NiCrSiBC Alloy Processed by SPS

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Abstract

Nickel superalloys of the Ni-Cr-Si-B-C system, known as the Colmonoy family, stand out for their high wear and corrosion resistance at high temperatures. These alloys are typically deposited onto stainless steel substrates for use as coating. Typically, deposition occurs by welding processes such as PTA (Plasma Transferred Arc) and Laser Cladding. The main objective of this work was to study the effectiveness of Spark Plasma Sintering in the processing of the Colmonoy-5 alloy. In the processing of samples, Colmonoy- 5 alloy powders were used, with average granulometry in the range of 44 to 105 µm. For the SPS sintering of the Colmonoy-5 alloy, the following parameters were used: pressure of 50 MPa, temperature of 900º C and sintering time of 15 minutes. The density of the sintered alloy was determined by the Archimedes method. Vickers hardness measurements were made, with load of 10 N. The structural characterization of the sintered alloy included microstructural analysis, performed by scanning electron microscopy (SEM), and phase composition analysis, where the present phases were identified by X-ray diffraction (XRD). The SPS sintering of Colmonoy-5 alloy powders was effective, achieving alloy densification above 90%.

Keywords: *Colmonoy, Sintering, Spark Plasma Sintering.*

I. Introduction

Hardfacing alloys are commonly categorized by Fe-based, Co-based and Ni-based. However, Fe-based hardfacing alloys should not be used for high temperature applications, due to their softening at service temperatures (>1000ºC). Similarly, hard Co-based alloys become radioactive in nuclear environments, and this phenomenon has restricted the use of Co-based coatings for high-temperature applications. Thus, nickel-based hardfacing alloys hardened primarily by borides, also known as Colmonoy, were developed. Currently, these alloys are popularly used for cladding materials. Among the hard Ni-based alloys, Colmonoy can be highlighted, which are in abundant use and with a wide variety of compositions [1,2].

Alloys from the NiCrSiBC family, such as Colmonoy, have as their main characteristic high resistance to wear and corrosion at high temperatures. These alloys were basically developed for deposition using some welding processes. Due to their excellent characteristics and lower cost compared to Co superalloys, Ni-based alloys have been deposited by various welding processes, such as plasma transferred arc (PTA), Tungsten Inerg Gas (TIG) and Laser Cladding [3-5].

The strength of NiCrSiBC alloys can be increased by the formation of precipitates such as borides and carbides. Some studies of the NiCrSiBC alloy deposited by laser cladding on steel substrate showed the presence predominantly of precipitated phases rich in chromium, such as chromium borides and carbides [6,7].

As already mentioned, NiCrSiBC alloys are normally deposited on a steel substrate by welding processes. There are numerous studies that report the negative influence of Fe dilution on the properties

of these alloys, as well as an increase in the ZTA (thermally affected zone) when these alloys are deposited by welding methods.
Spark plasma sintering (SPS) can also be a processing route for Nickel-based alloys, although it is still little explored [8].
The SPS process uses high pulsed current simultaneously with the application of uniaxial pressure to consolidate the powders and may use vacuum in the sample chamber or use a protective atmosphere [9]. The process scheme is shown in figure 1.

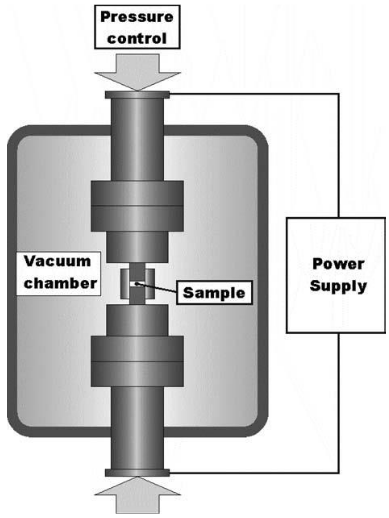

Figure 1. SPS process schematic. The matrix, as well as the pistons that transmit the pressure, are made of graphite [9].

