have been considered and HVOF and plasma spray (PS) methods have been employed for the deposition. All powders used for the coating have been dried in an electric furnace at 100°C for about 30 min, to avoid any internal humidity, while the steel substrate has been sandblasted with corundum sand and then has been cleaned with acetone previous to the treatment. Pressed-air has been used to cool the substrate.

Ni-based and WC-Co coatings have been developed by HVOF technique and finally both ceramic coatings have been realized by plasma spray method.

On the starting powders morphological and structural analysis have been carried out, while on the coated surfaces morphological and structural characterizations have been realized. Morphological observation and the adhesion between the substrate and the coating has been carried out by Optical Microscopy (OM, MeF4 Reichart-Jung) and by Scanning Electron Microscopy (SEM, Leo 1450VP). The distribution of the elements has been verified by Energy-dispersive X-ray Spectrometry (EDS, Oxford microprobe) and X-ray diffraction spectroscopy (X-ray, PANanalytical tool). Microhardness measurements have been performed on the transversal section of the polished samples using a Volpert DU01 tester. A force of 10 N (for the metallic powders) and 20 N (for the ceramic powders) has been applied for 15 s for both types of measurement and a minimum of 5 indentations were performed on each samples. Also the surface roughness of deposited protective coatings has been examined using stylus roughness tester (Hommelwerke T1000) and obtaining as a result Ra and Rz parameters. X-ray technique has been employed for phase identification and for residual stress measurements on the steel substrate before and after the deposition treatment.

Table 1 Chemical composition (% wt) of the powders employed for the coating

Type of coating used	Ni	Cr	Fe	Si	B	C	Co	W	ZrO_2	Y_2O_3	MgO
Ni-based	bal.	17.0	4.0	4.0	3.5	1.0	-	-	-	-	-
WC-Co	-	-	1.0	-	-	4.0	12.0	bal.	-	-	-
ZrO_2 - Y_2O_3	-	-	-	-	-	-	-	-	92.0	8.0	-
ZrO_2 - MgO	-	-	-	-	-	-	-	-	bal.	-	24.0

3 Results and discussion

3.1 Analysis of the used powders

Physical characteristics of the particles made up the powder (i.e. their size, shape, orientation, porosity, hardness, etc.) and other external factors (i.e. humidity of the surrounding environment) can influence the fluidity during the coating procedures. For these reasons, firstly, morphological analysis on the employed powders has been carried by SEM observation.

As shown in **Fig. 1a** the Ni-based powders are homogeneous and a well-embedded distribution of the particles has been observed. A spherical grain shape and a regular variation of the grains size can be evidenced (10÷40 μm).

As concern the ceramic particles and the WC-Co-based alloy a more complex polyhedral shape particles (Fig.1b, c, d) with a relatively homogeneous dispersion of the different parts made up the structure. As reveals the EDS analysis (**Fig. 2**) in addition to the expected elements the presence of Cr has been detected, even if this element could not be really present in all compositions (some contamination has been created due to the use of the same device for other deposition previously realized). The provided powders composition has been confirmed by X-ray analysis (**Fig. 3**).

