

α -SiC-induced embrittlement in WC-(Co, Ni) hardmetals: Role of silicide formation and residual stress intensification

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ABSTRACT

This study systematically investigates the effect of adding α -SiC (0, 0.7, 1.3, and 3.2 wt%) on the microstructure, residual stresses, and mechanical performance of WC-11(Co, Ni)-based hardmetal processed by liquid-phase sintering at 1400 °C. A slight increase in hardness was observed, rising from 12.64 to 13.24 GPa with the addition of 0.7 wt% α -SiC. However, the transverse rupture strength (TRS) dropped by approximately 71% (from 1219 ± 114 MPa to 355 ± 87 MPa) at 1.3 wt% α -SiC, far exceeding the 10–20% losses typically associated with conventional grain growth inhibitors. Fracture toughness (K_{IC}) decreased by 57% (from 26.0 ± 5.6 to 11.2 ± 1.9 MPa m^{1/2}), accompanied by a transition from the Palmqvist crack regime to the radial-medial crack regime, indicating pronounced embrittlement. Densification was progressively impaired, with the apparent density falling by 3.4%. XRD and SEM analyses revealed the underlying degradation mechanism: partial dissolution of α -SiC promotes the formation of brittle $\text{Co}_{0.85}\text{Si}_{0.15}$, Co_2Si and Ni_2Si silicides, which consume the ductile binder phase, promote abnormal WC grain growth, and intensify compressive residual stresses (from -150 to -1000 MPa). These combined effects result in a pronounced reduction in mechanical strength and toughness. These combined effects result in a marked loss of mechanical strength and toughness. Overall, the results demonstrate that α -SiC, under the evaluated conditions, does not function as an effective reinforcement or grain growth inhibitor, but rather promotes microstructural instability through binder modification, silicide formation, and increased residual stresses, underscoring the need for careful control of composition and processing parameters for industrial applications.

1. Introduction

Common wear-resistant materials, such as Ni and Co, are used with varying proportions of carbides to improve wear resistance in engineering components [1]. This approach combines WC carbide with a Co–Ni metallic binder phase, forming a WC-(Ni, Co) composite [2]. The mixture of Ni and Co is advantageous because, in some engineering

applications, the applied load is transferred to the ductile metallic matrix (toughness) and to the hard phase (WC), providing high wear resistance [3]. In nickel-based hardmetal, such as WC-Ni, hardness increases significantly with the addition of SiC reinforcements. This increase can also be attributed to solid solution reinforcement in the nickel binder phase, promoted by silicon [4].

Cobalt plays a fundamental role as a binder phase in the liquid-phase

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sintering (LPS) process for traditional WC–Co alloys, with emphasis on densification mechanisms, wettability, dissolution-precipitation, and microstructural evolution during the process [5]. However, being a relatively scarce metal [6], expensive, and harmful to human health [7], there is a growing concern about restricting its use to applications (critical raw materials) where its presence is indispensable [2]. This scenario has led several researchers to investigate the partial or total replacement of cobalt with other metals to meet increasing technical and regulatory demands [8]. Among the metals studied, nickel has proven to be the most suitable for replacing cobalt as the binder phase. However, during sintering, nickel dissolves smaller amounts of W and C than cobalt during cooling, which causes the Ni–W–C alloy to exhibit lower hardness and strength properties than those observed in WC–Co hardmetals. The sintering of WC–Co composites occurs at temperatures between 1360 °C and 1600 °C, depending on the binder content, which ranges from 3 wt% and 30 wt% [9,10].

Compared with traditional WC–Co composites, WC–Ni alloys exhibit better corrosion and oxidation resistance [11]. Correia et al. [12] studied the effect of adding metallic silicon to the WC–Ni composite (10 wt% of Ni). They found that hardness, flexural strength, and fracture toughness were superior to those of a similar WC–10Co-based composite. Comparative studies indicate that WC composites alloyed with nickel and cobalt exhibit broadly similar mechanical properties [13], owing to the similar physicochemical characteristics of these metals, which differ mainly in their crystalline structure. Cobalt is allotropic, with an HCP structure below approximately 450 °C and FCC at higher temperatures, while nickel exhibits a stable FCC structure throughout the range of interest [14]. Thus, in Co–W–C alloys, the HCP↔FCC transformations of cobalt influence the mechanical behavior of the binder phase and, consequently, the performance of the composite.