Spark Plasma Sintering (SPS) is a recent technique, which offers some advantages over other sintering techniques. It is a successful route in consolidating a wide range of materials, such as metals and metallic nanomaterials, composites, solid materials, electronic materials, biomaterials [10,11]. Furthermore, the processing of thermoelectric materials by SPS is also considered viable and consolidated technique [12,13]. The positive points include ease of operation, precise sintering energy control, high sintering speeds, safety, and reliability [14,15].
The properties of Colmonoy alloys are strongly related to the processing technique. Therefore, this work investigated the processing of the Colmonoy-5 alloy via SPS as an alternative technique to conventional deposition welding processes.

II. METHODOLOGY

For samples processing, commercial Colmonoy-5 alloy powders (NiCrSiBC) were used, produced by the manufacturer WallColmonoy Corporation. The powders were produced using the atomization technique. The average particle size of the powders was provided by the manufacturer. To analyze the morphology of the powders, images were taken via confocal microscopy. XRD analysis was also carried out in order to identify the phases present in the initial powders.
The Colmonoy-5 alloy was sintered using the SPS technique, maintaining pre-determined technological parameters in the work of [16], as shown in table 1. SPS sintering was carried out under vacuum.

Table 1. Sintering parameters by SPS.

Processing Technology	Pressure	Temperature	Sintering Time
Spark Plasma Sintering	50 MPa	900º C	15 minutes

Graphite matrix and pistons were used to obtain the samples. Before starting sintering, the matrix assembly stage takes place. The alloy powder is inserted into the matrix and ends closed with pistons that will transmit pressure to the sample (powder). After the assembly stage, this system is taken to the

SPS equipment to start heating by pulsed current with simultaneous application of pressure. Cylindrical samples with diameter of 5 mm and average height of around 10 mm were generated (Figure 2).

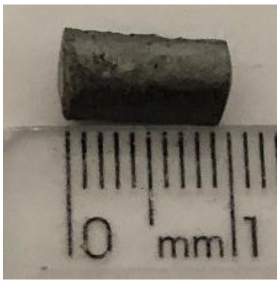

Figure 2. Sample after powder consolidation by SPS.

After sintering, the density of the sintered bodies was first determined using the Archimedes Method, as shown in equation 1. The calculation of the bulk density was based on the value of the dry mass of the sintered material (dm), mass of the same immersed in water (im) and the saturated mass (sm) that is obtained after the sample is subjected to boiling for a period of 20 minutes. The relative density (%), was obtained by the quotient between the experimental bulk density (sintered material) and theoretical density of alloy (8.14 g/cm³).

$$Density = \frac{dm}{(sm - im)}\ x\ \rho_{H2O} \tag{1}$$

To evaluate the microstructural aspect of the sintered body after SPS, Scanning Electron Microscopy (SEM) images were obtained. Before SEM analysis, the samples were metallographically prepared, first being sanded (100 to 1200 mesh), then polished and subjected to chemical attack. Phase identification was carried out through X-ray diffraction (XRD) analysis. The samples were analyzed under Cu-Kα radiation in a 2θ range of 20º to 90ºC, at a step of 0.05º for 3 seconds.
The characteristic peaks in the diffractograms obtained were analyzed, and the results were compared with the ICDD (International Center Diffraction Data) database, to help identify the phases present.
The Vickers hardness tests were carried out using a digital microhardness, making 5 indentations in each sample and applying a load of 10 N during the tests, for a period of 10 seconds.

III. Results and Discussion

The images of the Colmonoy-5 alloy powders used in sintering are shown in figure 3. Predominantly spherical shape of the alloy powder particles is observed, indicating a very regular morphology. The average powder size was predominantly in the range of 44 to 105 µm.