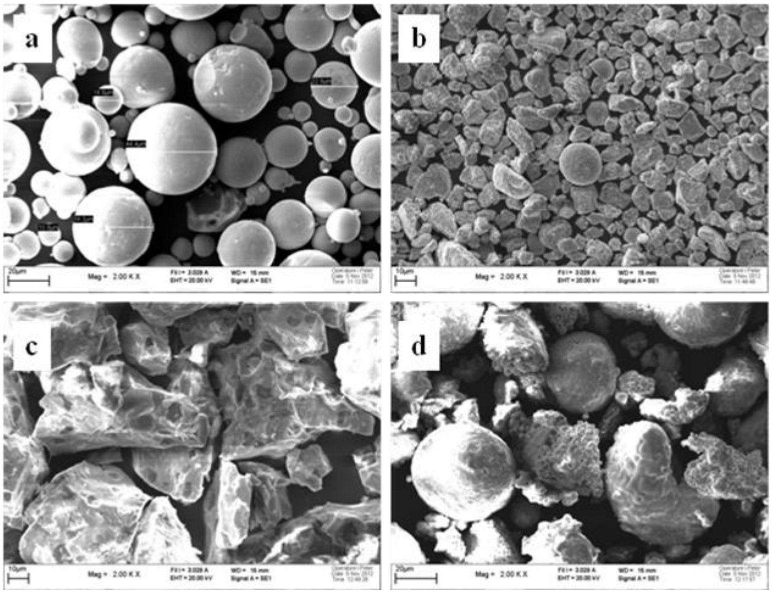


Fig. 1 SEM micrographs for the powders used for coating: a) Ni-based alloy, b) WC-Co-based alloy, c) ZrO_2 - MgO, d) ZrO_2 - Y_2O_3

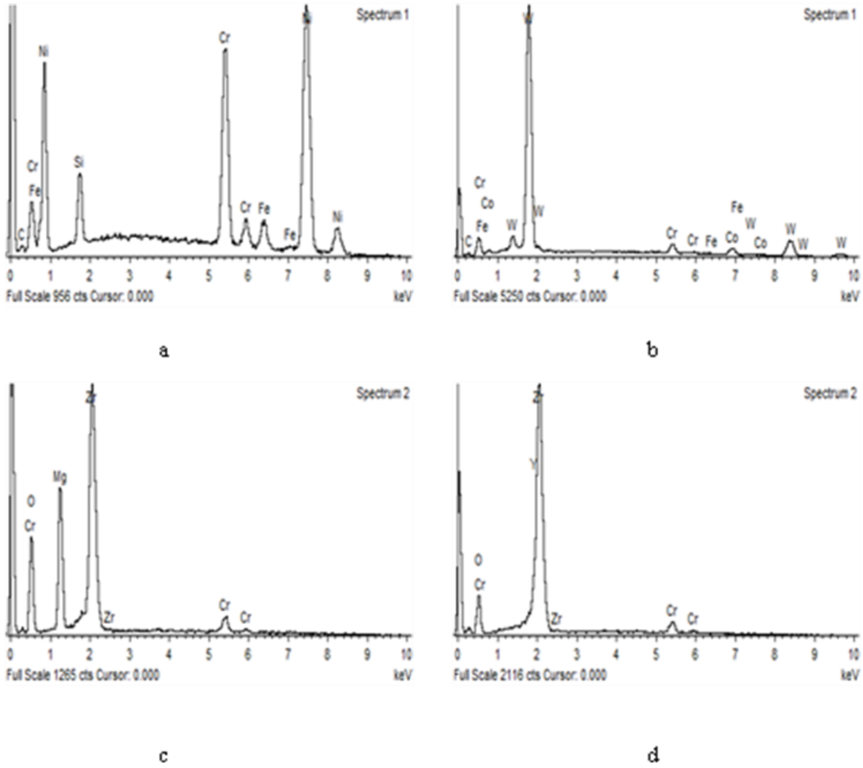


Fig. 2 EDS analysis results for the coating powders used: a) Ni-based alloy, b) WC-Co-based alloy, c) ZrO_2 - MgO, d) ZrO_2 - Y_2O_3