The use of these Ni–Co combinations, as well as the inclusion of Fe as a binder phase in WC-based composites, has attracted considerable and frequent attention [8]. Co–Ni-based hardmetals exhibited slightly lower hardness and superior fracture toughness compared to WC–Co binder systems. At the same time, flexural strength proved to be relatively insensitive to variations in binder composition. Furthermore, the crack propagation threshold (K_{IC}) was higher in materials with coarser grains, a result associated with the greater effectiveness of crack deflection mechanisms promoted by the microstructure [15].

Some attempts to replace Co and add various carbides, in small quantities, to improve or reinforce the binder phase have been successful, but not always [16]. In many cases, these attempts failed due to several factors, including poor mechanical properties—including fracture toughness, hardness, and transverse rupture strength (TRS)—a lack of densification, and microstructural heterogeneity. Examples of this heterogeneity include abnormal WC grain growth and the formation of ternary phases, such as eta phases (M_6C or $M_{12}C$) [8]. The mechanical performance of these materials is strongly dependent on microstructural control during liquid phase sintering (LPS), especially regarding WC grain growth and binder phase distribution [17,18]. Abnormal grain growth significantly compromises transverse rupture strength (TRS) and fracture toughness [5].

Classical grain growth inhibitors, such as NbC, VC, and Cr_3C_2 , are already industrially established [19,20]. However, the addition of chromium intensifies the effect of η phases (M_6C or $M_{12}C$) formation compared to pure WC–Co [21]. Silicon carbide (SiC), in turn, has been proposed as an alternative additive due to its high hardness and thermodynamic stability. Some studies suggest that SiC can act as an inhibitor through grain-boundary anchoring. However, other studies report partial dissolution of SiC in the binder phase, formation of secondary phases, increased porosity, and even intensification of abnormal grain growth, depending on the sintering conditions [4]. These divergent results highlight that the role of α -SiC in WC-based systems is not yet fully understood. Furthermore, most research focuses on WC–Co systems and predominantly emphasizes increased hardness as the main performance indicator [20]. Systematic evaluations involving

densification, residual stress development, fracture toughness, and shear strength in WC–Co–Ni systems [14] are well established. However, WC–Co–Ni alloys containing SiC are still limited in the literature.

WC–Co based alloys with 10 wt% Co, known as grade DIN G20 or ISO K30/K40 grade [22], is widely used for cutting, machining, and rock drilling tools, due to its excellent hardness, fracture toughness, and wear resistance properties over a wide temperature range [23]. These materials exhibit high hardness, ranging from 15 to 20 GPa, depending on the applied load (10 to 45 kgf), a density of 14.45 g/cm³, a relative density of 99%, fracture toughness exceeding 10 MPa·m^{1/2} for loads of 15 and 30 kgf—a property that depends on the average grain size of WC—and transverse rupture strength (TRS) above 3000 MPa [21,22,24,25]. This unique combination of properties makes hardmetals the most recognized materials for numerous applications [16,26].

It is known that the binder phase plays an important role in the deformation behavior of hardmetals and it is important to investigate new alloys with alternative binder phases [16], such as Ni or Co–Ni combinations, with α -SiC additions [4], and compare them with traditional WC–Co alloys.

Silicon carbide (α -SiC) is a ceramic material widely used in the refractory [27], foundry, and abrasive industries. Its formation occurs in two phases, through the carbothermic reduction of silica: at 1700 °C, SiC- β (with a cubic crystal structure) is formed, and carbon monoxide (CO) is generated; and at approximately 2100 °C, the β -SiC structure is transformed into α -SiC, with a predominance of hexagonal crystal structure [4].

There is no consensus in the literature on the effectiveness of α -SiC as a grain growth inhibitor in WC–Co–Ni systems without compromising densification and overall mechanical integrity, especially regarding the evolution of residual stresses. The incorporation of new additives requires a balance between microstructural refinement and maintaining mechanical strength. In the case of SiC, the absence of a clear correlation between microstructure, residual stresses, and mechanical properties limits its safe technological application. The available literature focuses predominantly on WC–Co systems [22,24,25], prioritizing increased hardness as the main performance parameter and neglecting comprehensive evaluations of transverse rupture strength (TRS) and fracture toughness (K_{IC}). Furthermore, studies correlating the addition of α -SiC with the development of residual stresses are scarce, as are systematic investigations involving systems with a mixed Co–Ni binder phase, which limits the integrated understanding of the microstructural and mechanical effects associated with these composites.

