**Microstructure and Wear Properties of CoCrMoSi alloy Coatings on AISI 316L**

**Wear performance as well as the low toughness of CoCrMoSi alloys is associated to the presence of Laves intermetallic phase. Alloying elements have been changed to reduce brittleness on newly cast alloys. This work evaluated coatings by plasma transferred arc (PTA) with different interaction with the AISI 316L steel substrate (dilution) thru the variation of processing current intensity. Coatings were deposited with 120, 150 and 180 A and characterized by light and scanning electron microscopy, X-ray diffraction and Vickers hardness. Wear behavior was assessed by pin-on-disc and ball-on-flat tests. Laves phase and Cobalt solid solution eutectic lamellar microstructure was observed for coating processed with 120A (18 % dilution). The chemical composition was displaced to hypoeutectic showing Cobalt solid solution dendrites and interdendrictic eutectic lamellar for coatings processed with higher current intensity, 150 and 180A, due to the higher interaction with the substrate (26 and 38 % dilution, respectively). Dilution increased linearly with the deposition current, inducing hardness decrease from 702 to 526 HV0.5. The wear mass loss rate increased up to 41.7 % as the chemical composition changed from eutectic to hypoeutectic. The friction coefficient (μ) ranged from 0.45 to 1.06 for eutectic and hypoeutectic microstructure, respectively. The interaction with the substrate dictated developed phases rate, determining the volume fraction of Laves phase and, as a consequence, coatings properties.**

**Keywords**: CoMoCrSi Alloy, Plasma Transferred Arc, Dilution, Microstructure, Wear Behavior.

**1. Introduction**

High performance coatings have been applied to protect components which operate under aggressive environments, aiming to reduce material cost and maintenance stops. Recent review on Plasma Transferred Arc (PTA) has pointed out the features that make the technique an attractive and competitive procedure (Ref 1).

Co-based alloys are utilized to increase life service of mechanical components, including valves and valve seats, bearings and bushings, sleeves, dies and punches. These alloys are applied for withstand wear in corrosive mediums because of their high corrosion resistance, meeting application in chemical, petrochemical and steelmaking facilities. Chromium acts as a solid solution strengthener, contributing to enhance corrosion resistance. However, service condition involving corrosion-wear phenomena is still a challenge. Corrosion-wear can cause surface material loss as a result of mechanical-chemical interaction and the produced wear debris will cause components life service reduction, like it can be observed on Hot-Dip Galvanizing bearings (Ref 2-4).

Co-based CoCrMoSi system has been shown better results operating under harsh environments. This alloy system exhibits hypereutectic composition composed by a primary Laves phase and a lamellar eutectic phase. The Laves intermetallic is a close-packed hexagonal (hcp) compound containing Co, Mo and Si, as Co3Mo2Si and/or CoMoSi stoichiometry (Ref 5).

Despite exhibitting better results for wear and corrosion-wear, CoCrMoSi alloy system has a limited ductility and toughness due to the hard intermetallic Laves phase fraction which can compromise processing. In order to increase alloys ductility and toughness , current intensity was varied from 120 to 180A to increase interaction with the substrate, promoting the decrease of proportional Silicon and Molybdenum contents reducing therefore the fraction of Laves brittle phase (Ref 6-8). As toughness improves, wear performance is expected to reduce.

This work studied CoCrMoSi alloy (Tribaloy T400) coatings by Plasma Transferred Arc evaluating dilution effect as an alternative to reduce the nature excessively brittle of coatings. The higher the dilution, the higher Iron, Chromium and Nickel contents proceeding from substrate. As a consequence, Silicon and Molybdenum contents will proportionally reduce and, therefore, the hard Laves phase fraction.

As processing parameters can alter significantly the chemical composition, understanding the interaction with the substrate is of great relevance on previewing coatings features and performance. Therefore, the aim of this work is to assess the relationship between dilution level and microstructure, hardness and wear behavior.

**2. Materials and Methods**

Atomized CoCrMoSi alloy (Tribaloy T400) with grain size ranging from 90to150 μm was Plasma Transferred Arc (PTA) deposited ,Table 1. The deposition of a 100 mm length single track on 12.5 mm thick AISI 316L stainless steel plate was carried out, Table 2. Track extremities were 20 mm discarded and characterization was performed in the middle of deposited layer.

