MICROSTRUCTURE OF SPRAY FORMED 2.9%C-22%Cr HIGH CHROMIUM WHITE CAST IRON

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ABSTRACT
In the present work a 2.9%C-22%Cr white cast iron was processed by spray forming aiming to investigate the potential of achieving novel microstructure by the high cooling rate involved in this process. Two gas flow rate to metal flow rate ratios (0.12 and 0.23) were used. The microstructural characterization was performed by using X-ray diffractometry, optical and scanning electron microscopy.The conventional microstructure of this alloy shows M_7C_3 carbides (about 300μm in length) embedded in a matrix of austenite and martensite dendrites; on the other hand the spray formed deposit showed a microstructure formed by fine M_7C_3 carbides (< 10μm in length) in a martensitic matrix. The overspray powders showed a microstructure composed mainly by carbides and austenite; the relatively rapid solidification of the droplets enhanced the chromium and carbon solubility in austenite changing the M_s temperature.
Keywords: *spray forming, white cast iron, carbides, wear, chromium*

INTRODUCTION
High chromium white cast irons are used when high wear resistance is necessary. This characteristic is guaranteed by the microstructure of high volumetric fraction of chromium carbides (in range of 20-35%) distributed in an austenitic/ martensitic matrix. By conventional cast techniques these alloys present coarse microstructures with interconnected eutectic carbides type M_7C_3 (M⇒Cr, Fe), leading to decrease of impact resistance, ductility and fatigue resistance [1]. The microstructural control of eutectic carbides has been a strategy in order to improve mechanical properties of these alloys. However, studies on morphological modification and carbide distribution by means of conventional foundry parameters, addition of alloying elements and heat treatments were not successful to solve this limitation [1, 2].
Prior studies have revealed that the grain size in spray formed deposits is determined by the conditions of the spray upon impact, the spatial distribution of solid particles after impact, the time required for complete solidification, and the cooling rate during and after solidification. Even not presenting so high solidification rates, such as melt-spinning or splat-cooling techniques, spray forming can produce refined microstructures with low segregation levels and supersaturated solid solutions with even metastable phases [3, 4].Equiaxial refined grains (10 to 100μm), low segregation levels, smaller dispersoids (0.5 to 15μm) and precipitated secondary phases are examples of typical microstructures of materials obtained by SF process. Porosities are usually very small and disperse, and can be, in some cases, eliminated by further conformation process. Due to the homogeneous and fine microstructure and extended solubility of some elements, heat treatments can be really shorter and even avoided. The workability of the deposits can be strongly improved and even non-workable alloys, such as high nickel and cobalt alloys can be hot rolled and forged [5-7].
The aim of the present study is to investigate the wear resistance of a high chromium white cast iron, obtained by spray forming. The performance of the spray formed deposit was evaluated by

means of standard wear resistance tests and the results compared with those of a similar alloy processed by conventional casting.

EXPERIMENTAL PROCEDURE

The molten alloy, whose composition is showed in table 1, was superheated to 1400°C and delivered through an alumina pouring tube and atomized by nitrogen, in a static close-coupled atomizer. The substrate was made of ceramic material, having 300mm of diameter and 30mm of thickness. Table 2 resumes the process parameters used (gas to metal flow rate ratio,GMR, and distances between pouring tube and substrate,flight distance) . In this table the codes presented in the first column indicate ***P*** the pressure (P_5 = 5 **bar,** $\mathbf{P_{10}}$**= 10 bar**) used during the related atomization and **H** its respective flight distance (H_{200} = 200mm, H_{325} = 325mm). The ceramic substrate had translation and rotation movements during atomizing. Details of the equipment used was described elsewhere [8]. In order to compare both spray formed and conventionally sand cast materials, the same superheating were used in both processes.

Table 1 - Chemical composition of the Conventionally Cast and Spray Formed white cast irons.