This study aims to systematically investigate the effect of α -SiC additions (0–3.2 wt%) on the densification behavior, microstructural evolution, residual stress state, hardness, fracture toughness, and shear strength of WC–11(Co,Ni) composites processed by liquid-phase sintering. The central scientific hypothesis is that, while α -SiC may induce a marginal increase in hardness via localized microstructural refinement, its interaction with the Co–Ni binder alters liquid-phase sintering kinetics, promotes porosity formation, and exacerbates residual stresses.

These effects are expected to outweigh potential benefits, leading to a pronounced deterioration in fracture toughness and overall mechanical strength. To substantiate this hypothesis, complementary analyses including SEM fractography, porosity quantification, XRD phase identification, residual stress evaluation, and fracture toughness (K_{IC}) measurements are proposed. These investigations aim to verify the possible formation of η phases, silicide compounds, or disruptions in the carbon balance—factors widely recognized as critical to the mechanical performance of hardmetals [17,24,28]. Fracture toughness will be evaluated by Vickers indentation using a modified Palmqvist approach, commonly applied to cemented carbides, with the results comparatively assessed against two conventional models, namely the Shetty (radial–median crack) and Niihara formulations [23,29,30].

2. Materials and methods

For the development of this research, the following ceramic powders were used: tungsten carbide (WC) with 99.53% purity and Black Silicon Carbide for abrasives (α -SiC, 9–10 Mohs) with 97.0% purity; and the metallic powders: electrolytic cobalt (Co) with 99.97% purity and nickel carbonyl (Ni) with 99.85% purity, presented in Table 1.

For α -SiC ceramic powder, the specification indicates a fine particle size of 1200 mesh (Tyler), being black silicon carbide for abrasives, with an angular grain shape, a specific gravity of $3.22 \text{ g}\cdot\text{cm}^{-3}$, and particle sizes ranging from 1.0 to $7.0 \mu\text{m}$ (80% of the particles around $1.0 \mu\text{m}$). This generic information was obtained from the α -SiC manufacturer and is presented in Table 2.

The particle size distribution of α -SiC, also provided by the manufacturer (Table 2), indicates a fine, controlled powder with a restricted upper size limit ($D_3 = 7.0 \mu\text{m}$), indicating a low fraction of coarse particles. The D_{50} value between 2.5 and $3.5 \mu\text{m}$ confirms the predominance of fine micrometric particles. In comparison, the indication that approximately 80% of the particles are above $1.0 \mu\text{m}$ (D_{94}) suggests a relatively concentrated, though still polydisperse, distribution. According to the FEPA F1200 specification, the α -SiC powder exhibits a median particle size (D_{50}) of approximately $3.0 \mu\text{m}$, with particle sizes ranging from about 1.0 to $7.0 \mu\text{m}$. In general, this particle size distribution is compatible with α -SiC intended for applications as a dispersed rigid phase, favoring high surface area and directly influencing the mixture's packing and homogeneity.

WC and α -SiC carbides, along with metal powders (Co, Ni), were mixed and homogenized (via mass balance) using a conventional stirrer for 1 h, using isopropyl alcohol (2 l) at 3000 rpm, and subsequently dried in an oven at 120°C for 2 h with dynamic synthetic air ($\text{N}_2 \sim 80\%$ and $\text{O}_2 \sim 20\%$, prepared with high purity to simulate atmospheric air, but free of moisture). The chemical composition of the mixtures is presented in Table 3. For this research, WC and α -SiC were used as ceramic phases, and Co and Ni as metallic binder phases. A total of 4 kg of WC-11 (Co, Ni) mixtures was produced, divided equally into 4 batches, with 1 batch of 1000 g without the addition of α -SiC and the other 3 batches with the addition of α -SiC of 7 g, 13 g and 33 g, respectively.

