Comparison of mechanical properties and microstructural characterization of CoCrMo alloy obtained via selective laser melting (SLM) and casting techniques

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Abstract: Advances in processes using the powder metallurgy techniques are making this technology competitive compared to the other traditional manufacturing processes, especially in medicine area. The additive manufacturing technique – selective laser melting (SLM) was applied in a biomaterial of CoCrMo alloy (ASTM F75), to study the mechanical properties and microstructural characterization in comparison between the conventional technique – lost wax casting. The gas atomized powder was investigated by their physical (as apparent density, bulk density and flow rate) and the chemical properties (SEM-EDS and X-ray fluorescence). Specimens of standard samples were manufactured to evaluate the mechanical properties as yield strength, maximum tensile, rupture tensile, elongation, elastic modulus, transverse rupture strength and the Vickers hardness. Before the mechanical tests the microstructure of specimens were examined using optical microscope (OM) and SEM-EDS. The results of mechanical properties showed a higher values in the SLM specimens compared with the obtained in the cast specimens. The micrographs revealed a typical morphology of consolidation process, like as the characterized by selected layer used in the SLM technique and the primary and secondary dendrites arms in the casting technique.
Keywords: CoCrMo alloy, selective laser melting, lost wax casting, biomaterial, powder metallurgy.

Introduction

Powder of Co-Cr alloys (*Stellite*) obtained by atomization gas have their use widespread in the automotive, aviation and aerospace industry, producing powders for use in coatings, since these alloys have excellent resistance to corrosion and wear. The high biocompatibility of these alloys has made this attractive material for the manufacture of components of medical and dental sectors (ASM INTERNACIONAL, 2000; CRAIG, 2012). In literature are reported several studies to consolidate the powder of Co-Cr alloy. The mechanical, physical and electrochemical properties of Co-Cr-Mo alloy for dental implants were evaluated for better determination of the production parameters on sintering with the improvement aimed at restoration and medical implants (FAZIRA et al., 2013; HENRIQUES et al., 2012; ÖRTORP et al., 2011). According (JABBARI et al., 2014), Co-Cr alloys are used almost exclusively in the manufacture of metal structures prosthesis and recently is replacing Ni-Cr alloy, or alternatively for the production of restorations in porcelain fused to metal

(PFM), due to the Co-Cr alloy is Ni-free does not have allergic responses or toxic effects related to Nickel.

At the end of the 80s emerged results from early research seeking a way to produce a physical model from a three-dimensional digital model. Rapid Prototyping (RP) is the term used to represent the great variety of technologies using the method to produce complex geometries from a three-dimensional (3D) model, obtained by Computer Aided Design (CAD) using: CT or MRI scan with the use of a Computer Aided Manufacturing (CAM). (GIBSON, 2005; GOUVEIA, 2009; VAN NOORT, 2012). The development of AM technologies, according to Noort, 2012, provided the manufacture of customized implants. Initially, techniques such as stereolithographic were implemented for the manufacture of models in resin for making dental implants (crowns and bridges) for the production via lost wax casting technique. The production of metal components by means of high power laser, known as Selective Laser Melting (SLM), was promising since it allows the manufacture of customized components and high final physical properties compared to conventional techniques. The aim of this study is to demonstrate the mechanical properties and microstructures of specimens manufactured by powder metallurgy techniques using the SLM, using the Co-Cr-Mo alloy in the form of particulate matter. Yet there is an important knowledge of performance properties, dimensional, mechanical and microstructural of this sintered alloy compared to casting, as reported recently (MERGULHÃO et al., 2015a, 2015b; PODESTÁ et al., 2015). Obtained properties must meet specific characteristics of health care performance.

Experimental Procedure

The Co-Cr-Mo alloy gas atomized (H.C Starck® Company) was provided by the HighBond company in three different particle sizes (granulometric range), respectively by terminologies D1 < 15 μm, D2 15-45 μm and D3 76-106 μm. The confirmation of the chemical composition by fluorescence spectrometer X-ray energy dispersive (Shimadzu EDX-720 equipment) of powders is presented in Table 1, in comparison with the chemical composition tolerance of standard ASTM F75(2012a). This study based on powders (HighBond®, Brazil) with certification of ANVISA for use in health care.

Table 1 – Chemical composition (weight %) of Co-Cr-Mo powder and the standard reference ASTM F75(2012a).