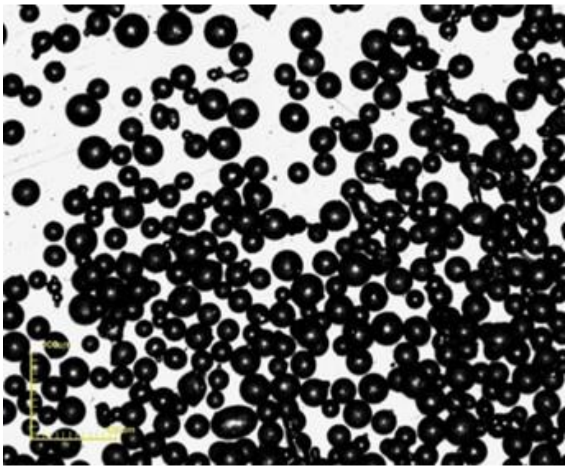

Figure 3. Confocal Microscopy showing regular morphology of the powders.

The XRD results of the initial powders are presented in figure 4. The presence of nickel can first be highlighted, which is base element of the Colmonoy-5 alloy. In addition, several borides (CrB, Ni_2B, Cr_2B, Ni_3B and Cr_5B_3) were identified, as well as chromium carbide Cr_7C_3.

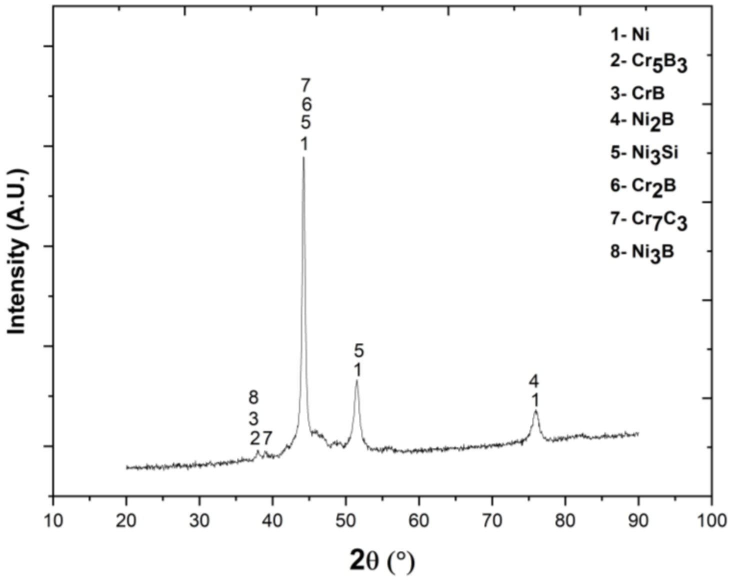

Figure 4. XRD of Colmonoy-5 alloy initial powders.

Figure 5 shows the diffractogram of the Colmonoy-5 alloy after SPS sintering. In all sintered samples, in addition to nickel, the presence of several important phases was identified, such as borides (CrB, Ni_2B, Cr_2B, Ni_3B and Cr_5B_3), as well as chromium carbide Cr_7C_3. The phases verified in the XRD analysis of bodies sintered by SPS are the same as those obtained in the diffractograms of the initial powders, which is in perfect agreement with the work of [17]. It is worth mentioning that there are practically no scientific studies reporting such phases for sintered Colmonoy-5 alloy, because most articles study the alloy deposited by welding processes. The presence of carbon peak can also be attributed to the graphite matrix used in the alloy sintering process.