Table 3 presents the weight balance (wt%) of four WC-11(Co, Ni)-based hardmetal compositions with progressive additions of α -SiC. Composition I (WC-11(Co, Ni)) is the reference alloy, containing 90.0% by weight of WC and 10% by weight of metallic binder phase, composed of 7.0 wt% Co and 4.0 wt% Ni. In compositions II, III, and IV, the addition of α -SiC (0.7, 1.3, and 3.2 wt%, respectively) occurs with a consequent proportional reduction in the WC content, while maintaining a constant fraction of the metallic binder phase (Co + Ni). This strategy ensures that microstructural and property variations are predominantly attributable to the incorporation of α -SiC, rather than to changes in binder content.

The theoretical specific gravity values presented in Table 3, 14.43; 14.20; 13.90 and $13.10 \text{ g}\cdot\text{cm}^{-3}$, respectively, are physically consistent

Table 1
Properties of metallic powders.

Powders (Symbol)	Theoretical density ($\text{g}\cdot\text{cm}^{-3}$)	Average grain size FSSS* (μm)	Purity (wt%)	BD ($\text{g}\cdot\text{cm}^{-3}$)	Origin (manufacturer)
WC	15.63	$3.5 \mu\text{m}$	99.530	4.0	Buffalo Tungsten Inc.
α -SiC	3.21	$\sim 3 \mu\text{m}$	96.800	–	Treibacher Alodur®
Co	8.90	$2.0 \mu\text{m}$	99.970	2.0	Nanjing Henri Cobalt
Ni	8.91	$4.8 \mu\text{m}$	99.847	2.5	CVMR Corporation

* Information obtained from quality certificates provided by manufacturers. FSSS refers to Fisher Sub-Sieve Sizer.

Table 2
Characteristic particle size data for α -SiC powder.*

Mesh	D_3	D_{50}	D_{94}
FEPA F1200	7.0 máx.	2.5–3.5	1.0 mín. (80%)

* Information obtained from quality certificates provided by the company Imerys Minerals Fused, Treibacher Alodur®.

Table 3
Properties of metallic powders.

Designations		Weight balance				Theoretical Specific Gravity (g cm ⁻³)
		Ceramic carbides		Binder phase		
		WC (wt%)	α-SiC (wt%)	Co (wt %)	Ni (wt %)	
I	WC-11(Co, Ni)-0SiC	89.0	0.0	7.0	4.0	14.43
II	WC-11(Co, Ni)-0.7SiC	88.3	0.7			14.20
III	WC-11(Co, Ni)-1.3SiC	87.7	1.3			13.90
IV	WC-11(Co, Ni)-3.2SiC	85.8	3.2			13.10

with the reported mass balance, showing the expected trend of density reduction with increasing α -SiC content. The increase in α -SiC content results in a progressive reduction in the theoretical specific gravity of the alloys, due to the lower density of α -SiC ($3.22 \text{ g}\cdot\text{cm}^{-3}$) compared to WC ($15.63 \text{ g}\cdot\text{cm}^{-3}$), directly reflecting the effect of the adopted mass balance. The theoretical specific gravity was calculated based on the rule of mixtures by mass fraction, according to Eq. (1).

$$\rho = \frac{1}{\sum_i \left(\frac{w_i}{\rho_i} \right)} \quad (1)$$

2.1. Characterization of ceramic and metallic powders

The characterization of WC, α -SiC, Ni, and Co powders was performed by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) for morphological and compositional analysis. A TESCAN microscope (Czech Republic) equipped with EDS and backscattered electron diffraction (BSE) systems was used. The equipment has a resolution of 1.4 nm at 30 kV and 3.0 nm at 3 kV in high-vacuum (SE) mode, and 2.5 nm at 30 kV in low-vacuum (BSE and SE) mode.

The particle size distribution was determined by laser diffraction using a Microtrac S3550 analyzer (USA), suitable for non-spherical particles, with a resolution of 25 nm and a measurement range of 0.02 to $2800 \mu\text{m}$. The actual densities of the powders were obtained using a helium pycnometer (AccuPyc II 1350, USA), while the specific surface area and average pore diameter were determined by N_2 physisorption using the Gemini II instrument (USA).