	Chemical Composition (wt. %)							
Material	***C***	***Cr***	***Si***	***Ni***	***Mn***	***Mo***	***V***	***S***
Conventional	2.98	19.70	0.79	0.76	0.68	1.88	0.04	0.02
Spray Formed	2.83	22.50	1.12	0.91	0.65	1.70	0.03	0.02

Table 2 – Process parameter used in the spray forming experiment.

Experiment	Gas flow (kg/s)	Metal flow (kg/s)	GMR	Flight Distance H (mm)
$\mathbf{P_{10}H_{200}}$	0.080	0.35	0.23	200
$\mathbf{P_5H_{200}}$	0.035	0.30	0.12	200
$\mathbf{P_5H_{325}}$	0.035	0.30	0.12	325
$\mathbf{P_{10}H_{325}}$	0.080	0.35	0.23	325

The overspray powder (droplets which do not impact on the preform top surface or/and bounce off impacting droplets or powder from the deposit surface) was separated and classified, by sieving, according to their sizes as fine range (less than 45µm) and middle range (between 150 and 180µm). Phase characterization of the samples was done by X-ray diffraction, using a D5000 Siemens™ diffractometer. A Netzsch™ STA409, differential scanning calorimeter (DSC), was used to measure the final transformation temperature of retained austenite to martensite ($\mathbf{M_s}$) . Optical microscopy and scanning electron microscopy (SEM) were used for microstructural characterization
Vickers hardness was measured for each experiment, using a load of 1kg. Wear resistance pin-on-disk tests were performed, according to ASTM G99-90, under load of 515g, using cylindrical samples pressed against a rotating (53 rpm) disc. Abrasive papers, 220 and 600 mesh, were glued at the disc surface before each test and the mass loss of each sample was measured after abrasion test. It were also preformed abrasion tests using a dry sand/ rubber wheel apparatus, following the procedure indicated by ASTM G65-91 (procedure A) standard.

RESULTS

The X-ray difractograms for both conventionally cast material and spray formed deposits revealed the presence of M_7C_3 type carbides, austenite and martensite. Figure 1a shows the microstructure of the conventionally cast white cast iron. It can be observed a dendritic microstructure with interconnected acicular M_7C_3 type carbides (100 to 300 µm in length) in a matrix composed by martensite and retained austenite. The literature report that the high chromium white cast irons ranging from 10-30%Cr and 2-3.3%C, as is in the present case, solidifies with primary austenite dendrites (γ) until the eutectic temperature is reached, where the reaction ($liquid \Rightarrow \gamma + M_7C_3$) occurs [9].
The microstructures of deposits are shown in figure 1b-e, presenting acicular carbides in a mainly martensitic matrix. The quantity of porosity is low. By comparison with the microstructure of figure

1a the benefit of the spray forming process producing refined microstructure with fine and homogeneously distributed carbides can be observed. In all deposits herein produced the carbides are surrounded by martensite (α'). The shorter mean free path necessary for diffusion of alloying elements from the austenitic matrix to the carbides can explain the higher amount of martensite surrounding the small carbides after solidification. Higher GMR value resulted in a more refined microstructure when deposits processed with same flight distances (figs. 1b,c and 1d,e) are compared. In the same manner the influence of the flight distance can be observed comparing Figs.1b-e and Figs 1c-d (same GMR). One can observe that the differences are not so accentuated and therefore it can be stated that the GMR values herein studied resulted in more significant microstructural changes than flight distance. The coarse carbides distribution presented in figure 1-d, among other microstructural features (largest volumetric fraction of carbides), led to the highest value of Hardness (960HV) of all studied parameters (see Table 3 for comparison).