	Cobalt	Chromium	Molybdenum	Iron
Powder	63,86 ± 0,07	28,96 ± 0,04	7,02 ± 0,01	0,16 ± 0,01
Cast	62,601 ± 0,06	27,998 ± 0,04	6,02 ± 0,01	0,213 ± 0,01
ASTM F75	Balance	30,00 - 27,00 ± 0,30	7,00 - 5,00 ± 0,15	0,75 ± 0,03

Several physical properties of gas-atomized powders were obtained such as flow time, apparent density, tap density of powders were performed according respectively to ASTM ASTM B212 (2013a), B213 (2013b) and ASTM B527 (2014). The particle size distribution was performed using a particular analyzer by laser scattering (Cilas - Model 1064). The particle format was analyzed by SEM - Philips XL30. The characterization by Helium pycnometry was performed in the Co-Cr-Mo powders used the Micromeritics machine -

Model Accu PYC 1330 Pycnometer, located in the Nuclear Fuel Center (NFC/IPEN). The consolidation of SLM samples was carried out by SLM Solutions™ using a selective laser melting machine SLM®280HL with a single Ytterbium laser beam (30 µm - trick laser and 400W – laser power). The lost-was casting tensile samples was performed according to ASTM F75(2012a), in standard dimensions of ASTM E8/E8M (2015). Mechanical characterization of consolidated samples by lost wax casting and SLM techniques was held in standardized tensile test samples (according to ISO 22674 (2006)). Bending tests samples were consolidated in the SLM technique (according to ASTM B528 (2012b)) to obtain the transversal rupture strength (TRS). The TRS relates the applied load (P) and the distance between the supports (L), over the cross area of the sample (T - thickness and w - width), as show the Equation (1). The mechanical tests were performed using a universal testing machine (Instron 3366) under a crosshead speed of 0,2 mm/min at room temperature.

$$TRS = \frac{(3 \,.\, P \,.\, L)}{(2 \,.\, t^2 \,.\, w)} \quad (1)$$

The microstructural characterization and fracture analysis of consolidated Co-Cr was performed after tensile test. The tensile test specimens was sectioned the vertical direction and was prepared mechanical grinding (SiC paper # 1200) and final polishing (OP-S 0,02µm). The specimens were etching in solution: 100ml HCl and 2ml H2O2 (1-2 minutes at room temperature). The microstructural characterization was performed using an optical microscope (Olympus - BX51M) and scanning electron microscope (SEM-EDS Philips XL30). To evaluate the internal porosity of cast and SLM sample were measured the pycnometer density in comparison by the theoretical density. The density by pycnometer Helium, considered only the internal porosity (excluding the open porosity) was measure using the Micromeritics equipment - Model Accu PYC 1330 Pycnometer.

Results and Discussion

In Figure 1 it is possible to analyze, the samples have spherical morphology, as well as the presence of satellites. This format is characteristic of the gas atomization process. The cross section of Co-Cr-Mo powders (after the chemical etch) reveals dendritic formation and segregation of the primary and secondary arms (see Figure 1d). The spectrogram by EDS (Figure 1e) shows the chemical elements present in the alloy of Co-Cr-Mo, confirming the chemical composition by X-ray fluorescence. The physical properties obtained according with powder metallurgy standardizations are shown in the Table 2**.**

Table 2 – Physical properties results (mean and desviations) of CoCrMo powders.

Physical Properties of Powder		*D1*	*D2*	*D3*
Granulometric Distribuition [µm]	Diameter 10%	5,67	20,88	-
	Diameter 50%	12,73	31,11	-
	Diameter 90%	19,64	46,10	-
	Medium Diameter	12,76	32,36	92,81
Flow Time [s/50g]		-	15,85 ± 0,11	22,89 ± 0,03
Apparent Density [g/cm³]		4,12 ± 0,01	4,51 ± 0,01	4,55 ± < 0,01
Tap Density [g/cm³]		5,00 ± 0,02	5,26 ± 0,05	5,09 ± 0,02
Theorical Density (g/cm³)			8,37	
Pycnometer Density by Helium (g/cm³)		8,28 ± 0,001	8,30 ± 0,001	8,27 ± 0,001
Specific Surface (m²/g)		0,66757	0,01114	0,35287