2.2. Compacted in green

The experimental procedure involved the fabrication of carbide-based test specimens and machining inserts using conventional powder metallurgy techniques. The WC-Co-Ni based mixtures, with and without the addition of α -SiC, were compacted by single-action, dry uniaxial pressing, without the use of polymeric or paraffinic binders. Compaction was performed in a steel die under uniaxial pressure of 100 MPa applied to all specimens, with a holding time of 30 s to ensure stabilization of the compaction process and uniform green density. Two distinct shapes were produced for each composition: rectangular geometry test specimens, with nominal dimensions of $10.0 \times 12.7 \times 31.8$

mm, for density, HV1 hardness, transverse fracture strength (TRS) and microstructural characterization tests; and machining inserts in the SMS E16 (F6) standard style, according to DIN 4966, for residual stress, XRD, HV30 hardness and fracture toughness (K_{IC}) tests. For each alloy, ten samples of each format were compacted.

It is worth highlighting that the chosen insert style, SMS E16 (F6), is a high-strength insert designed for medium-to-heavy roughing applications in ferrous materials and stands out for its versatility in machining operations. These inserts were produced to enable the performance of turning tests (at two points), which will be addressed at a later stage of this research and presented in a future publication. The choice of this format is aligned with the procedures established by the ISO 3685 standard, which defines methodologies for tool life tests in turning operations, including criteria for wear assessment, determination of tool end-of-life (TE), selection of workpiece material, and cutting conditions. In this way, the preparation of the inserts at this stage ensures the traceability and compatibility of the developed materials with standardized machining performance tests.

2.3. Differential scanning calorimetry and dilatometry

Differential scanning calorimetry (DSC) analysis was performed on the WC–11(Co, Ni) sample, without the addition of α -SiC, to identify thermal events associated with the melting of the binder phase, phase transformations, and possible formation of intermetallic phases. The tests were conducted on a SETARAM SETSYS Evolution instrument (KEP Technologies, France), under a dynamic argon flow of 20 mL·min⁻¹ and a heating rate of 10 °C·min⁻¹.

Dilatometry tests were performed on the WC–11(Co, Ni) alloys without the addition of α -SiC up to 1420 °C and on WC–11(Co, Ni)–1.3SiC up to 1400 °C, both with an isothermal plateau of 60 min. Additionally, the WC–11(Co, Ni)–1.3SiC alloy was evaluated at 1400 °C for holding times of 60 and 120 min to analyze variations in dimensional shrinkage. Dilatometric analyses were conducted on the same equipment, under a dynamic argon flow of 20 mL·min⁻¹ and a heating rate of 10 °C·min⁻¹.

2.4. Liquid phase sintering under vacuum

All green compacts (test specimens), without the addition of polymeric binders, were sintered simultaneously in a vacuum furnace with graphite heating elements (Thermal Technology Inc., Nevada, United States). The sintering cycle was conducted under a vacuum of 2×10^{-5} mbar (corresponding to <50 ppm O₂), beginning with a stage for isopropyl alcohol removal at approximately 200 °C. Subsequently, the temperature was increased at an average heating rate of 10 °C·min⁻¹ up to 1400 °C, where it was held for 60 min to promote adequate densification and microstructural evolution. After this stage, the samples were slowly cooled inside the furnace to minimize thermal gradients and the development of residual stresses.

2.5. Microstructural characterization via optical microscope and scanning Electron microscopy

Apparent porosity was evaluated by optical microscopy (Olympus, GX series) at 100× magnification, while microstructural analysis was conducted at 1500× magnification. Additional micrographs of the polished sections were obtained by SEM using SE and BSE detectors under high vacuum with a TESCAN Vega LMU microscope (Czech Republic) and a Quanta 650 FEG-SEM for morphological analysis and semi-quantitative chemical characterization.

Microstructural characterization of the WC–11(Co, Ni)– α -SiC samples sintered by liquid phase (LPS) was performed by scanning electron microscopy (SEM) using a Quanta 650 FEG microscope (FEI, USA), equipped with energy-dispersive X-ray spectroscopy (EDXS) and electron backscatter diffraction (EBSD). The system provides a resolution of

1.4 nm at 30 kV and 3.0 nm at 3 kV in high-vacuum (SE) mode, and 2.5 nm at 30 kV in low-vacuum (BSE/SE) mode. Grain size was determined on transverse sections by optical microscopy (Olympus) at 1000× magnification (20 μ m scale). The mean WC grain size was obtained using the linear intercept method combined with automated circular intercept analysis, employing *AxioVision Release 4.9.1* software, in accordance with ASTM E112. Test lines and concentric circles were superimposed on the micrographs, and the number of intersections with grain boundaries was automatically counted. The mean grain size was calculated as the ratio between the total test line length and the number of intercepts, with results reported as mean $\pm$ standard deviation.