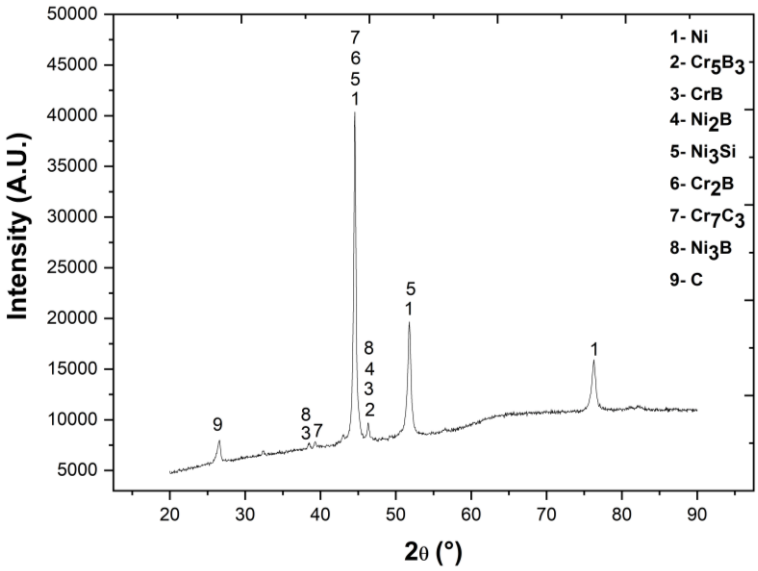

Figure 5. XRD of Colmonoy-5 alloy after sintering SPS.

The microstructural aspect of the bodies sintered by SPS can be observed in figure 6, which is an SEM micrograph using backscattered electrons and magnification of 4000x. It can be noted that the phases are well distributed in the Ni-matrix and there is little porosity. It is also observed the presence of phases with different morphologies, such as the shape of needles and rods with darker tone, and another greyish tone (half tone) in the lighter matrix.

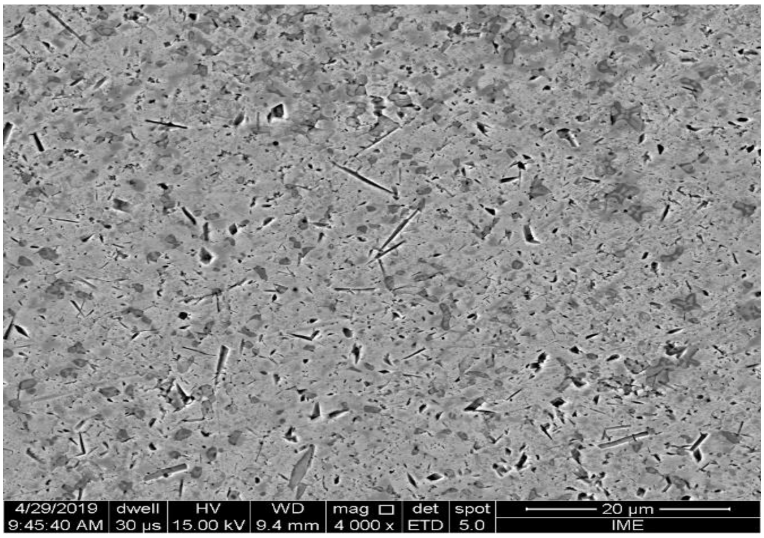

Figure 6. SEM of Colmonoy alloy sintered by SPS at 50 MPa (4000x).

Comparing with the results of the work of [6,7,17], it can be said that the darker phases are probably borides, and the carbides are presented in the form of plates or slats in a lighter tone (half tone).
The mentioned phases can also be observed in a broader way in the micrograph of figure 7 with a lower magnification (2000x), but now, secondary electrons were used to obtain the micrograph in the SEM. Again, we have some dark phases in the form of small needles (see arrows) and the half-tone phases can be seen as interconnected islands (see circles) spread across the matrix phase, with the same observations as in figure 6.

