Fracture toughness of different PVD coatings

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Abstract

Indentation technique was used to characterize the mechanical properties (elastic modulus, hardness and toughness) both of PVD coatings and autocatalitic chemical deposition ones. TiN and TiCN films were respectively deposited on a duplex stainless steel substrate using PVD technique; moreover a NiP films (P content about 8%) and a NiP/B_4C composite ones were used as comparison materials. The effect of different substrate surface finishing (polishing and shot peening) was evaluated.

1 Introduction

Nowadays several treatments of the surface and near-surface are available and therefore the designer, in function of the final properties of the component, can select among different processes all similar as final purpose: modifying the surface to increase the required in-service properties.
The choice of the proper surface technology enables the production of coatings having different chemical composition and/or microstructure appearance, thickness, hardness, adhesion with the substrate material, etc.
Even if one limits the investigation to the thin films a high versatility can be reported both for the types of technology used (chemical vapor deposition-CVD, physical vapor deposition PVD, and electrochemical deposition processes) and for the nature of the deposed coating, different in the chemical composition and for the presence of single or multi-layered films. Therefore, the difference in deposition surface treatments can be considered responsible for the variety in the mechanical and physical properties characterizing the industrial thin coatings today available [1-5].

In order to select the surface finishing method it is necessary to take in account the bulk material, the applied stress during the service life of the treated components and the type of the environmental in which the coated part has be used. Therefore it is not satisfactory to know the coating thickness and its microhardness, but it is essential the collection of data regarding porosity, roughness, adhesion with the bulk, and, if it is possible, residual stress and toughness. In particular the residual stress field consists of a combination of two components: intrinsic stresses and thermal stresses. The intrinsic stresses originate from the growth process as a result of in-growth defects and structural mismatch between the substrate and the coating lattices. The thermal stress es originates from the difference in the thermal expansion coefficients of the coating and the substrate lattices. Hence, any fluctuation in the deposition temperature or cooling rate during the coating process will cause changes in the thermal induced stresses of the system and therefore affect the effective load capability of the coated part. For a good working of the component during its service life, it is essential to avoid reaching the critical load intending with critical load the load that enables the nucleation of cracks inside the coating. Different values of the thermal expansion coefficients of the coating and the bulk material are in fact responsible for high stresses generated in the coating after cooling to room temperature. The presence of steep gradient in the tensile stresses inside the coating thickness often leads to the nucleation and growth of cracks and, therefore, to a bad in-service condition responsible for short term life of the coated component due to the possibility of the environmental of using cracks as a damage preferential way of the substrate material, or, in the presence of wear conditions, of promoting the detach of small amounts of hard film working as abrasive particles. Furthermore the presence of surface residual tensile stresses is responsible for stress-corrosion cracking in several corrosive environments and can promote crack initiation under cycling loads causing a reduction in the fatigue strength of the coated component [6]. besides the coating adhesion depends on the surface and interface properties of the substrate, and, therefore, on the residual stresses distribution [7]. Mechanical pre-treatments like shot peening or micro blasting affect the bulk residual stress state and, in the case of thin films, can influence not only the adhesion with the substrate but also the toughness of the coating.

The analysis of fracture mechanics behavior of thin films is therefore of great importance in order to improve the coating serviceability. However it is difficult to curry out the fracture mechanics characterization of different thin films, in fact the traditional tests based on the fracture mechanics approach, K_{Ic}, are not suitable for the determination of the toughness behavior of a thin film, and, therefore, tailored techniques able to distinguish the toughness of the coating from the toughness of the substrate material, have to be used. Some of these methods can be found in the literature: nanoindentation techniques [8-9] and three-point bending tests plus in situ microtensile tests [3] are some of the proposed experimental approaches.

Starting from these concepts, the effects of bulk preparation and deposition surface treatments, including physical vapor deposition and autocatalitic

chemical deposition processes, on the mechanical properties (microhardness, stiffness and toughness) of the thin films were evaluated in this paper. Independently from the type of coating a stainless steel plate was used as substrate. The choice of such a material is related to applications where wear and corrosion resistance properties are fundamental, the first due to the hardness of the coating, the second demanded not only to the high Chromium alloyed steel but mainly to the thin surface deposed film (typical is the case of control valves electroless nickel plated in chemical and petroleum plants).

