

## Microstructural Control of Co-based PTA Coatings

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Cobalt-based alloys are widely used as hardfacing materials when wear resistance is required at room temperature or high temperature applications. However, their performance is a consequence of their microstructures that depends on the processing conditions. This work focused on the influence of solidification rate on the structure development by processing the alloys with and without the interference of the substrate. The coatings were characterized by scanning electron microscopy, energy dispersive spectrometer, optical microscopy and instrument indentation tests. Results showed that despite the same phases developed in tested conditions, differences in the solidification microstructure and the influence of Fe diffusing from the substrate accounted for the measured variation in hardness. Higher hardness values were obtained for the samples processed free-standing (mini billets) with respect to the coatings and they were independent of the processing parameters, indicating that the substrate compromise the properties of hardness, as expected.

**Keywords:** cobalt-based alloys, high temperature, sliding wear

### 1. Introduction

Hardfacing refers to processing procedures used to process hard coatings by a welding technique. Cobalt-based alloys are frequently used for high temperature application and known by their high resistance to wear and corrosion under severe conditions<sup>7</sup>. Cobalt-based coatings processed by Plasma Transferred Arc (PTA) are frequently referred for good surface finish, high hardness at elevated temperature, low dilution and excellent corrosion resistance<sup>5</sup>.

A typical solidification structure is observed with dendrites of a Co-rich matrix and a carbide interdendritic region<sup>2</sup>. The characteristics of these coatings are determined by the solidification kinetics and dilution with the substrate. However, chemical composition changes imposed by dilution may play an important role in the degradation of mechanical properties.

To better understand the performance of cobalt-based coatings a different approach to analyze PTA coatings was carried out. Two atomized Co-based alloys (CoCrWC - Stellite #1 and #6) were processed with the same parameters by Plasma Transferred Arc on a steel substrate and a chilled Cu mold. The relation between coating features and properties was analyzed for the effect of the solidification rate imposed by the processing parameters on the microstructure, Iron content, elastic modulus and hardness of Co-based alloys.

### 2. Experimental

#### 2.1. Material and methods

The atomized commercial Cobalt-based alloys Stellite#1 and Stellite#6 were used in this study. Their nominal composition are listed: Stellite#1: 2.45 C, 31% Cr, 13% W, 2.5% Fe, 3% Ni, 1% Mn, 1% Si, Co(bal) and Stellite#6: 1.2 C, 28% Cr, 4.5% W, 3% Fe, 3% Ni, 1% Mn, 1.1% Si, Co(bal). Both alloys were processed by PTA technique, in two different conditions: a coating processed on a carbon steel AISI 1020 plate (100 mm × 100 mm × 10 mm) and a mini cast billet processed on a cavity of a chilled cooper mold (free-standing).

The substrate of carbon steel plate was selected due to its higher coefficient of thermal exchange. The water flow of chilled mold was kept constant in value of 600 L/h.

In order to impose different solidification rates, two different velocities deposition were selected: 50 mm/min and 150 mm/min. Other process parameters were kept constant, as related: Plasma gas: Ar 2 L/min; Shielding gas: Ar 15 L/min; Feeding gas: Ar L/min; Current intensity: 120 A; Distance torch work-piece: 100 mm; Rate Feeding: Volume constant.

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2.2. Characterization

Mechanical features were evaluated by measurement of *E* (Young’s modulus), and Vickers (0.3) by microhardness instrumented tests of transversal sectional of coatings and free-standing specimens in three different regions: a) next to fusion line for coatings and next to interface between cooper mold wall and the mini billets, b) center and c) top of coatings and mini billets.

The specimens were etched electrolycally in oxalic acid (3 V by 1 second) for coatings samples and in solution of reagent 100 mL distilled water + 10 mL HCl 32% + 10 g CrO3 (1,5 V by 1 second) fo mini billets. Microstructure of each related regions and conditions was analysed by laser confocal and Scanning Electron Microscopy (SEM).

The dilution effect was analyzed evaluating the iron content of each region and condition described by energy dispersive eletrosopy (EDS) observation.

3. Results

One of the major differences between coatings and the mini-billets is the dilution with the substrate experienced by coatings which alters their composition. Within the elements that affect the properties of Co-based alloys the iron content has an important role and is known to reduce their hardness. Iron content measured in coatings and mini-billets is shown in Figure 1. It is observed that the iron content in the mini-billets agrees with the nominal composition of both alloys. However, iron content in coatings reached a much higher level confirming the incorporation of Fe from the substrate in to the coating. Also, a decreasing the iron profile from the fusion line to the external surface was measured.

Analysis of the microstructure as observed in the transverse cross section of coatings and mini-billets is shown in Figure 2, respectively.