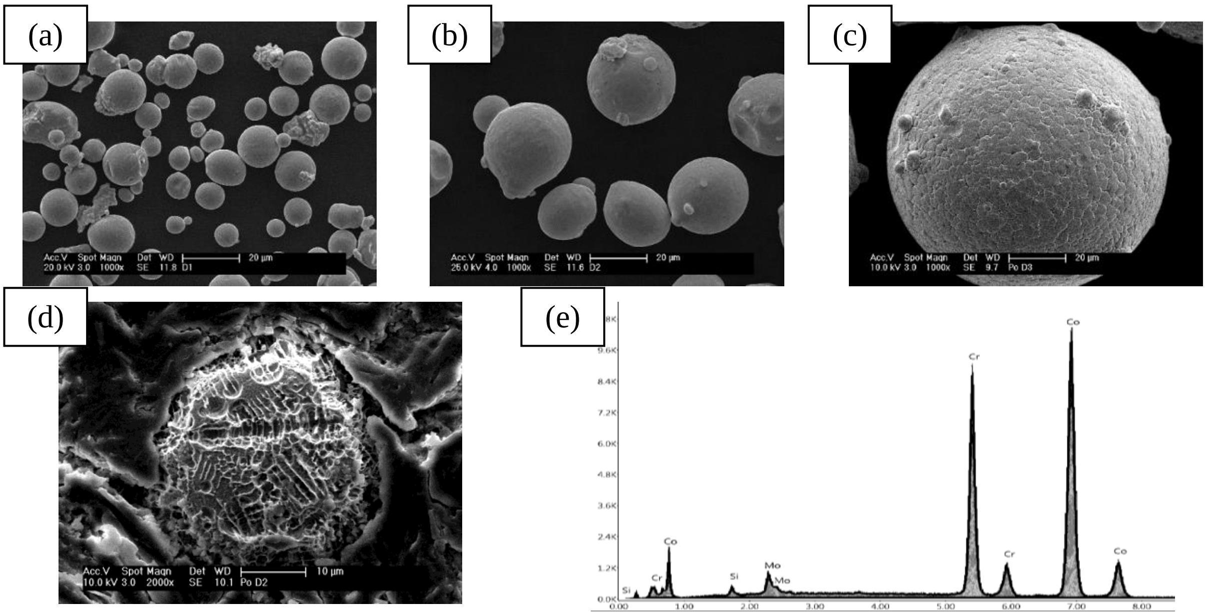

Figure 1: MEV images of CoCrMo powders. (a) D1; (b) D2; (c) D3; (d) cross-section of D2 powder after chemical etch; (e) EDS spectrogram of powders.

According to the results, the flow time of powders were measured: D2 equal to 15,85 s/50g and D3 equal to 22.89 s/50g. The sample of the ratio D1 powder having a very fine granulometry and was characterize as no flow powder. According to the comparison between the average diameter of the D2 and D3 powders, respectively 32,36 µm and 92,81 µm it is concluded that the flow time of the finer powder (D2) is better than the flow time of the coarser powder (D3). The results of tap density showed that the values obtained are directly related to the particle size, respectively 4,12g/cm³, 4,51g/cm³ and 4,55g/cm³ for D1, D2 and D3 powder, which it increases relative to the increase of particle size range. According to Haan, *et al.,* (2015), powder flow time and apparent density of the alloy Co-Cr-Mo study showed relevant results to those obtained respectively for powders with D90 diameter equal to 39 µm, the flow time was 18,6 s/cm³ and bulk density was 4,38 g/cm³. The results of tap density of powders of samples show the increased density relative to density. According to the methodology to obtained the tap density, obtained by "hits" or vibration of a graduated tube, the particles occurs complacency and decreasing the gaps between them and consequently implies increasing density. The Co-Cr-Mo powders characterized by theoretical density related to pycnometer Helium density shows a presence of closed porosity detected.

The data of mechanical properties presented in the Table 3, compared the results of tests with the minimum mechanical properties required by the standards. The ratio of the mechanical properties obtained and the referenced by standards indicates that the cast samples are approved (see Table 3) only by the yield stress in type 2 of ISO22674(2006), but not obtained the minimum mechanical properties required by the ASTM F75(2012a). In the consolidated samples by SLM technique, the results of mechanical properties fall with type 5 of standard ISO22674(2006), as well as meet the minimum values of ASTM F75(2012a). The data obtained for the modulus of elasticity for both techniques accord with the minimum required by standard ISO22674(2006). The Co-Cr-Mo alloy consolidated by casting technique required a heat treatment to improve the mechanical properties, due to the presence of brute fusion structure. However, the mechanical properties obtained for the consolidation of the alloy Co-Cr-Mo by SLM technique, fits the type 5 as manufactured. According

Takaichi, *et al.*, (2013), the mechanical properties of SLM and casting samples have values similar to those obtained in the test samples, respectively: 516 MPa for the yield strength, 912 MPa for maximum tension and 10,7% elongation to consolidated by SLM and 296 MPa for yield strength, 591 MPa for maximum voltage and 9,6% elongation for the consolidated by casting.