2 Experimental procedures

Four coatings, different in terms of applied coating technology (PVD and autocatalic chemical deposition) were deposited on a SAF 2205 duplex stainless steel 11mm thick plate. Four different surface finishing conditions of the substrate were considered: hot-rolled status and solution annealed at 1050°C (henceforward denoted by TQ sample), polishing with diamond paste (named L), shot peening carried out with glass beats (henceforward denoted by P), and shot peening plus polishing respectively (henceforward denoted by P+L).
In order to investigate the effect of the chemical composition of the coating both TiN and TiCN-films obtained by using an arc evaporation technique were tested. Furthermore a NiP (P content about 8%) coating obtained from the autocatalytic chemical deposition (ACD) bath and a NiP/B_4C composite film with 25% volumetric fraction of ceramic dispersoid plated according to an industrial process described in [10] were used as comparison materials.
All the tested coatings are commercial ones, in the sense that industrial coating plants were used to produce them and therefore the thickness of the coatings depends on the practical production needs.
Roughness, hardness and surface residual stresses were measured on the substrate bulk material in the four finishing conditions, while all the coatings investigated were characterized in terms of roughness, hardness and elastic modulus. The residual stress field of the coated samples was not measured because the depth of the PVD coating is too small with respect to the thickness of the XRD spectrum.
Both bulk and coated samples microhardness were measured on by means of a Vickers indenter coupled with a MeF3 microscope under an applied load of 0.1N for 10s, Young's modulus was calculated by measuring the penetration depth decrease during unloading.
Chemical composition and surface morphology, as well as coating thickness, were evaluated by using a Scanning Electron Microscopy (SEM) equipped with a disperse probe (EDS). Analysis both on the surface and along the cross section of the coatings were performed, in the last condition a sample of each coating was sawed up to 2mm of residual ligament left and then was broken by an impact load in order to obtain a fracture surface used to measure the thickness of the coating.
Crystallographic structure was examined using the X-Ray Diffraction (XRD) method with a Philips PW 1830, PW 3020 automatic diffractometer with Cu Kα target in a Bragg configuration.

X-ray stress measurements carried out by a XRD diffractometer were also executed. Cu Kα radiation was used with a 2mm point collimator; the working parameters assured a penetration depth of 0,01mm.
Surface roughness both of the bulk material in the different surface conditions and of the coated samples was evaluated by using a laser profilometer.
The toughness of the coatings was evaluated by using the Palmquist indentation crack analyses originally proposed for ceramics [11] and recently applied to NiP coating [12], nitride steels [13] and WC-Co cermets [14].Vickers hardness indentations with an applied load ranging from 1N to 600N were performed on sample surfaces without any mechanical polishing to roughness reduce. Crack lengths at the corners of the Vickers hardness indentation were measured by SEM and the relationship $K_{Ic} = \alpha\ (E/H)^{1/2}(P/c^{3/2})$ [1] where α is a constant dependent on the indenter geometry, E the Young's modulus, H the coating hardness, P the load applied on the indenter, and c the crack length, was used to evaluate the coating toughness.

3 Results and discussion

3.1 Bulk material

The SAF 2205 duplex stainless steel used as substrate material was characterized in previous papers [15-16] in terms of fracture mechanics behavior, microstructure and phases microhardness. The bulk microhardness and roughness data are shown as reference values in figures 1 and 2 respectively.