The effects of dilution can be observed as coatings processed with both alloys exhibit hypoeutectic structures

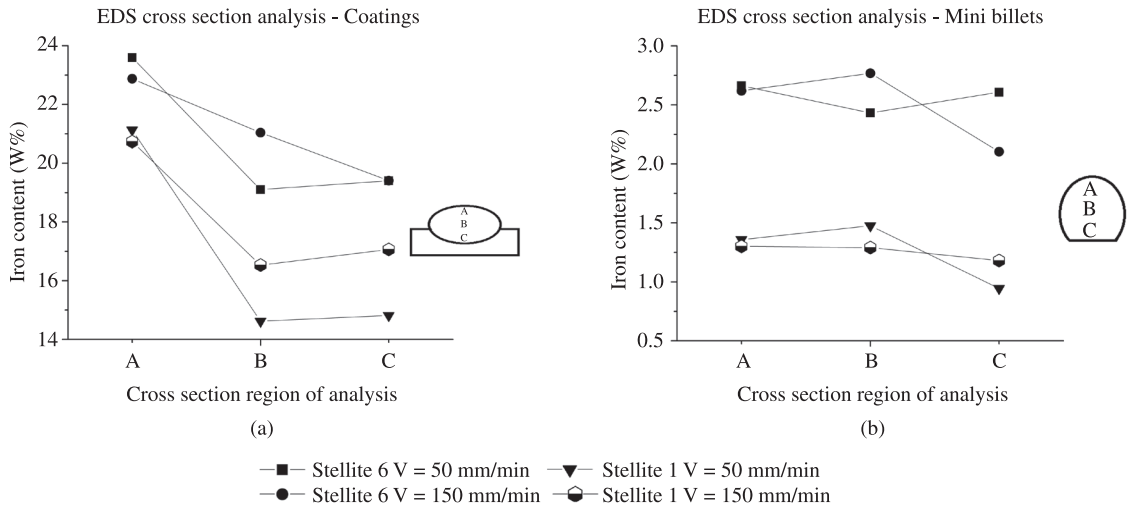


Figure 1. Iron content in the transverse section of coatings (a) and mini-billets (b).

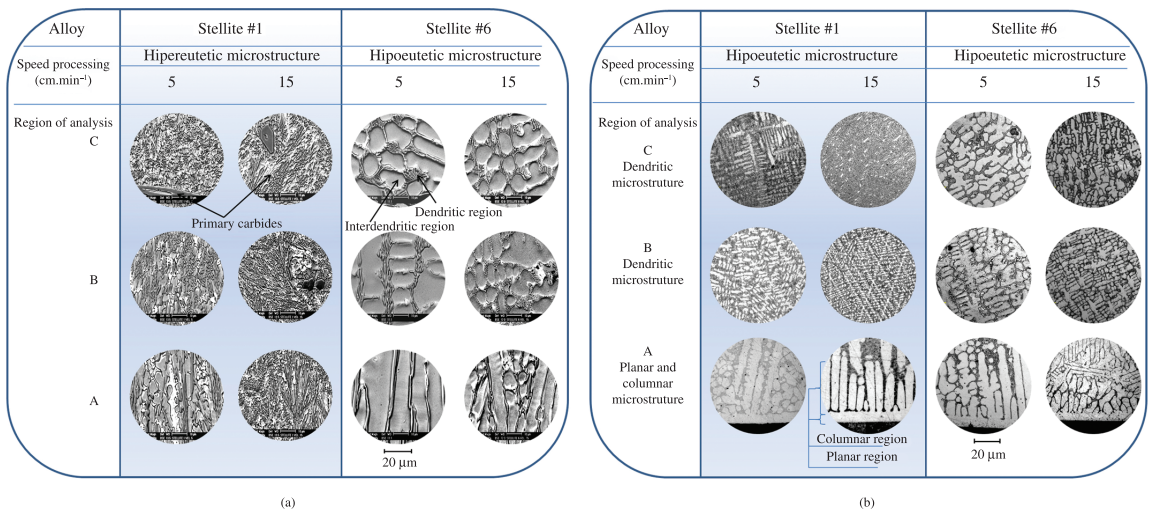


Figure 2. Microstructures relative to cross-section for coatings (a) and mini-billets (b) species.

with co rich dendrites and a interdendritic net of carbides whereas in mini-billets a hipereutectic structure with primary carbides was observed in the richer carbon Co alloy - Stellite 1 and hypoeutectic structure in the Stellite 6.