Table 3 –Results (mean and standard deviation) of mechanical properties of Co-Cr-Mo alloy manufactured by cast and SLM according to ISO 22674(2006) *and ASTM F75*(2012a, p. 75).

Reference	*Type*	*0.2% YS [MPa]*	*Elongation [%]*	*E [GPa]*	*UTS [MPa]*	*TRS [MPa]*
Co-Cr-Mo alloy	CAST	276,20 ± 43,60	8,37 ± 4,45	291,21 ± 15,22	453,62 ± 75,91	-
	SLM	731,50 ± 40,31	13,73 ± 5,32	276,70 ± 12,63	1136,95 ± 0,92	1127,91 ± 0,15
ISO 22674:06	1	80	18			
	2	180	10	-		
	3	270	5		-	
	4	360	2			-
	5	500	2	150		
ASTM F75		450	8	-	655	

The TRS values of bending tests on samples consolidated by SLM, results a TRS equal to 2501,2 MPa with a standard deviation of 9,61%. According Mengucci, *et al.*, (2016), using a composition similar to Co-Cr-Mo alloy, after treatment shoot-peened followed by heat treatment for stress relief obtained a TRS result approximately to 2700 MPa with a standard deviation of 25%. Therefore, comparing the data obtained in the study (MENGUCCI et al., 2016) it is verify that the result is satisfactory, as it our samples prepared in this study were not subjected to heat treatment.

The OM images of the consolidated casting and SLM samples can be seen in Figure 2. As in cast micrographs (Figure 2a) it is possible to identify the dendritic structure in the sample having different orientations solidification and the presence of porous (indicated by arrows). The formation of the microstructure observed was reported recently (MERGULHÃO et al., 2015a, 2015b; PODESTÁ et al., 2015). In the SLM samples (Figure 2b) presents a homogeneous microstructure characteristic of process, represented by the laser beam, as a slightly elliptical morphology. Authors (HAAN et al., 2015; RIVERA et al., 2011; XIN et al., 2012) describes the same microstructures observed in the samples.

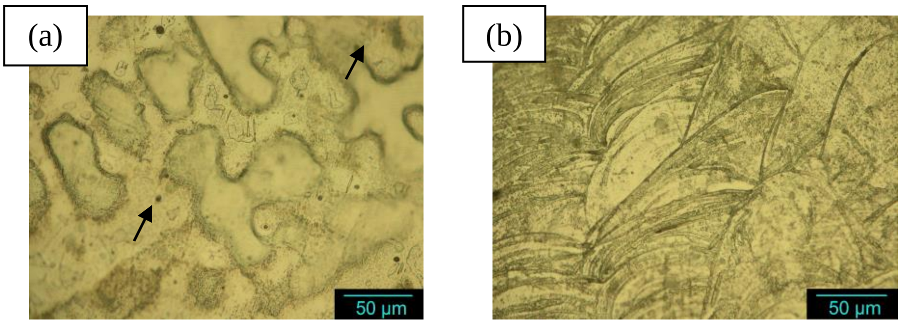

Figure 2: OM micrographies of Co-Cr-Mo specimens after chemical etch. (a) cast sample (arrows indicate porous); (b) SLM sample.

The images obtained by SEM in the casting sample can analyze possible formations or pitting as well as increasing the pore diameter (highlighted by arrows - Figure 3a). It is possible to analyze the presence of a second phase, represented by the lighter region. The points of interest (Figure 3b) of the microstructure were selected and analyzed by EDS (Figure 3c and Figure 3d), and respectively show a carbide ($M_{23}C_6$) rich in Cr and Mo.