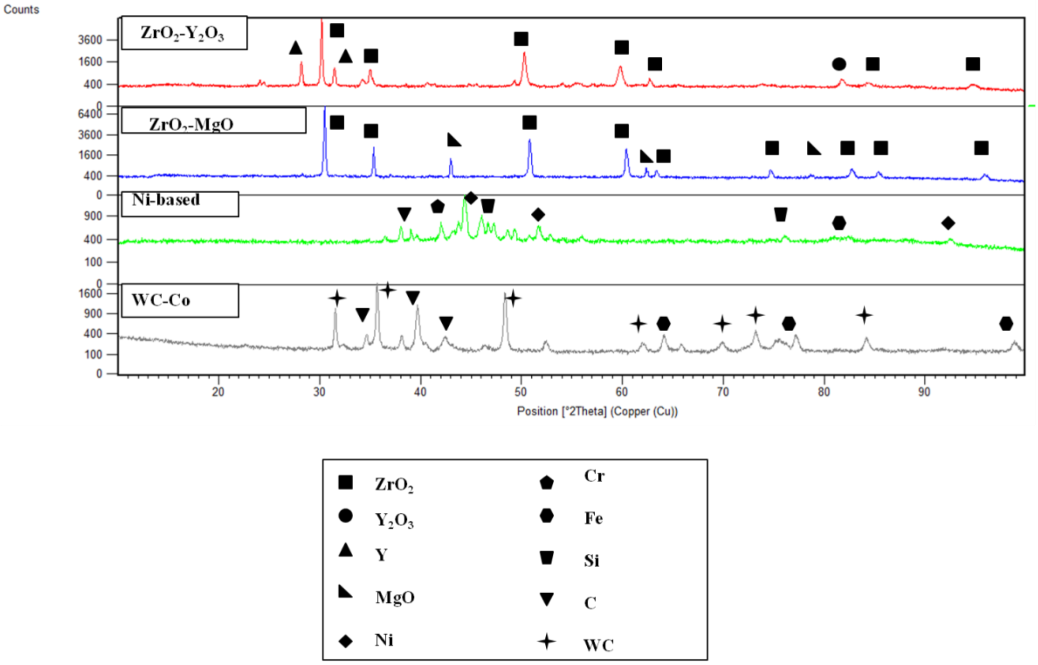


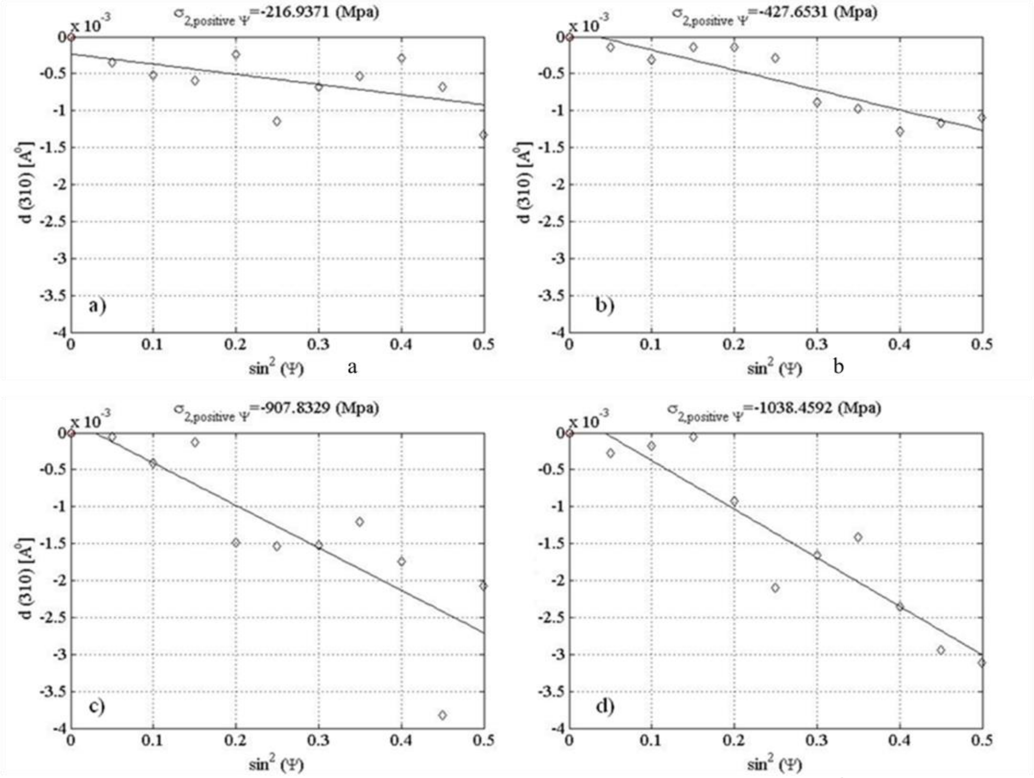
Fig. 3 X-ray diffraction patterns of the substrate steel material and powders employed for the coating

3.2 Residual stress measurements on the un-coated and coated substrate

Residual stresses can be defined as the strain which remain in the material in the absence of any external forces. In this paper X-ray techniques and a d sin2 ψ method (ψ being the tilt angle) has been applied on the (3 1 0) diffraction plane of H11 substrate prior and after coating, for ψ ranging from 0 to 45°. Comparison between the different conditions has been performed by evaluating the stresses measured in the un-stressed steel, HVOF and plasma coated materials.

