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## Structural, mechanical and thermal characterization of an Al-Co-Fe-Cr alloy for wear and thermal barrier coating applications



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## ABSTRACT

A structural, mechanical and thermal characterization of an Al-Co-Fe-Cr coating alloy was performed. An atomized powder with atomic composition of  $Al_{71}Co_{13}Fe_8Cr_8$  was thermally sprayed by high velocity oxygen fuel (HVOF) on a steel substrate. X-ray diffraction, scanning and transmission electron microscopy and differential scanning calorimetry were used to characterize the atomized powder and the sprayed coating. Vickers microhardness and pin-on- plate wear test were carried out for mechanical and tribological characterization and an infrared camera was used to evaluate the insulation capacity of the coating material. The results show that both the atomized powder and the coating material were composed predominantly by a quaternary extension of the hexagonal  $Al_5Co_2$  phase and by the monoclinic  $Al_{13}Co_4$ . Both phases are quasicrystalline approximants of a decagonal Al-Co quasicrystal. The coating samples presented high values of micro-hardness, close to 500 HV and substantially low friction coefficient values, around 0.05. The coatings were good thermal insulators, decreasing by 30% the surface temperature of a sample exposed to a hot plate in comparison with the carbon steel substrate. © 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

Quasicrystalline and intermetallic approximant phases present interesting physical and transport properties for protective coating applications [1]. Quasicrystalline materials have very particular structures with crystallographic features very different from conventional crystalline materials. They present an ordered structure with rotational symmetries as fivefold, eightfold, tenfold and twelvefold [2] that are forbidden for crystalline solids.

Close to the quasicrystalline phase compositions, intermetallic approximants may be present and they show structure and properties similar to those of quasicrystalline phases [3]. The intermetallic approximants present complex crystalline structures, which usually consist of large unit cells. This is of great importance for the electronic properties, leading to low thermal and electron conductivity and applications as thermal barrier coatings [4].

Up to now, a large number of metallic systems were shown to form quasicrystalline and intermetallic approximant phases, most of them being aluminum based systems such as Al-Cu-Fe [2,5,6], Al-Co [7–9], Al-Cu-Fe-Cr [10,11], Al-Co-Ni [12–14].

In a recent publication [15], the phase formation in the system Al-Co-Fe-Cr has been assessed in detail, particularly for the  $Al_{71}Co_{13}Fe_8Cr_8$ (at.%) composition. It was shown that the main phase formed in this alloy was a quaternary extension of the hexagonal  $Al_5Co_2$  phase. The formation of the monoclinic  $Al_{13}Co_4$  was also observed at grain boundaries of the hexagonal phase. Those phases are intermetallic approximants of a decagonal Al-Co quasicrystalline phase [12].

Potential applications of the  $Al_{71}Co_{13}Fe_8Cr_8$  (at.%) alloy as thermal barrier coating (TBC) depends on its physical properties. A low thermal conductivity and a thermal expansion coefficient close to those of steels [3,5] make this alloy of interest for TBC applications. Indeed, thermal stress due to mismatch between substrate and coating material is the most important cause of failure of traditional ceramic thermal barrier coatings, such as the partially stabilized zirconia [16]. In addition to that, the  $Al_{71}Co_{13}Fe_8Cr_8$  alloy has been proven to have an excellent oxidation resistance [17], which is essential for high temperature applications. This alloy starts to form liquid phase around 1100 °C and thus maximum temperatures of 900 °C should be the limit for application of this composition. Also, when this TBC alloy is applied on a Fe-based substrate above 700 °C interfusion between coating and substrate becomes intense and application of an interfusion barrier is necessary [5].

As a result, the above-mentioned properties coupled to good wear properties make this alloy even more promising for protective coating applications. Intermetallic quasicrystalline approximants usually present similar properties to those of the related quasicrystals and therefore,

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it is expected that this Al<sub>71</sub>Co<sub>13</sub>Fe<sub>8</sub>Cr<sub>8</sub> alloy shows interesting wear properties such as low friction coefficient and high hardness.

Moreover, thermal insulation properties and tribological properties have not been characterized so far for this alloy in a coating form. This study aims at revealing these properties on coated samples of Al<sub>71</sub>Co<sub>13</sub>Fe<sub>8</sub>Cr<sub>8</sub> alloy made by HVOF thermal spray.

Both atomized and HVOF sprayed samples were structurally characterized to clarify some inconsistences in the literature regarding the phase formation of this  $Al_{71}Co_{13}Fe_8Cr_8$  alloy produced by these techniques. The formation of a single dodecagonal quasicrystalline phase was reported in reference [18]. However, the electron diffraction patterns presented showed no quasiperiodicity, which must be present for quasicrystalline structures. In another study [19], the same atomized composition was reported to form seven different phases, among them, intermetallic and quasicrystalline phases.