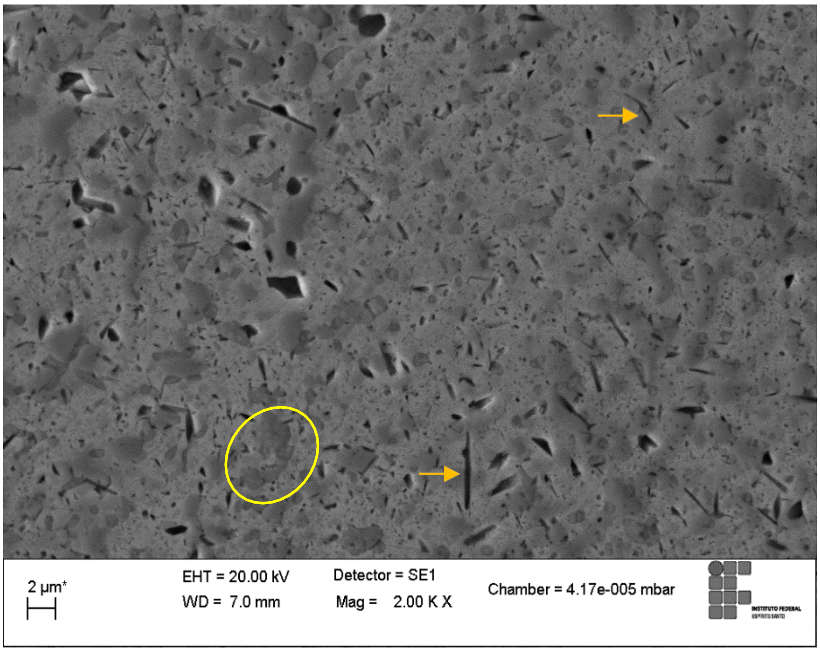

Figure 7. Phase distribution of sintered bodies by SPS.

Table 2 shows the average experimental density values, based on measurements of 4 samples, with their respective standard deviations. In general, it can be said that there was no significant variation in the density values verified, since the values were concentrated around 7.5 g/cm³ on average. This corresponds to approximately 92% densification (experimental density/theoretical density), which indicates that SPS sintering was effective.

Table 2. Bulk density calculated by the Archimedes Method.

Pressure (MPa)	Bulk Density (g/cm^3)	SD
50	7,50	±0,107

The average Vickers hardness value verified for the Colmonoy-5 alloy was around 625 HV, which agrees with several works reported in the literature for deposited alloy, such as in the studies by [6,7]. Figure 8 shows an indentation made on one of the samples in the hardness test. One can clearly observe the absence of cracks on the diagonals, which indicates good fracture toughness of the alloy after sintering.

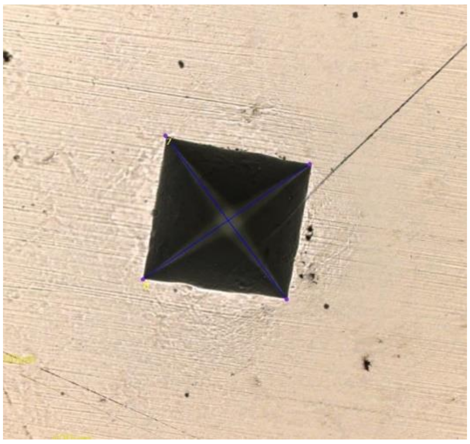

Figure 8. Indentation showing absence of cracks, as well as plastic deformation of the alloy on the diagonals.

IV. CONCLUSIONS

Microstructural analysis showed that the phases formed after SPS are the same as those found for the deposited Colmonoy alloy.

Colmonoy-5 alloy can be hardened by chromium borides and carbides. XRD analyzes confirmed the presence of such precipitated phases, justifying the satisfactory hardness values found.

The measured average hardness agrees with the literature on studies on Colmonoy alloys.

It can be said that the SPS sintering of the Colmonoy-5 alloy was effective, as 92% densification was achieved. Thus, the SPS process can be a promising processing route for NiCrSiBC system alloys.

The use of sintering (powder metallurgy) in the processing of NiCrSiBC family alloys is still an open field. Therefore, it is expected that the scientific results of this work will strongly contribute to more researchers developing scientific studies on this processing route for the alloys studied here.

ACKNOWLEDGEMENTS

The authors are grateful for the support of the Brazilian institutions FAPERJ, IME, and IFES campus Vitória/ES throughout the development of this study.

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