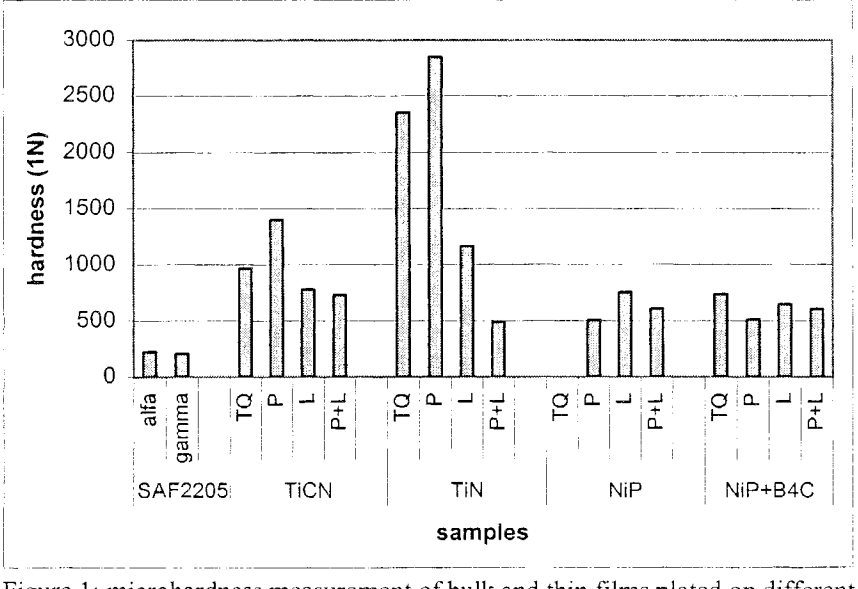

Figure 1: microhardness measurement of bulk and thin films plated on different finishing surface conditions

Residual stresses evaluated in the rolling condition as well as after shot peening show a strong difference between alfa and gamma phases. In particular the austenite in the solution annealed condition shows tensile residual stresses both in the longitudinal (+38MPa) and transverse (+83MPa) direction, while after shot peening a soft compressive residual stress field (-38MPa longitudinal; -134MPa transverse one) was observed. Compressive stresses were found in the ferrite phase independently from the surface finishing; although after shot peening an increase in the compression absolute value was detected (-669 MPa longitudinal; -660 MPa transverse direction).

3.2 Coatings behaviour

Samples chemical composition was investigated by means of EDS in order to find out the presence of elements due to coating impurities such as embedded particles or

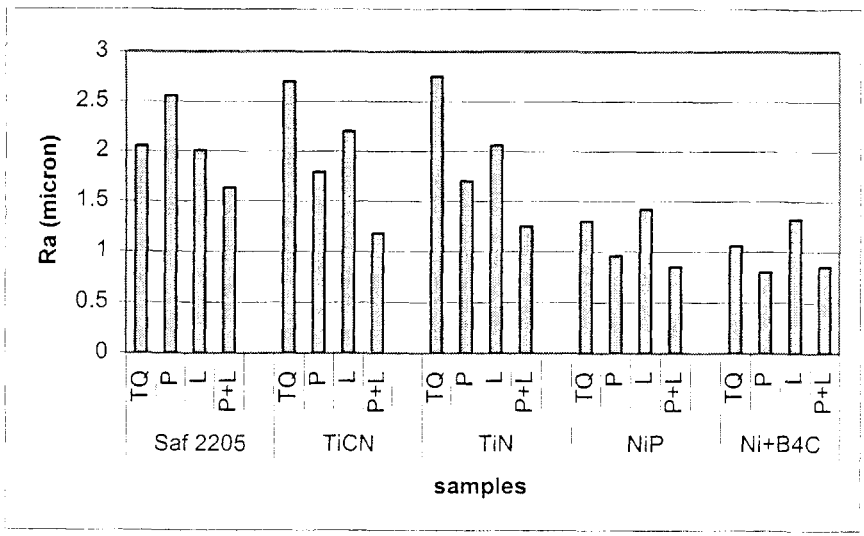

Figure 2: roughness measurement of bulk and thin film plated on different finishing surface conditions

particulate contamination. No evidence of such chemical contaminants was found with respect to the nominal composition.

The crystalline structure was analysed by XRD patterns for all coatings in the polishing (L) and shot peening (P) surface condition. A preferred orientation (PO) [111] stronger in the L case than in the P one, was detected in the TIN coating, as reported in literature for spattered ion plated [2].

NiP coating shows a typical X-ray amorphous metastable structure [17] with an amorphous phase of about 93% that decrease up to 82% when B_4C was added to the electrodeposition bath.

The microstructure of the different coating samples is shown in figures 3-4 both for the surface and for the cross section.