Thus, a more detailed structural characterization of this system is necessary and this is the object of the present work.

#### 2. Materials and methods

The Al<sub>71</sub>Co<sub>13</sub>Fe<sub>8</sub>Cr<sub>8</sub> (at.%) alloy was gas atomized using commercially pure elements. The alloy was atomized with an overheating of 120 °C above the melting temperature at a pressure of 10 bar. Nitrogen gas and a 4 mm nozzle were used to produce powder for the high velocity oxygen fuel (HVOF) process. Afterward the as-atomized powder was sieved to a particle size ranging from 20 to 53  $\mu$ m and thermally sprayed by HVOF. The coating was applied on a 1020 steel plate with dimensions of 120 × 30 × 4 mm. The substrate was previously sand blasted in order to improve adherence of the coating material. Roughness of Ra = 1.16 ± 0.11  $\mu$ m was obtained from the sand blasting process. An Olympus LEXT OLS4100 confocal microscope with laser scanning was used to measure the roughness. Fig. 1 shows the topography of the sand blasted substrate. Table 1 summarizes the HVOF spraying parameters.

The atomized sieved powder, ranging from 20 to 53  $\mu$ m, and the coating were characterized by X-ray diffraction (XRD) with a Siemens D5005 X-ray diffractometer using a Cu-K $\alpha$  radiation. XRD analysis of the coating sample was performed in the surface of the as deposited material. Scanning electron microscopy (SEM) with a Philips XL-30 FEG and transmission electron microscopy (TEM) with a FEI TECNAI G2 F20 200 kV were used for this study. Samples of the coating and of the powder, for microstructural analysis by SEM were prepared by grinding up to a 1500 grit sand paper and then by polishing using a 1  $\mu$ m alumina. The porosity content of the coating samples was measured on 10 SEM images with magnification ranging from 1000 to 2000×, with use of the Image J software for measurement of the area fraction of pores. For TEM analysis, coating samples were carefully scratched from the substrate and then crushed into powdery form with the use of a mortar.

Table 1

HVOF spraying parameters used. A Praxair JP8000 HVOF torch was used for deposition.

HVOF parameters	
Substrate	1020 Steel
Powder size range (µm)	20-53
Oxygen flow (slpm)	826
Kerosene flow (l/h)	22.7
Oxygen/Kerosene equivalence ratio	1.2
Carrier gas	Argon
Scanning velocity (mm/s)	375
Step size (mm)	10
Standoff distance (cm)	38.1
Barrel (inch/mm)	2.5/63.5
Number of passes	12
Coating thickness (µm)	30

The powdery coating samples were then prepared by dripping a suspension of powder sample and methyl alcohol on a carbon grid. The atomized powder was also prepared by dripping a suspension of powder and methyl alcohol on a carbon grid.

The powder was also analyzed by differential scanning calorimetry (DSC) with a NETZSCH 404 DSC, under argon atmosphere. In addition to that, the powder was annealed at 1000 °C for 30 min under an argon atmosphere, in the DSC equipment. This experiment was performed in order to study the thermal stability of the phases observed in the ascast atomized powder. An inductively coupled plasma - optical emission spectrometry (ICP-OES) chemical analysis, in a VISTA Varian equipment, was used to analyze the chemical composition of the atomized powder. The ICP-OES analysis was performed in liquid medium. The powder was dissolved in a solution of 5 ml of HCl + 3 ml of H<sub>2</sub>O<sub>2</sub> + 100 ml of H<sub>2</sub>O.

The mechanical properties of the coatings were investigated by Vickers micro hardness using a load of 50 g and a Stiefelmayer KL2 micro-indenter. The coating was also submitted to a wear test using a pin-on-plate configuration with reciprocating motion conditions. The pin used was a 4140 steel with 595 HV and 8 mm of diameter. The stroke length was 50 mm. Loads, average velocities and stroke frequencies of the tests were 12 N:10 cm/s:1 Hz and 32 N:20 cm/s:2 Hz respectively. The wear tests were performed up to 1000 m or up to the failure of the coating samples. In the latter case, a sharp transition of friction coefficient values was used as an indicator of the failure of the coatings. The 1020 carbon steel substrates were also submitted to the same wear test for comparison. Wear test samples were sanded up to 1500 grit and then were polished with alumina. The coated sample was only smoothly sanded due to the low thickness of the coating. Surface roughness of the polished uncoated sample was  $Ra = 0.20 \pm 0.07 \mu m$ . Surface roughness of the polished coated sample was higher due to the irregular surface of the coating,  $Ra = 1.43 \pm 0.27 \,\mu m$ . The worn surfaces of the coating material were analyzed by SEM coupled to EDX in order to understand the wear mechanisms of the coating material.



Fig. 1. Surface topography of the sand blasted substrate. Roughness  $Ra = 1.16 \,\mu m$ .

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