The microstructures of the samples processed via Liquid Phase Sintering (LPS) were revealed by electrolytic corrosion, applying a voltage of 5 V for 5 s in a solution composed of 10 g of potassium hydroxide (KOH) dissolved in 100 mL of distilled water, due to the high corrosion resistance of tungsten-based alloys with a nickel matrix.

2.6. Evaluation of the density and porosity of the alloys produced

The density of the sintered bodies was determined by Archimedes' method using the ratio of the mass to the volume of the test specimen. Measurements were performed using dry samples, without impregnation. The volume was obtained indirectly by immersion in fluid, from the difference between the mass measured in air and the apparent mass in the fluid, according to Archimedes' principle. The specific mass of the sintered bodies was calculated according to Eq. (2).

$$\rho_{app} = \frac{m_d}{m_s - m_i} \cdot \rho_{fluid} \quad (2)$$

where, ρ_{app} : is the apparent density of the sintered composite (g cm⁻³); m_d : is the dry mass of the specimen (g), m_s is the saturated mass of the specimen measured in air (g), m_i is the apparent mass of the specimen immersed in water (g), and ρ_{fluid} is the density of water (≈ 0.998 g cm⁻³ at 20 °C). Based on the apparent density obtained by the Archimedes method, the total porosity (%) was determined from the relationship between the measured apparent density and the theoretical density of the material, according to Eq. (3).

$$\rho_{total}(\%) = \left(1 - \frac{\rho_{app}}{\rho_{real}}\right) \times 100 \quad (3)$$

2.7. Vickers hardness (HV) and fracture toughness measured using the indentation test

Vickers hardness tests were performed with loads of 1 kgf (HV1) and 30 kgf (HV30). Measurements at HV1 were conducted using a Mitutoyo HM-100-810 durometer. At the same time, tests at HV30 were performed using a Buehler VMT-7 durometer equipped with a square-based pyramidal Vickers indenter at an angle of 136° between faces. For each experimental condition, ten indentations were made, distributed to avoid overlapping stress fields and interference between impressions.

Hardness was determined from the average of 10 indentations per sample, with the associated standard deviation calculated to assess reproducibility. All procedures followed the recommendations of ISO 6507-1:2018 (Vickers hardness) and ISO 28079 (microindentation fracture toughness) standards. Vickers hardness (HV) was calculated using expression (4):

$$HV_c = \frac{1.854 \times F}{D^2} \quad (4)$$

where HV is the Vickers Hardness (GPa), c is the applied load (HV1 for 1 kg = 9.807 N and HV30 for 30 kgf = 294.2 N), F is the indentation load (kgf), and d is the average diagonal of the indentation (mm²).

Vickers hardness (HV) and fracture toughness (K_{IC}) will be compared with those of hardmetals alloys WC-10Co (grade G20, DIN or ISO K30/K40). Samples were prepared with sequential polishing to a 1 μ m finish.

Vickers indentations were performed with a load of 31.25 kgf (HV30) applied for 20 s, and the diagonals of the indentations were measured to calculate HV and crack length.

Fracture toughness (K_{IC}) was determined by the Vickers indentation method under a load of 30 kgf. Measurements of the indentation diagonals (2a) and crack lengths (c) were performed by optical microscopy immediately after indentation. The crack regime was classified based on the geometric ratio c/a , distinguishing between Palmqvist-type cracks ($c/a \leq 2.5$) and radial-median-type cracks ($c/a > 2.5$), according to criteria consolidated in the literature [29,30].

The K_{IC} values were estimated using the *Palmqvist* [23], *Niihara* [29], and *Shetty* [30] models, enabling comparison across different empirical approaches applicable to brittle materials and hardmetals. Only indentations that presented four well-defined, symmetrical, non-coalesced cracks, free from interaction with pores or surface defects, were considered valid. The coefficient of variation (CV%) was calculated as a criterion for statistical reliability. Fracture toughness is related to the critical stress intensity factor K_{IC} , a property that describes a material's resistance to crack propagation under applied stresses.