Samples thickness is in the range 1,5 - 2 μm for PVD specimens, while the ACD ones are thicker being 65μm in the NiP/B_4C case and 150 μm for the NiP one.
In the TiCN PVD coating a non homogeneous layer was detected; several surface droplets can be observed on the layer surface (figure 3). These inhomogeneities strongly affect the mechanical properties of the coating; this fact can be evidenced trough the analysis of the hardness values characterizing the PVD coating that are lower than the one that can be found in the literature [2].

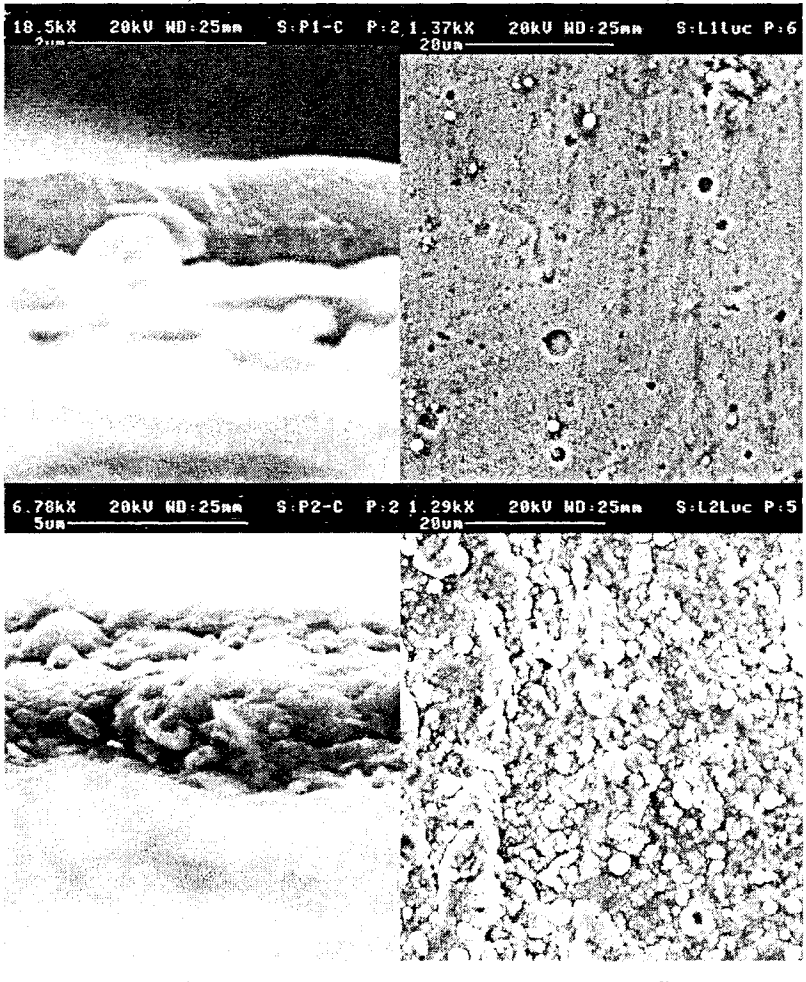

Figure 3: TiN coating: a) cross section, b) surface morphology; TiCN coating: c) cross section, and d) surface morphology.