Differences were observed near the fusion line for coatings and in interface mould-mini-billets. In coatings as one moves away from the fusion line, a columnar structure follows the planar region which is replaced by a dendritic structure observed in the most of the area of coatings, in agreement with previous observed by Hidouci et al.<sup>6</sup>. It is also interesting to notice that finer hypoeutectic structures were formed in coatings. Processing parameters also influenced the formation of microstructures with the higher processing speed resulting in finer microstructures both in coatings and mini-billets. In Mini billets a hipereutectic matrix oriented parallel to heat flow with primary carbides was observed for Stellite 1 and a typically hipoeutectic corse

microstructure comprising columnar dendrites (region A of Figure 2a) followed by equiaxed dendrites (region B of Figure 2a) was observed for Stellite 6.

The effect of solidification kinetics and dilution can also be observed in the hardness (Figure 3) and elastic modulus (Figure 4) of coatings and mini-billets.

The effect of dilution can also be observed in the lower measured hardness of coatings compared to the mini-billets for each of the alloys processed. The effect of processing parameters is more significant on the hardness of coatings which showed a lower hardness for coatings processed with a slower processing speed.

Elastic modulus showed decreasing values from the faster solidification regions, near the fusion line and mold wall, to the center of samples. This trend is more significant in the mini billets also the effect of processing parameters is more significant in the mini-billets.

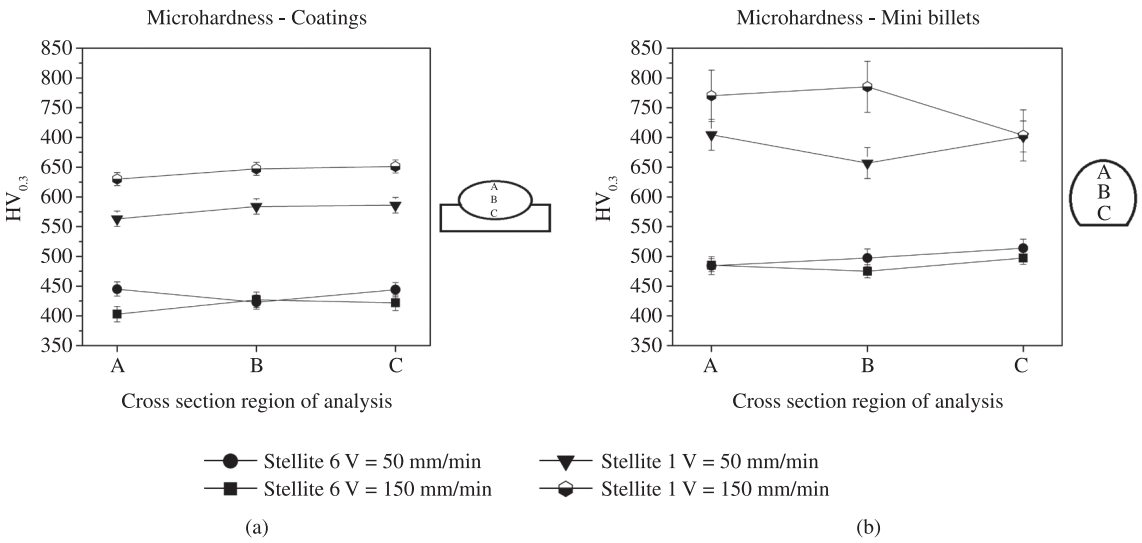


Figure 3. Microhardness of transverse section of coatings (a) and mini-billets (b).

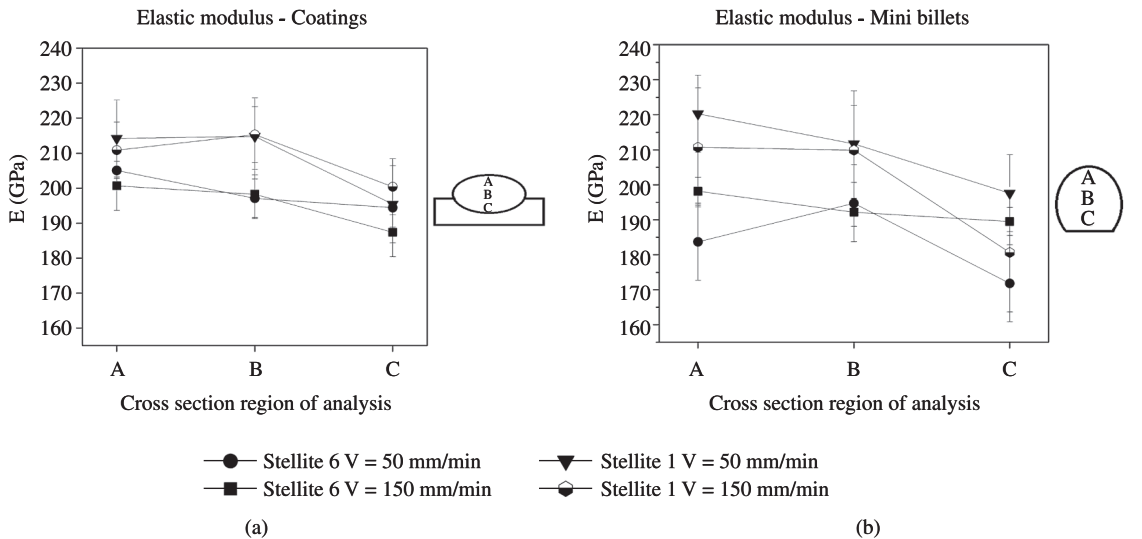


Figure 4. Elastic Modulus of transverse section of coatings (a) and mini-billets (b).