Averages of the diagonals without cracks (2a_{μm}) and with cracks (2c_{μm}) were determined from two impressions per sample, ensuring reproducibility. The crack regime classification was established by the geometric ratio $c/a \leq 2.5 \rightarrow$ Palmqvist regime and $c/a > 2.5 \rightarrow$ radial-median regime, as described by Niihara, Morena, and Hasselman [29] and Shetty et al. [30]. According to the classic formulation, expression (5), presented in the Palmqvist method, Applicable to short surface cracks:

$$K_{IC} = 0.0028 \sqrt{HV30} \sqrt{\frac{P}{T}} \quad (5)$$

According to the Shetty/Radia-median (Anstis) model, expression (6), this model is widely used for WC-Co hardmetals due to its better fit to the Palmqvist regime [30]. Shetty and radial-median have the same basis, with small differences in constants. For simplification, we will adopt the classical constants.

$$K_{IC} = 0.016 \left(\frac{E}{HV} \right)^{1/2} \frac{P}{c^{3/2}} \quad (6)$$

According to the Niihara Model (radial-median regime), expression (7) applies when the cracks exhibit radial-median behavior [29].

$$K_{IC} = 0.018 \left(\frac{E}{HV} \right)^{0.4} \frac{P}{c^{3/2}} \quad (7)$$

Where: HV30 is the Vickers hardness value (N/mm² or MPa) for a 30 kgf load, P is the indentation load in N (typically high loads such as 30 kgf are used in hardmetals) converted to Newtons (N), and T is the total sum of the crack lengths measured from the indentation corners (4 l), in millimeters (mm). The same test used to obtain the HV₃₀ results was used to evaluate fracture toughness (K_{IC}) using the Palmqvist method and alternative models (Shetty, Niihara, radial-median), considering an elastic modulus (E) of 580 GPa for WC alloys with 10 wt% binder phase [22,24].

Only indentations that presented four well-defined, symmetrical, non-coalesced cracks free from interaction with pores or surface defects were considered valid. The coefficient of variation (CV%) was calculated for each composition as a criterion for statistical reliability. All procedures followed the recommendations of the ISO 6507 (Vickers hardness) and ISO 28079 (microindentation toughness) standards.

2.8. Transverse Rupture Stress (TRS)

Transverse Rupture Strength (TRS) was determined using a three-point bending test on specimens with dimensions of 10.0 × 12.7 × 32.0 mm. The tests were performed on a properly calibrated EMIC universal testing machine at room temperature. Before testing, the

specimens were ground on all faces to ensure parallelism and adequate surface finish. For each chemical composition, corresponding to WC mixtures with 11 wt% of binder phase, 10 specimens were tested. The specimens were positioned on the supports of the three-point bending device, with a support spacing of 25.4 mm, and the load was applied at a constant displacement rate until fracture. The transverse rupture strength was calculated from the maximum recorded load, according to expression (8):

$$TRS = \frac{3}{2} \times \frac{P}{W} \times \frac{L}{t^2} \quad (8)$$

where, TRS: is the shear strength (MPa), P: is the breaking load (N), L: is the distance between the supports (mm), W is the width of the sample (mm), and t is the thickness of the sample (mm).

2.9. Analysis of residual thermal stresses and phase composition via X-ray diffraction XRD

X-ray diffraction (XRD) measurements were performed on a *Rigaku Ultima IV* diffractometer (Japan) using Cu-Kα radiation. Analyses were conducted in θ–2θ scanning mode over the angular range 25° to 125°, with a step size of 0.025°, a counting time of 2 s per step, a voltage of 40 kV, and a current of 30 mA. For the WC-based samples, considering a WC-10Co alloy (10 wt% Co), an elastic modulus (E) of 580 GPa and a Poisson's ratio of 0.23 were adopted [24], considering a 2θ diffraction angle of 136.63°.

Residual Thermal Stresses (RTS) were evaluated by X-ray diffraction (XRD) using a *Rigaku Automate II* diffractometer (Japan). X-rays were generated by a chrome tube (λ = 2.291 Å), operating at 40 kV and 20 mA. Residual stresses were determined using the $\sin^2\psi$ method [31]. The diffraction peaks were smoothed using the *Savitzky–Golay* algorithm [32].