The diffraction angle, 2θ, is measured experimentally and then the lattice spacing (d) is calculated from the diffraction angle and the known X-ray wavelength (λ) using Bragg's Law ($n\lambda = 2d\sin\theta$, where n=1, 2, 3…). If residual stresses are present inside the material, the d spacing will be different compared to the un-stressed state. The difference is proportional to the level of the residual stress. Once the d-spacing values are identified, they can be plotted versus sin2 ψ. The plot of d vs. sin2 ψ is a straight line which slope is proportional to the stress present in the analysed steel material.

The most common problems in using X-ray measurements arise due to the location of the diffraction peak. For peak fitting scope, a high precision is indispensable. For this reason a correct sample alignment and precise methods of diffraction sign location has been involved. Unfortunately, many parameters can contribute to the introduction of errors in the measurements and consequently in the data acquisition. Some of them are related to the collection time, the number of ψ angle used for the analysis, the position of the peak, etc. In this paper the analysis has been performed on the cross section of the samples after consecutive elimination of the coated layer from the substrate by polishing procedures (operated very carefully in order to avoid further mechanical solicitation). The preparation procedure has an influence on the values of the residual stress. As reveals **Fig. 4** for all samples analysed a quite linear dependence of d vs. sin2 ψ has been obtained. The presence of a compressive stresses has been identified for all samples, which change progressively toward higher values moving from the un-coated condition to the coated samples. Generally, the presence of a compressive residual stresses increases both the fatigue strength and the resistance to some undesirable phenomenon (i.e. stress-corrosion cracking). The presence of the residual stress in the un-coated steel is probably originated from the manufacturing process, the successive industrial steps and also from the laboratory preparation route. The high temperatures involved in plasma spray process determine the appearance of residual stresses inside both the protective coating and the substrate: during cooling (solidification) the particles that make contact with the surface are subjected to a contraction and as a consequence can cause the appearance of residual tensile stresses within the protective coating and compressive residual stresses within the substrate (Figure 4c-d). In correspondence to a maximum thickness, when the total tensile stress exceeds the adhesion force at the interface between the coating and the substrate, cracking of coating layer takes place.



c d

Fig. 4 Linear dipendence of d (3 1 0) upon sin^2 *ψ* for H11 steel prior and following deposition: a) H11 substrate without coating, b) H11 substrate following HVOF treatment, c) and d) H11 substrate following plasma treatments

During the deposition techniques such as HVOF or cold spray characterized by a high kinetic energy and a limited thermal energy the tensile residual stresses inside the coating can be reduced. In fact the particles that arrive on the samples with high velocity generate compressive residual stresses and operate in opposition to the tensile stresses caused by the solidification. As a result of this the compressive residual stresses measured in the substrate following by HVOF results to be lower than those detected in the same substrate following by plasma spray deposition technique (Figs. 4b-c-d). However, the magnitude of the residual stress created in the plasma treated samples are comparable.

An annealing treatment, prior to the deposition process, should be one way to reduce the internal stress in the starting material.

3.3 Characterization of the coated layers

On the polished section of each samples SEM observation has been carried out to detect the quality of the coating layers. The morphology, thickness and the adhesion has been monitored.

Observing **Fig. 5** is possible to note that the thickness of the deposited layers are different: the highest thickness (about 800 μm), even more porous, has been developed using ZrO2 - MgO powders. For the Ni-based coating and ZrO2 - Y2O3 type coating the thickness corresponds to about 200 μm and finally the thickness of WC-Co-based coating is about 130 μm.