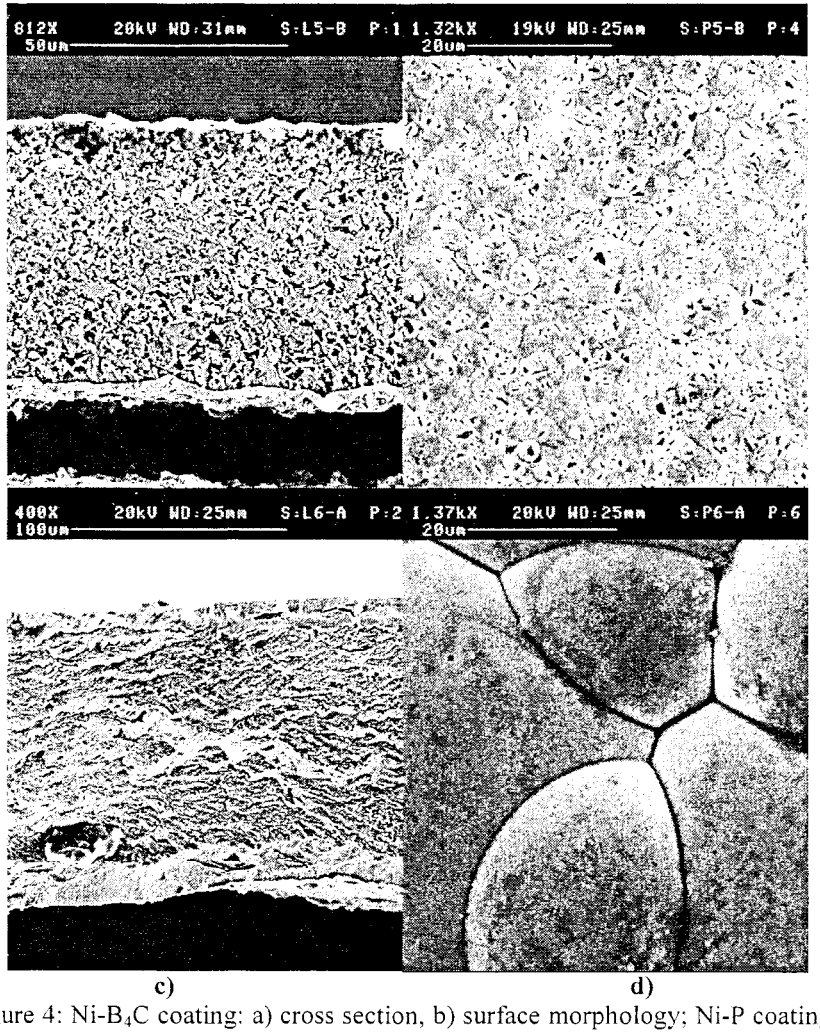

Figure 4: Ni-B_4C coating: a) cross section, b) surface morphology; Ni-P coating: c) cross section, and d) surface morphology.

All the ACD coatings have a continuous and homogeneous layer that was found to be detached from the substrate after impact test in liquid N_2 showing a worst adhesion than that obtained from the tested PVD coatings.

The different bulk finishing processes affects not only the roughness of the steel plate, but, also, the roughness of the PVD coatings too. In fact using as substrate shot peened samples the coating surface shows a decrease in the roughness with respect to the coating deposed on TQ samples.

The higher thickness of the ACD coatings excludes the bulk finishing effect, while it is responsible for a smoother surface morphology. The low hardness of steel bulk material is the cause of the increase of the roughness measured after

shot peening. The increase in the hardness in the shot peening and PVD conditions is related to the surface compressive stress field due to the cold working process, compressive stress field that affects the mechanical properties of the PVD coatings. The decrease in the hardness obtained in the PVD coated and polished samples is therefore an evidence of the absence of compressive surface stresses due to the polishing technique.
Young's modulus data obtained from the indentation measurements are summarized in figure 5. The elastic modulus is affected by the surface finishing only in the case of PVD coatings, while no effect associated to the surface finishing can be reported in the case of ACD coatings.