Tribaloy T400 alloy exhibits hypereutectic chemical composition and the microstructure is composed by primary intermetallic Laves phase and lamellar eutectic. The Laves hexagonal close-packed (hcp) structure contains Co, Mo and Si, as a Co3Mo2Si and/or CoMoSi stoichiometry compound. The T400 alloy was designed with lower amount of Chromium and Silicon compared to T800. Laves Phase volume fraction may reach up to 50 % on the cast alloy and, as a consequence, higher ductility and toughness is reported (Ref 5, 7, 9).

Visual inspection was performed and no nondestructive technique on coatings surface was done to evaluate the presence of welding defects. Optical microscopy on the transverse cross section of the deposits was done. The track geometry was measured by light microscopy for reinforcement thickness (t), width (W) and wettability angle (Θ), Fig. 1. The interaction with the substrate (dilution) was determined on transverse cross-section by the ratio between melted area of the substrate and the total melted area.

The coatings were characterized in the as-deposited condition concerning microstructure description and volume fraction measurement was performed with Olympus Soft Imaging Solutions ® software. X-ray diffraction (XRD) analysis on coatings top surface was carried out with KαCu radiation from 20 to 120º and exposure channel of 1 s. Coatings hardness was measured on the transverse cross-section under 4.9 N load and results as an average of 10 measurements.

The effect of processing on wear performance was evaluated by abrasive sliding tests on pin-on-disc sliding apparatus. Samples slide against silicon carbide paper (#220) assembled on a 63 HRC hardness metal disc with an axial load of 4.9 N and tangential speed of 1.5 m/s. Pins with 4 x 4 mm were machined out of transverse section of deposited coatings. The wear behavior was measured thru the mass loss, weighing the samples before every test and after each 250 m sliding distance at room temperature. The friction coefficient was measured utilizing ball-on-flat sliding test against 6 mm diameter ZrO2 sphere with 4.9 N axial load, 150 m total distance and 20 mm/s maximum travel speed.

**3. Results and discussion**

**3.1. Soundness**

Coatings visual inspection revealed a smooth surface with no welding defects. Evidence of spatter, undercut, porosity or cracks was not found. This macroscopic evaluation is coherent with literature prediction that Tribaloy T400 has an improved weldability decorrent of the lower volume fraction of the Laves hard phase compared to Chromium and Silicon richer alloys (Ref 9). However, limited data is available relating Tribaloy T400 interaction with the substrate (dilution) and its effect on coatings chemical composition, microstructure and properties.

Differences on geometry due to current intensity variation were measured and are presented on table 3 and Fig. 1. Coatings processed as single track with 120 A exhibited the lowest wettability, confirmed by the highest wettability angle (Θ) and reinforcement thickness (t) and shallowest width compared to that processed with the higher current (180A), Table 3. As deposition current increases, dilution levels rise from 18 to 38 %, as a consequence of the higher temperature of the system (alloy and substrate). The higher interaction with the substrate induces coatings chemical composition variation (Ref 10, 11).

**3.2. Interaction with the substrate and Microstructure**

X-ray diffraction analysis showed that Cobalt solid solution (Co SS: FCC), CoMoSi / Co3Mo2Si Laves phase and Co2Mo3 / Co7Mo6 (Co-Mo intermetallics) are the main phases formed for each deposition current. It might suggest that Iron, Chromium and Nickel contents variation due to dilution did not alter the developed phase, but just their proportion, following the same trend as observed recently on cast alloy, Fig. 2 (Ref 5, 8, 12).

The dilution displaced the chemical composition of coatings and changed the hypereutectic composed by primary Laves phase and eutectic lamellar (Co SS + Laves phase) microstructure reported for cast CoCrMoSi T400 alloy to eutectic and hypoeutectic composition, for 150 and 180A, respectively, Fig. 3, Fig. 4 and Fig. 5 (Ref 8, 9). For 18 % dilution, an eutectic lamellar microstructure composed by Laves phase and Cobalt solid solution was observed. The chemical composition was altered as a consequence of higher Iron, Chromium and Nickel content on coatings.

A new cast alloy named T401 was developed based on T400, to improve especially toughness. Chemical composition was altered by reducing Silicon to the half, Molybdenum to 22.8 wt % and Chromium was doubled, changing the composition to a hypoeutectic. Chromium is mostly in Cobalt solid solution while Silicon is concentrated in Laves phase. Molybdenum can be in both Cobalt solid solution and Laves phase (Ref 8). So, the interaction with the AISI 316L steel substrate on microstructure of T400 alloy and its consequence on hardness and wear behavior of the coatings was investigated.

The main elements of AISI 316L steel substrate are Iron, Chromium and Nickel and, therefore, it is expected that the presence of these elements on coatings due to dilution alter the proportion of Cobalt solid solution phase on coatings microstructure. The interaction with the substrate was directly related to dilution, as previously reported by the literature (Ref 11).