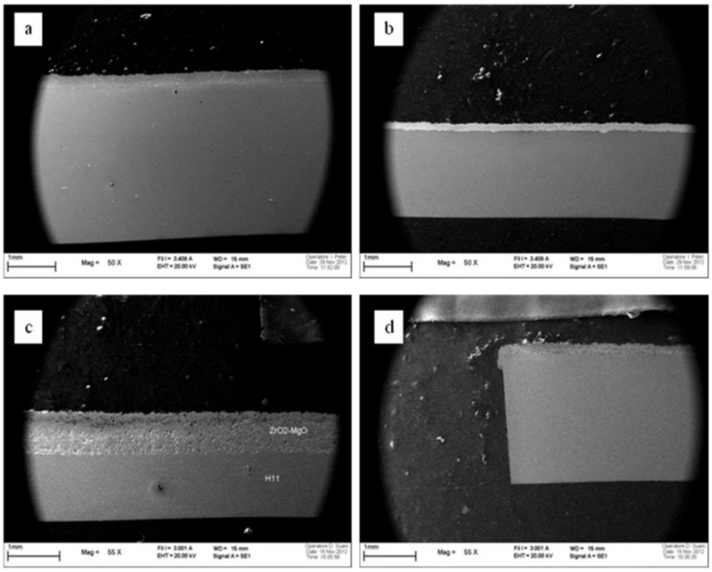


Fig. 5 SEM micrographs showing a general view of the coated layers: a) Ni-based alloy, b) WC-Co-based alloy, c) ZrO_2 - MgO, d) ZrO_2 - Y_2O_3

The SEM micrographs of the samples reported in **Fig. 6** allow evidencing the differences, in terms of morphology and adhesion to the substrate, between the metallic and the ceramic protective coatings. Employing Ni-based alloy and WC-Co-based alloy powders (Fig.6a and b) a more compact deposition has been obtained, compared to the ceramic layers (Fig. 6c and d) partially due to the higher velocity employed in the HVOF thermal spray method. Moreover thank to the higher velocity both the two metallic coatings show a superior adhesion characteristics compared to the ceramic coatings where some discontinuities has been observed at the interface region. The presence of some porosity in the deposited ceramic layers, caused by the collision of the particles on the substrate at lower velocity compared to HVOF process, can represent an important limitation in terms of resistant to heat cycling: the molten aluminum can penetrate through these pores and can react with the iron reducing service life of the die. However, using a very high temperature in the case of plasma spray method the eventually difficulty arising from the dissimilarity of the particles size and shape can be reduced.

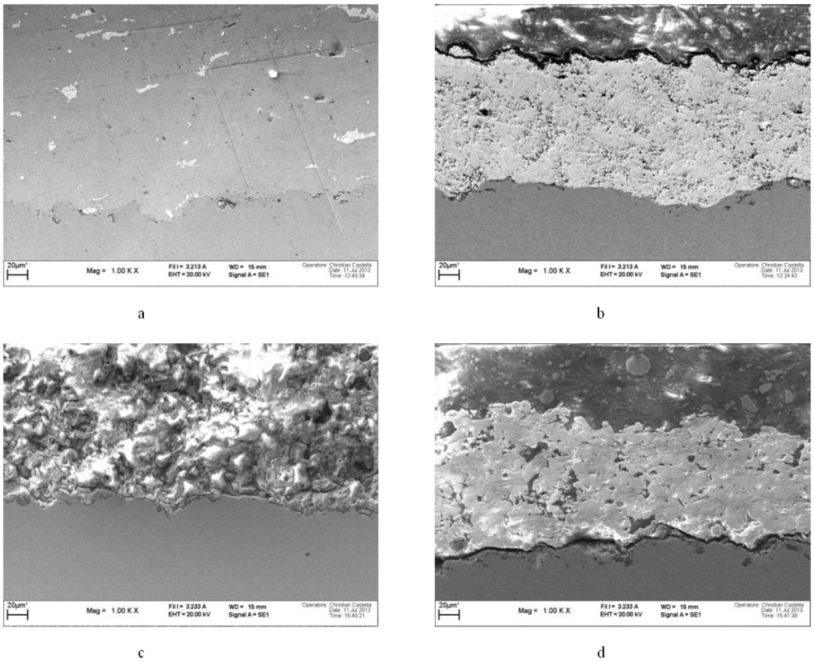


Fig. 6 SEM micrographs of the coated layers:a) Ni-based alloy, b) WC-Co-based alloy, c) ZrO_2 - MgO, d) ZrO_2 - Y_2O_3

The microhardness of the coating has been measured and the results have been reported in **Fig.7**.