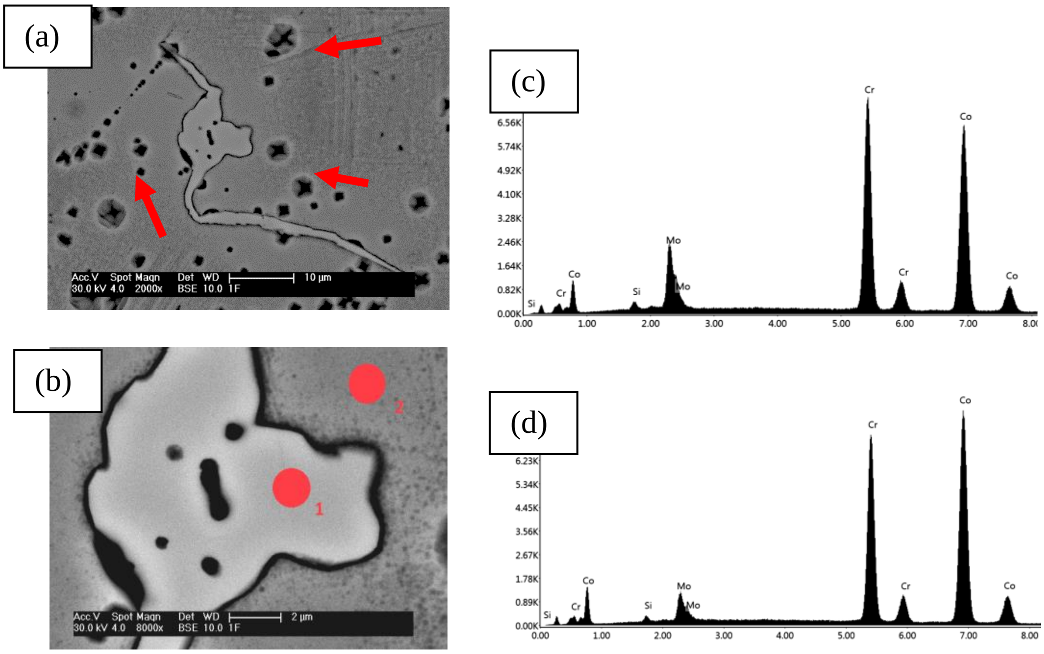

Figure 3: (a) ; (b) SEM micrographics of cast sample; (c) EDS spectrogram of point 1 and (d) EDS spectrogram of point 2.

In Figure 4 can be see the SLM sample examined by SEM-EDS. As in OM images, it is possible to observe the ellipsoid geometry structure of incidence of the laser beam, highlighted by the arrows on the images. This typical laser beam configuration is described by several authors (GIRARDIN et al., 2016; MERGULHÃO et al., 2015a, 2015b; PODESTÁ et al., 2015). It is possible to observe the homogeneous microstructure and absence of second phases in the microstructure, as can be observed in the cast samples.

The SLM technique provides formation of ultrafine grains within ellipsoid geometry formed by the fusion laser beam action. The semi-quantitative chemical analysis by EDS (points 1 and point 2 in the Figure 4b) shows that there was no difference in the chemical composition of light and dark regions of ultrafine grain structure. On analyzing the microstructure with respect to cutting section, it is observe that in the horizontal section view to casting selective layer by layer by the laser beam action. It can be seen that the MA layer formation technique of the layer, as seen cross section parallel to the laser beam (Figure 4b) having thickness of 20 to 50 micron.

To determine the porosity of the consolidated samples was established the comparison of the pycnometer density between the theoretical density. The results of analysis are show in the Table 3.