The chemical composition of the T400 alloy coatings was displaced to hypoeutectic for 26 and 38 % dilution. It induced to a microstructure of Cobalt solid solution dendrites and interdendrictic eutectic lamellar region. The chemical composition of coatings with highest interaction with the substrate showed similar solidification microstructure to the newly developed cast T401 alloy, confirming the distribution of elements from substrate (Fe, Cr and Ni) mostly as Cobalt solid solution (Ref 8).

Once Iron, Chromium and Nickel form substitutional solid solution in Cobalt, coatings composition changed from hypereutectic T400 (Ref 9) to eutectic and hypoeutectic coatings as dilution increases. The lowest dilution (18 %) reduced Silicon and Molybdenum contents leading to the primary Laves phase suppression and to a fully eutectic microstructure. Hypoeutectic microstructure exhibiting Cobalt solid solution dendrites and interdendrictic eutectic lamellar was observed for 26 and 38 % dilution, Fig. 6 and Table 4.

**3.3. Effect of Microstructure on Hardness and Wear Performance**

CoCrMoSi alloys are intermetallic reinforced materials and the chemical composition of these alloys is the most important factor dictating Laves phase volume fraction and, thus, mechanical properties (Ref 9). In this context, as important differences on chemical composition occurred during processing altering microstructure, changes on coatings properties are expected.

Higher dilution leaded to a microstructure with reduced intermetallic Laves phase volume fraction, inducing hardness to decrease, Fig. 7. The most significant reduction of the eutectic volume fraction (40 % reduction) was observed comparing 18 % (120 A) to 26 % (150 A) dilution and larger hardness decrease was measured on CoCrMoSi alloy coatings. Furthermore, the higher Iron content in solid solution presented deleterious effect, reducing the hardness. For the higher dilution (38 %) of coatings processed with 180 A, eutectic volume fraction decreased even more (6 %) leading to the lowest hardness. Thus, the hardness was influenced firstly by the volume fraction of the hard phase (eutectic lamellar containing Laves phase) followed by the reduction of alloying in solid solution, following the same behavior previously observed on cast alloy (Ref 7, 8, 12).

Microstructure of as deposited condition available a better understanding of the hardness variation. Co-based T400 coatings mean hardness ranged from 702 to 526 HV0.5, as a result of increasing dilution which increased the volume of the lower hardness phase, Cobalt solid solution. Higher deposition current led to higher Iron, Chromium and Nickel contents on the melted pool, reducing Molybdenum proportionally and, therefore, the solid solution hardening effect (Table 4). Developed microstructure and phase distribution observed as well as the measured coatings hardness are in agreement with literature prediction (Ref 8).

Coatings wear behavior was assessed to evaluate the response of the T400 in a hardfacing condition, according to the interaction degree with the substarte (dilution). The coatings were tested in the as deposited condition with constant test parameters. The higher current intensity (180A) changes microstructure and hardness and induced to an increase on mass loss rate, Fig. 8a. Under tested conditions, a linear correlation between sliding distance and mass loss was measured by varying sliding distance (Ref 10). As expected, the result abided by Holm-Archard equation which establishes that the volume wear is inversely proportional to the hardness (Ref 13).

Coatings differences on chemical composition influenced wear mass loss rate. The lowest wear rate (0.1908 mg/m) was obtained for 18 % dilution. The mass loss rate increased to 0.2435 and 0.2703 mg/m as dilution reached 26 and 38 %, respectively. Better wear behavior can be related with the volume fraction of the eutectic lamellar and, consequently, with the hard Laves phase fraction (Ref 6, 8, 9).

Chemical composition displacement to hypoeutectic leaded to higher volume fraction of Cobalt solid solution and higher Iron content on such phase, inducing poor wear performance. Results followed the previous reports obtained on the cast CoCrMoSi T400 alloy (Ref 12). Dilution increase from 18 % to 26 % promoted an increase of 27.6 % on wear mass loss rate and, finally, 38 % dilution resulted increment of 41.7 % on wear rate, Fig. 8b.

The eutectic microstructure developed the lower friction coefficient (μ = 0.45), while the mixture of Cobalt solid solution dendrites and interdendrictic eutectic lamellar areas presented the higher values (μ = 0.90 and μ = 1.06), Fig. 9. Forged CoCrMo alloy presented friction coefficient (μ) varying from 1.0 and 1.1 against ceramic ball, while cast T400C alloy presented 0.6 (Ref 14-16).