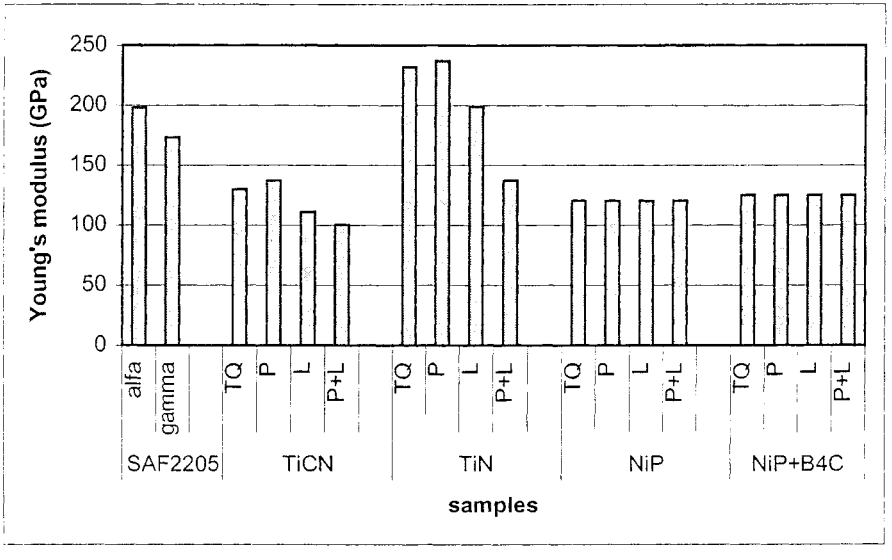

Figure 5: Young's modulus of bulk and thin film plated on different finishing surface conditions

In Table I the data regarding the coating toughness obtained as estimate from the measurement of the crack length emanating from the microhardness indentations are shown.

Table 1: K_{cr}= critical stress intensity factor characterizing the coating fracture toughness.

Finishing condition	TiN coating	NiP-B_4C coating
TQ	K^*_{cr}= 5,2 MPa$\sqrt{m}$	K_{cr}= 5,5 MPa$\sqrt{m}$
P	K_{cr}= 8,8 MPa$\sqrt{m}$	K_{cr}= 5,3 MPa$\sqrt{m}$
L	K_{cr}= 7,3MPa$\sqrt{m}$	K_{cr}= 5,8 MPa$\sqrt{m}$
P+L	K_{cr}= 7,4 MPa$\sqrt{m}$	K_{cr}= 5,0 MPa$\sqrt{m}$

In the table I the toughness data regard only two coatings because of for the TiCN coating it was impossible to measure the cracks emanating from the corners of the indenter. For all the applied load tested multi cracks were always detected and some of them nucleated away from the indenter corners. A complete different situation was detected for the NiP coating that, in the presence of low and medium applied load levels (< 150 N) does not show cracks, while for higher applied loads shows excessive penetration.

The experimental results obtained by using the indenter methodology show an increase in the toughness in the presence of thin films (TiN coating) due to the shot peening treatment. This result can be interpreted partially with the presence of a compressive surface stress field indirectly valuable by the hardness data and partially by the smooth surface that, in presence of low applied load, can be considered a further parameter able to delay the crack nucleation. The decrease in the hardness values measured in case of polishing and shot peening plus polishing, changes probably due to a partial relaxation of the compressive stresses induced by the polishing process. This can be considered the main reason for the decrease of measured facture toughness. No significant effect of the mechanical pre-treatment of the bulk material can be reported, and the data are consistent with the value of hardness and of roughness that, for the Ni-B_4C coatings are independent from the surface morphology of the bulk material.

Conclusions

The need of increase the expected in-service properties of thin films in applications where fatigue, stress corrosion or wear and corrosion resistance are required suggests tailored characterization of the coatings not only based on microhardness and thickness data.

Nanoindentation has proved to be a reliable tool of assessing the hardness and elastic modulus of thin films, while indentation tests can be used to measure, in a simple but quite reliable way, the fracture toughness of the coatings. This tool is useful also in the presence of films, like the ones investigated in the present work, having a quite rough morphology induced by a shot peening or a mechanical polishing pre-treatment of the substrate. The analysis of the fracture properties obtained by the measure of the cracks length produced at the corners of the indenter is however possible only under specified conditions. The thin film should be sufficiently compact (for low values of applied load no multiple cracks should be obtained) and the deposed surface layer should have a brittle behaviour; the presence of such conditions enable the nucleation of only radial cracks emanating from the corner of the indentation.

The indentation technique was used to evaluate the fracture toughness behaviour of a TiN PVD coatings and a NiP-B_4C composite films obtained from the autocatalytic chemical deposition process, while in the case of TiCN PVD coatings or NiP films the indentation technique was not a suitable approach because of the impossibility to point out radial cracks by means of load-indentation tests. The shot peened samples coated with a TiN PVD film (2 μm depth) showed an increase in the toughness due to the presence of compressive residual stress field induced by the mechanical pre-treatment of the substrate. Shot peening does not affect the toughness in the case of NiP-B_4C coatings

65μm depth. Further analyses on the residual stress distribution in thin coatings are therefore of great interest to better interpret the toughness data.

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