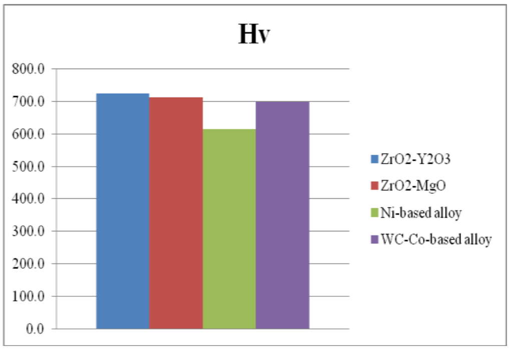


Fig. 7 Vickers hardness of the deposited protective coating

As illustrated in figure the hardness of the ceramic layers and WC-Co-based coating layer reveals a comparable behaviour (for the first cases a hardness value is just a little bit higher than 700 HV). However, as a result of the porous nature of the ceramic layer the hardness measurements became more difficult for these samples in particular for accurate results more measurmenets vave been realized. As expected, the presence of the hard WC particles amplifies the hardness compared to the samples coated with Ni-based alloy, (HV≈ 600) even if the same deposition procedures have been adopted. Roughness measurement has been carried out since this parameter can determine the surface quality of the components. In the case of roughness which is situated as much as possible near to the final required roughness allows to reduce the machining operations after the casting (as a consequence reducing the production cost and can decrease the risk to induce residual stress inside the components). The obtained results are reported in **Fig. 8**. The metallic and the cermet coatings (WC-Co) reveal lower roughness compared to the ceramic coatings in terms of both Rz and Ra parameters, due to the high impact velocity of the particles in the HVOF process.

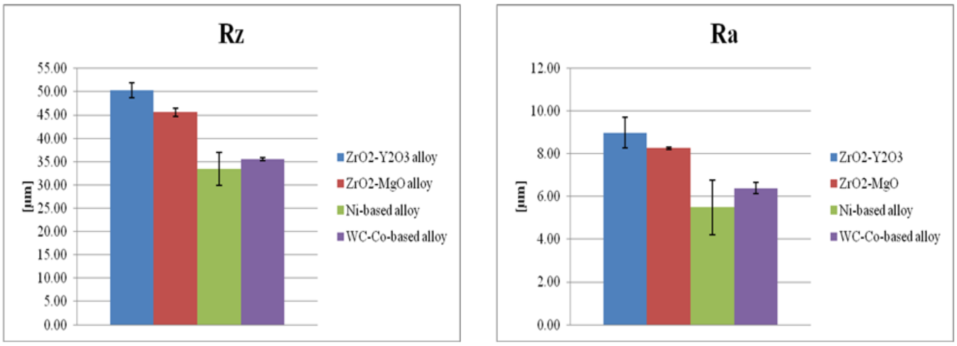


Fig. 8 Surface roughness parameters R_z and R_a of the four protective coatings

4 Conclusions

In the present paper some conditions, as concern the materials used and the more appropriate deposition techniques, were identified in order to obtain higher quality dies usable in the innovative squeeze casting and/or some related modified processes.

The presence of a compressive residual stresses was established for all materials and the obtained values results to be higher in the coated samples. Caution has to be paid to reduce the presence of the residual stress in the un-coated steel deriving from the manufacturing process and from the laboratory preparation route. This condition gives an additional benefit.

On the basis of this study regarding the employed powders for the deposition, WC-Co-based and Ni-based alloy powders results to be more suitable compared to the ceramic powders. Contrarily, as concern the deposition technique, due to the lower temperature and the big velocity employed, HVOF technique seem to be the more appropriate method with respect to plasma deposition technique because permitted to realize dense coatings with a good adhesion with the substrate. Further research should investigate the wear and the corrosion resistance of the coating, directly on some real part.

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