Coatings eutectic microstructure showed that the wear debris are a result of detaching small lamellar areas of the hard intermetallic Laves phase, Fig. 10a. The presence of dendrictic Cobalt solid solution areas induced higher mass loss rate. Moreover, the Cobalt solid solution free of Laves changed detaching intensity because this phase does not support adequately the interdendrictic eutectic lamellar higher hardness phase, which was worn out as large debris, as observed on sliding track of the ball-on-flat test, Fig. 10b and Fig. 10c.

 The interaction with the substrate by PTA processing altered significantly coatings chemical composition. It displaced the composition from hypereutectic to eutectic or hypoeutectic, depending on dilution degree. The Laves phase volume fraction and Cobalt solid solution alloying dictated coatings hardness. Therefore, the wear behavior was influenced showing an increase on mass loss rate as well as on friction coefficient.

**4. Conclusions**

This study analyzed the effect of the interaction with the substrate on microstructure, hardness and wear performance of the Co-based T400 alloy coatings by PTA. The main contributions are presented as follows:

* The interaction with the substrate leaded to higher amount of Iron-Chromium-Nickel on coatings, displacing chemical composition of CoCrMoSi alloy from hypereutectic to eutectic or hypoeutectic.
* The higher interaction with the substrate the lower coatings hardness due to the reduction of Laves phase volume fraction and also Cobalt solid solution alloying.
* Hypoeutectic microstructure presented lower Laves phase volume fraction and solid solution alloying, leading to a poorer wear performance of the CoCrMoSi alloy coatings. Differences also affected negatively the friction coefficient and the intensity of the wear detaching debris.
* For the specific CoCrMoSi alloy system, the interaction with the substrate can be designed to control coatings microstructure and properties. Coatings processing reduced the amount of alloying elements, following the principles developed to obtain higher ductility cast Tribaloy alloys.

**5. References**

[1] R. H. Gonçalves, J. C. Dutra. PTA-P Process - A Literature Review as Basis for Innovations. Part 1 of 2: Constructive Elements. Soldag. Insp. 17 (1), 2012, 076-085, In Portuguese.

[2] M. J. Donachie, S. J. Donachie, Superalloys: A Technical Guide, Second ed., ASM International, Ohio, 2002, 25-38.

[3] H. Kim, B. Yoon, C. Lee. Sliding wear performance in molten Zn-Al bath of cobalt-based overlayers produced by plasma transferred arc weld-surfacing. Wear. 254 (5-6), 2003, 408-414.

[4] Q. Y. Hou, J. S. Gao, F. Zhou. Microstructure and wear characteristics of cobalt-based alloy deposited by plasma transferred arc weld surfacing. Surf. Coat. Technol. 194 (2-3), 2005, 238-243.

[5] A. Scheid, A. S. C. M. D’Oliveira. Analysis of PTA hardfacing with CoCrWC and CoCrMoSi alloys. Soldag. Insp. 18 (4), 2013, 322-328.

[6] F. Gao, R. Liu, X. J. Wu. Triballoy alloy reinforced tin-bronze composite coating for journal bearing applications. Thin Solid Films. 519, 2011, 4809-4817.

[7] J. Przybylowicz, J. Kusinski. Laser Cladding and erosive wear of Co-Mo-Cr-Si coatings. Surf. Coat. Technol. 125 (1-3), 2000, 13-18.

[8] R. Liu, W. Xu, M. X. Yao, P. C. Patnaik, X. J. Wu. A newly developed Tribaloy alloy with increased ductility. Scripta Materialia. 53 (12), 2005, 1351-1355.

[9] W. Xu, R. Liu, P. C. Patnaik, M. X. Yao, X. J. Wu. Mechanical and Tribological properties of newly developed Tribaloy alloys. Mater. Sci. Eng. A. (452-453), 2007, 427-436.

[10] R. H. Gonçalves , J. C. Dutra. PTA-P Process - A Literature Review as Basis for Innovations. Part 2 of 2: Powder Thermal and Kinematic Behavior, Process Parameters and Consumables. Soldag. Insp. 17 (2), 2012, 173-183, in Portuguese.

[11] T. J. Antoszczyszyn, R. M. G. Paes, A. S. C. M. D’Oliveira, A. Scheid. Impact of dilution on the Microstructure and Properties of Ni-Based 625 Alloy Coatings. Soldag. Insp. 19 (2), 2014, 134-144.

[12] A. Scheid, A. S. C. M. D’Oliveira. Effect of processing on microstructure and properties of CoCrMoSi alloy. Mater. Res. 16 (6), 2013, 1325-1330.