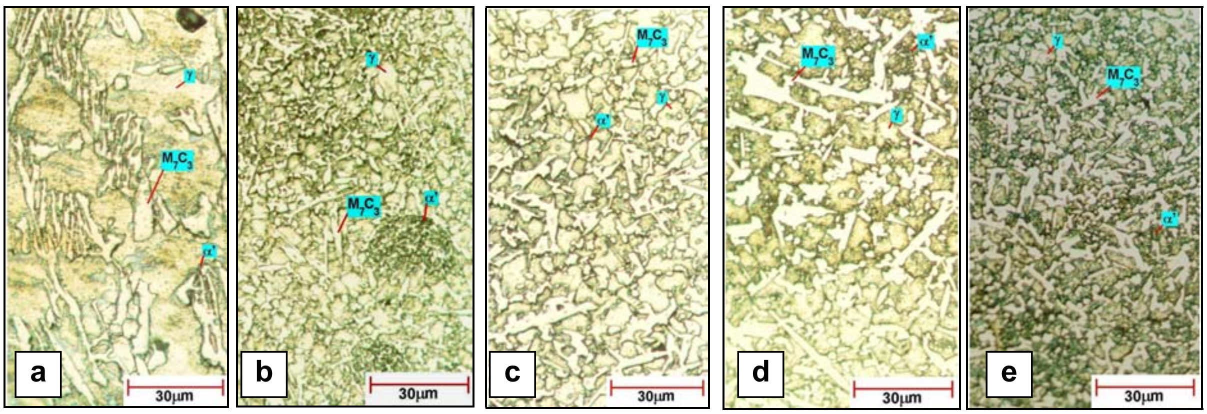

Figure 1 - Optical micrographs: (a) conventionally cast white cast iron showing interconnected M_7C_3 carbides in a dendritic matrix, composed by austenite and martensite, and of SF white cast iron; b) $P_{10}H_{200}$. c) P_5H_{200}. d) P_5H_{325}. e) $P_{10}H_{325}$, showing M_7C_3 carbides, smaller than that shown in conventionally cast, in a matrix, composed by martensite (α') and retained austenite (γ).

Figure 2 shows a typical small size (around 30 µm in diameter) overspray powder microstructure, which presented a very fine dendritic structure having secondary arm spacing ranging from 1 to 3µm. The middle size (50 to 180 µm) powder presented a dispersion of carbides in an austenitic matrix, similar to the matrix of deposits. The X-ray diffractograms of both small and middle size overspray powders revealed the presence of some peaks which are not present in the deposits or in the conventionally cast material, and that could not be indexed by the *JCPDS* cards, indicating the probable existence of metastable phases. To understand the present results it must be considered that chromium has been known as an alloying element, in white cast irons and steels, which decreases the starting temperature of austenite to martensite transformation (M_s) and also displace the TTT curve to the right, retarding the transformations from austenite to ferrite, pearlite and etc [1, 10]. According to the literature, it has been found higher amount of martensite, than austenite, in the matrix, for the conventionally cast materials, due to both: middle cooling rate in solid state and low amount of chromium in solid solution.

The microstructures of the overspray (figure 3) revealed the presence of fine and homogeneous distribution of carbides, but without the presence of martensite in the matrix. It could be expected a higher amount of martensite than austenite in their matrices, due to the higher cooling rates imposed. However, due to the high solidification rates imposed during atomization, some alloying elements, such as carbon and chromium, might be retained in solid solution in the matrix. In this case, the matrix could be supersaturated with chromium and carbon to lower M_s temperature below the room temperature, resulting in a matrix mainly composed by austenite. The cooling rates, lower in the deposit than in the powders, might allowed the chromium carbides formation and therefore decreasing the content of both carbon and chromium in solid solution. This fact leads, in a more easy way, the subsequent transformation of austenite to martensite in the deposits.