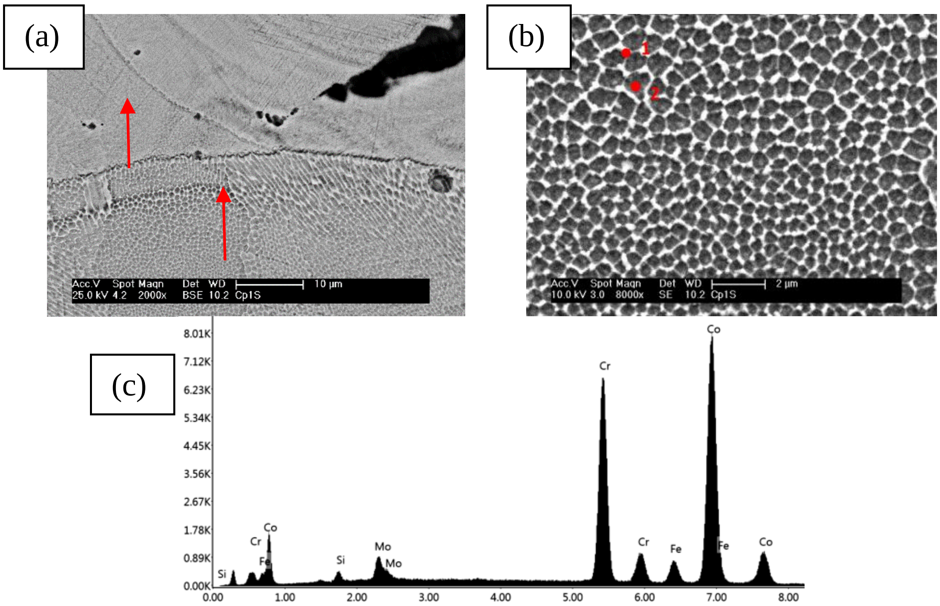

Figure 4: (a) and (b) SEM micrographics of SLM sample; (c) EDS spectrogram point 1 and point 2.

Table 3 –Results (mean and desviations) of porosity analysis methods applied in specimens Co-Cr-Mo.

Specimens	*Porosity methods [g/cm³]*	
	Picnometer by Helium	*Theorical*
CAST	8,193 ± 0,007	8,37
SLM	8,244 ± 0,006	

The results of pycnometer density appointed lower values of density in cast samples relation to the SLM samples. Upon measurement of pycnometer density regard the open porosity of the sample, but also takes into account the internal closed porosity of the sample. Comparing to the theoretical density is proposed to assess the internal porosity of the consolidated sample by SLM. Therefore, the cast and SLM samples, results approximately 97,90 % and 98,50 % of real density. The presence of porosity influence the mechanical properties of samples, however is possible to identify by the lower values of casting mechanical results (as showed in Table 3.)

The fractures of the tensile samples were SEM analyzed. In the fracture imaging is showed a homogeneous formation fracture surface of the cast and SLM (Figure 5). Fractures are observed the formation of "dimples" homogeneously distributed in the microstructure of the samples. Regions with presence of dimples are more ductiles and higher toughness. However, it is apparent that the dimple formation on the SLM sample extends completely by the fracture planes, and that these are of finer size, compared to the fracture cast geometrically larger. The occurrences of geometrically higher fracture regions are observe in the fused sample. Some smooth planar regions indicated by arrows show this morphology. The formation of finer dimples is characteristic of a ductile fracture and which features mechanical properties and higher toughness, and it can be see on the SLM sample according to the results shown (Table 3). The type of fracture observed in the samples, according to Takaichi *et al.*, (2013), describes the formation of dimples along the fracture surface, as well as cracking of the wedge, as can be clearly seen in Figure 5 is appointed as a possible formation of cleavage fracture over favorable crystallographic planes.

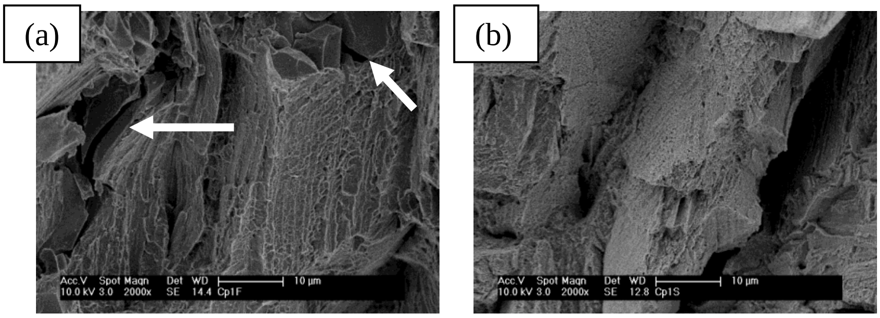

Figure 5: SEM images of tensile fractures. (a) cast sample; (b) SLM sample.

Conclusions

The particles in the study produced by gas atomization showed spherical particle geometry with satellites and internal porosity, which can compromise the additive manufacturing process. The SLM technique allowed obtaining samples with superior mechanical properties of the cast technique. In this case, the yield strength and elongation were respectively 69,73% and 39,04% greater than the yield strength and elongation obtained in the cast samples. The microstructural characterization of the casting samples showed formation of rich carbide molybdenum. The selective laser melting allowed to obtain samples with improved chemical homogeneity over the molten sample, as discussed in the microstructural characterization of the samples and confirmed by fracture analysis. The processing using laser sintering proved superior to casting processing technique, allowing the use of this technique in the manufacturing area of prosthetics and dental implants.

Acknowledgments

This study was financially support by CNPq. The authors also thank to Ms. Amed Belaid and SLM® Solution for tensile and bending specimens.

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