[13] E. Rabinowicz, Friction and Wear of Materials, Second ed., Wiley Interscience, New York, 1995, 143-190.

[14] A. Çelik, Ö. Bayrak, A. Alsaran, Í. Kaymaz, A. F. Yetim. Effects of plasma nitriding on mechanical and tribological properties of CoCrMo alloy. Surf. Coat. Technol. 202 (11), 2008, 2433-2438.

[15] R. Wei, T. Booker, C. Rincon, J. Arps. High-intensity plasma ion nitriding of orthopedic materials Part I. Tribological study. Surf. Coat. Technol. 186 (1-2), 2004, 305 -313.

[16] K. Jiang, R. Liu, K. Chen, M. Liang. Microstructure and tribological properties of solution-treated tribaloy alloy. Wear. 307 (1-2), 2013, 22-27.

**Table 1 Chemical Composition of the materials used (wt %).**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Alloy** | **Co** | **Cr** | **W** | **Mo** | **C** | **Fe** | **Ni** | **Si** | **Mn** |
| CoMoCrSi | Bal. | 8.8 | .... | 29.1 | 0.05 | 0.4 | 0.6 | 2.4 | .... |
| **Substrate** | **C** | **Mn** | **Si** | **P** | **S** | **Cr** | **Ni** | **Mo** | **Al** |
| AISI 316L | 0.02 | 1.35 | 0.43 | 0.03 | 0.01 | 16.78 | 10.12 | 2.13 | 0.002 |

**Table 2 Plasma Transferred Arc processing parameters.**

|  |  |
| --- | --- |
| **Parameters** | **Values** |
| Shielding gas (l/min) | 2 |
| Protection gas (l/min) | 15 |
| Powder feeding gas (l/min) | 2 |
| Protection, shielding and feeding gas | Argon |
| Main arc current (A) | 120, 150, 180 |
| Powder feed rate | Constant in volume |
| Travel speed (mm/min) | 100 |
| Distance torch / substrate (mm) | 10 |
| Electrode diameter (mm) | 3.125 |

**Table 3 Geometry and dilution of welding track.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Substrate** | **Parameter** | **120 A** | **150 A** | **180 A** |
| AISI 316L | Dilution (%) | 18 | 26 | 38 |
| Thickness, t (mm) | 2.7 | 2.4 | 2.1 |
| Width, W (mm) | 7.7 | 11.2 | 12.0 |
| Wettability Angle, Θ (0) | 83.0 | 49.4 | 37.8 |

**Table 4 Chemical distribution measured on the microstructure of CoCrMoSi T400 alloy coatings (wt %).**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Current (A)** | **Alloy Powder** | **Si** | **Mo** | **Co** | **Cr** | **Fe** | **Ni** |
| 2.4 | 29.1 | Bal. | 8.8 | --- --- --- | --- --- --- |
| **120** | Eutectic | 2.23 | 29.42 | Bal.  | 9.02 | 9.75 |   |
| Cobalt Solid Solution | ---- | 14.04 | Bal. | 12.30 | 13.42 | 3.20 |
| **150** | Eutectic | 2.12 | 28.40 | Bal. | 9.32 | 18.08 |   |
| Cobalt Solid Solution | ---- | 11.84 | Bal. | 13.44 | 21.08 | 4.14 |
| **180** | Eutectic | 2.08 | 22.56 | Bal. | 11.08 | 26.63 |   |
| Cobalt Solid Solution | ---- | 11.54 | Bal. | 14.23 | 27.28 | 4.05 |

**Fig. 1** Geometry of welding overlays: thickness (t), width (w) and wettability angle (Θ).

**Fig. 2** X-ray diffraction analysis on CoCrMoSi coatings deposited with 120, 150 and 180 A.

**Fig. 3** Eutectic microstructure of CoCrMoSi PTA coatings (120 A).

**Fig. 4** Hypoeutectic microstructure of CoCrMoSi PTA coatings (150 A).

**Fig. 5** Hypoeutectic microstructure of CoCrMoSi PTA coatings (180 A).

**Fig. 6** Volume fraction of lamellar eutectic.

**Fig. 7** Vickers Hardness of coatings in the as-deposited condition.

**Fig. 8** Wear curves for CoCrMoSi alloy coatings (a) and Wear coefficient (b).

**Fig. 9** Ball-on-flat sliding friction coefficient for CoCrMoSi alloy coatings.

**Fig. 10** Grooving details of ball-on-flat sliding tracks: (a) 120 A (b) 150 A and (c) 180 A.