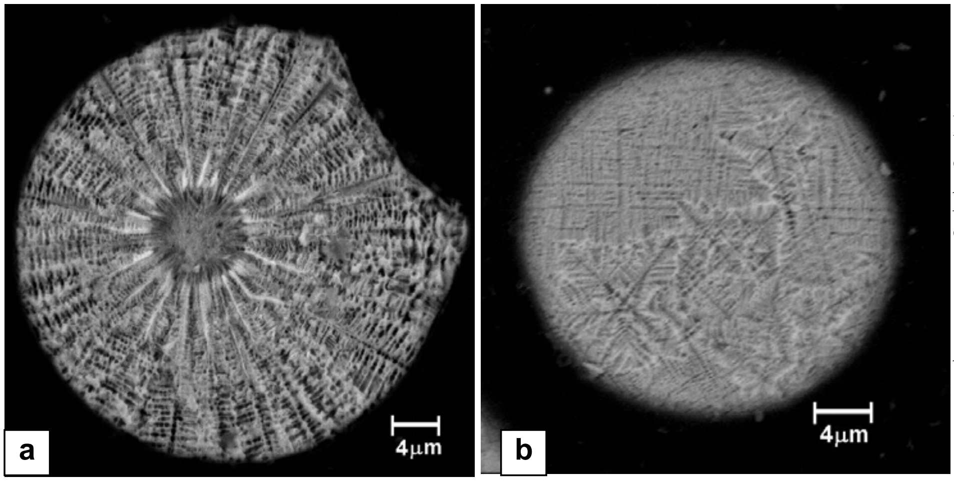

Figure 2 - Fine overspray powder particles, showing dendrites, having secondary arm spacing of about 1μm. a) P_5H_{200}. b) $P_{10}H_{325}$

The wear resistance tests performed using abrasive paper grit 220, indicate a better wear resistance of conventionally cast material and a very close result for the spray cast material P_5H_{200}. Considering the hardness and the microstructure these results might be related to the presence of similar amounts of austenite in their matrices and also to the effect of the ratio between the size of the abrasive particles and the carbides. The carbides present in conventionally cast material and in P_5H_{200} will act as a hard protection. For the other spray formed samples, these carbides would be removed easily by the abrasive material resulting in higher loss of mass. It has been stated [11] that if the matrix is ductile, for example, austenitic, this matrix can be deformed and the carbides are less intensely removed. The spray formed material P_5H_{200} presented smaller volumetric fraction of carbides disperse in the matrix and better wear resistance. This relationship between volumetric fraction of carbides and wear resistance has been reported by other studies [12] when using hard abrasive and has been attributed to the ductility of matrix.

For the wear resistance tests using abrasive paper grit 600 mesh, the deposits shown lower resistance when compared to the conventional cast material, indicating relationship between the carbides size, matrix and the size of the abrasive material. The presence of large carbides when compared to the size of abrasive particles resulted in better wear resistance of the conventionally cast material. The presence of fine carbides homogenously dispersed and having grit similar to the abrasive paper has shown the influence of the hardness, and consequently the matrix in the wear of the herein studied material. Similar to the wear resistance test using 220 mesh abrasive paper, the best wear result using 600 mesh abrasive paper were measured for the spray formed material P_5H_{200}, which presented higher amount of austenite. Spray cast materials having high amounts of martensite (P_5H_{325} e $P_{10}H_{325}$) have presented poor wear resistance. Figure 3a shows a surface after test in $P_{10}H_{200}$ material and was observed the microcutting wear mechanism.

Initial results in dry sand/rubber wheel wear test showed better performance for P_5H_{325} condition. This type of test presents less severe wear condition than the pin-on-disk test does and microfurrow should be the predominant wear mechanism (figure 3b). Therefore, by similar content and size of carbides, a matrix with a higher hardness value should present a better performance against wear, as is the case for the P_5H_{325} deposit (table 3).