#### 4. Discussion

Stellite alloys primarily comprise the group of quaternary alloys of the complex system Co-Cr-W-C system.

The hypoeutectic microstructure involves primary Co-rich dendrites matrix of metastable fcc austenitic gamma phase and eutectic interdendritic consisting of pseudo-hexagonal close-packed (hcp)  $M_7C_3$  carbide and fcc gamma phase, as related by<sup>1-2</sup>. Hypereutectic microstructure consisted of hcp  $M_7C_3$  primary carbides and eutectic similar to that formed in the hypoeutectic microstructure.

The pseudo-binary phase cobalt-rich FCC and chromium-rich  $M_7C_3$  carbide phase refers to an eutectic transformation at 2.6% carbon content which is also displaced depending on the content of other elements such as the iron content and accounts for the observed variations in microstructures of the mini-billets and coatings. As with other hypoeutectic structures, Co-rich dendrites formed enriching the remaining liquid in elements with a poorer solubility in this solid solution accounting for the eutectic (carbides and Co solid solution) solidification in the interdendritic regions<sup>3</sup>.

The Stellite 6 alloy which has nominal composition of carbon of around 1.2% basically tends to produce a hypoeutectic microstructure. While the alloy high carbon Stellite 1 by agreement with the nominal content of 2.45% carbon can be regarded as a eutectic or near eutectic alloy in the quaternary system<sup>4</sup>. According to the literature this alloy has been described as exhibiting a hypereutectic structure and also a hypoeutectic structure<sup>7</sup>, depending on the conditions of processing<sup>4</sup>, treatment<sup>5</sup> and dilution<sup>1</sup>.

Changes in the balance of the elements during deposition of coatings, especially the levels of iron, plays a major role on final microstructure and mechanical features<sup>1,4,5</sup>. The increased iron levels from substrate can shift the eutectic point of pseudo-binary diagram phase to lower carbon compositions, so a hypoeutectic microstructure can form instead of a hypereutectic microstructure. The dilution of stellite alloys by iron diffusion from substrate causes increased toughness, reduced hardness and corrosion resistance in many corrosive environments<sup>1</sup>.

Although a significant variation in the iron content was measured in coatings it did not affect their elastic modulus as significantly as the solidification texture of the mini-billets. The influence of the solidification texture on the measured modulus in the mini-billets is also identified

following the change in processing parameters for both alloys. The lower processing speed resulted in a more significant reduction in the  $E$  of the mini-billets and in coatings.

Hardness measurements also show the effect of processing conditions with the coatings exhibiting lower hardness than the mini-billets, differences associated with the dilution of coatings. The higher hardness is expected to hypereutectic microstructures and is attributed to the formation of  $M_7C_3$  primary carbides. The lower hardness of the hypoeutectic microstructures is related to the presence of gamma phase in the primary dendrites and low concentrations of chromium and carbon<sup>6</sup>. Therefore, the hardness of hypoeutectic Stellite 6 alloy tends to be generally lower than Stellite 1 alloy due to the lower carbon and tungsten content and fraction of the reinforcement phase precipitated.

Higher processing speed resulted in higher hardness due to the faster solidification rates imposed that account for the finer microstructures observed. However, for both alloys the higher processing speed resulted in more significant variations in mini-billets samples indicating that processing has a decisive role since the iron content did not vary along the profile.

Higher processing speeds impose elevated rates of solidification and consequent greater microstructural refinement, due to the higher heat input supplied by the arc, reflecting, as expected, an increase of hardness. This trend was observed for both alloys but a Stellite 1 alloy was more sensitive to variations.

#### 5. Conclusion

Elastic modulus decreases from region of high (mold wall and fusion line) to low solidification rate.

Iron content varies through the cross section of coatings but is not altered in the cross section of billets.

Lower processing speeds resounded on higher hardness values, but the elastic modulus was not changed to the mini-coatings and billets.

Higher hardness values were observed for the free-standing (mini-billets) in respect of coatings, as expected, due to dilution of substrate. The dilution of coatings did not lead to any change in the Modulus of elasticity.

The properties of hardness of Stellite 1 were more sensitive to a change of speed of processing according to the microstructure hypereutectic observed.

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