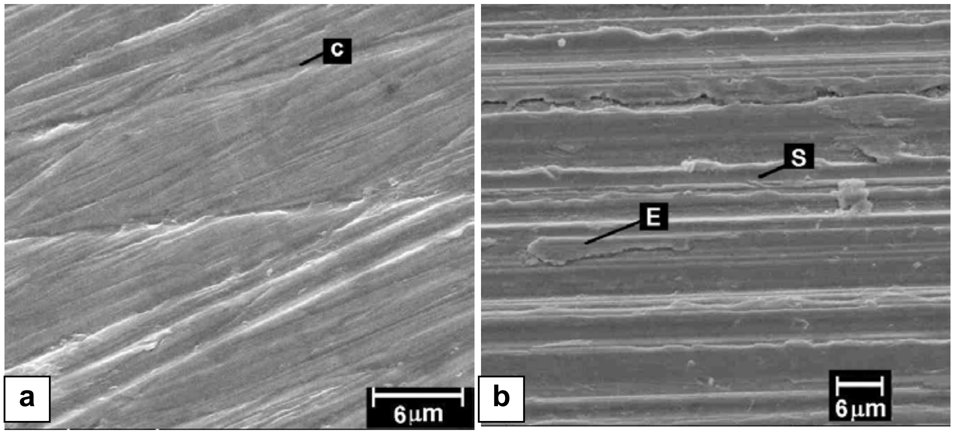

Figure 3 – Surfaces after wear tests, using grit 600, in $P_{10}H_{200}$ samples. a) Pin-on-disk, where (**C**) indicates microcutting; b) dry sand/rubber wheel tests, where (**E**) is squeeze of material, and (**S**) microfurrow.

Table 3 shows wear resistance test results for conventionally cast and spray formed samples, using abrasive paper grit 200, grit 600 mesh and dry sand/rubber wheel. The same table also presents the average values of measured porosity, average volumetric fraction of carbides and Vickers hardness. It can be observed a significant decrease of mass loss, and then, a decrease of wear for the tests performed using abrasive paper grit 600 mesh.

Table 3 - Measures of mass loss during wear resistance tests at room temperature, volumetric fraction of carbides and average Vickers hardness of both, conventionally cast and spray formed white cast irons

Material	Loss of mass 200mesh (mg)	Loss of mass 600mesh (mg)	Loss of mass Rubber Wheel (mg)	Carbides (%)	HV
C.C.	9,0 ± 0,4	3,6 ± 0,5	86,00 ± 17,45	23.06 ± 3.55	647 ± 25
$P_{10}H_{200}$	12,9 ± 1,5	4,4 ± 0,9	107,83 ± 5,69	24.40 ± 2.35	714 ± 32
P_5H_{200}	7,9 ± 0,8	4,0 ± 0,9	86,57 ± 13,19	21.84 ± 3.02	589 ± 10
P_5H_{325}	10,2 ± 1,0	5,5 ± 0,5	69,53 ± 9,48	25.54 ± 1.87	960 ± 51
$P_{10}H_{325}$	10,5 ± 1,0	4,6 ± 1,1	98,03 ± 9,03	23.52 ± 2.86	749 ± 89

CC- conventionally cast.

The spray formed material P_5H_{200} presented smaller volumetric fraction of carbides disperse in the matrix and better wear resistance when considering pin-on-disk results. This relationship between volumetric fraction of carbides and wear resistance has been reported by other studies [13] when using hard abrasive and has been attributed to the ductility of matrix.
In summary, the hardness attained for the spray formed white cast irons herein studied is substantially higher when compared to the materials produced by conventional casting. In the present wear evaluation conditions, it could be also verified that the spray cast material is slightly better for coarse abrasive paper and for fine abrasive material is similar to the conventionally cast white cast iron.

CONCLUSIONS

Spray forming process allowed the processing of high chromium white cast irons, producing higher hardness, when compared to the same material, conventionally cast, due to the presence of fine M_7C_3 type carbides homogeneously dispersed in a martensitic matrix. Nevertheless, a significant enhancement of the wear resistance, under the wear conditions analyzed, was not observed. Pin-on-disk results showed that the higher wear resistance is related to microstructures with higher volumetric fraction of austenite and lower values of hardness. Otherwise, a microstructure with a high volumetric fraction of carbide and higher values of hardness showed a better performance by sand/rubber wheel tests. These results are attributed to the wear mechanisms that prevail for the pin-on-disk test, microcutting, and the sand/rubber wheel test, microfurrow.

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