The identification of crystalline phases was performed by comparison with the *ICDD* powder diffraction pattern (PDF) databases and by patterns calculated from structural data from the *ICSD*, *AMCSD*, and *COD* databases. For this, the *Crystal Impact Match and Crystallographica Search-Match* software were used, which allowed the identification of the WC, α-SiC, Co, and Ni phases, as well as possible intermetallic phases and other crystalline constituents formed.

3. Results and discussion

3.1. Characterization of powders

Fig. 1(a) (SEM-BSE, 20 keV, 1000 x) reveals compositional phase differentiation based on different chemical elements. This image shows a mixture of metallic (Co, Ni) and ceramic (WC, α-SiC) powders, with marked differences in particle shape and size, directly associated with the synthesis routes of each material.

Fig. 1(b) (SEM-BSE, 20 keV, 10000 x) provides higher magnification and topographical contrast. The brightest particles correspond to WC, exhibiting predominantly angular to polygonal morphology, well-defined contours, relatively rough surfaces, and a tendency to form compact agglomerates. The cobalt particles are the smallest, with rounded and irregular shapes, smoother surfaces, and greater deformability, allowing better accommodation between the ceramic phases. The nickel particles are the largest, presenting a porous (sponge-like) morphology and higher surface area. The darkest particle, identified as α-SiC, is more clearly visible in the BSE image (Fig. 1(b)).

Regarding α-SiC powder, it exhibits irregular, angular hexagonal particles (Fig. 2 SEM-BSE, 20 keV, (a) 2000× and (b) 7500×), characteristic of the α-SiC phase [27], with sharp edges, faceted surfaces, and a fragmented appearance, predominantly in lamellar and prismatic shapes resulting from brittle fracture.

In general, these particle size differences directly influence packing,

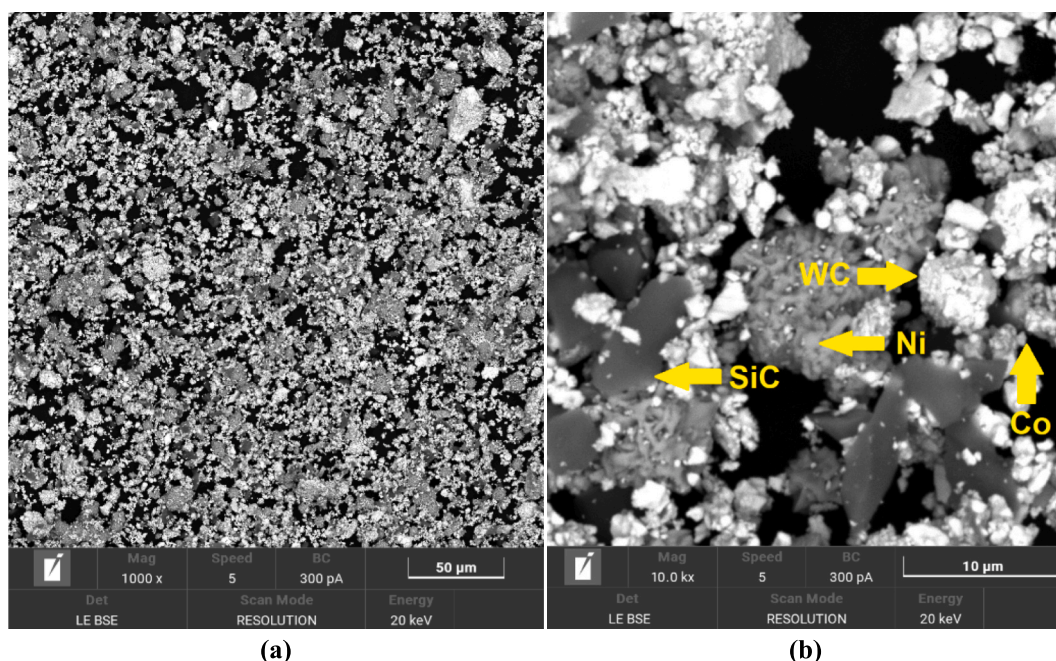


Fig. 1. Identification of the mixed constituents WC-11(Co, Ni)-1.3SiC: (a) BSE 1,000 $\times$, and (b) SEM-SE 10.0 kx magnifications.

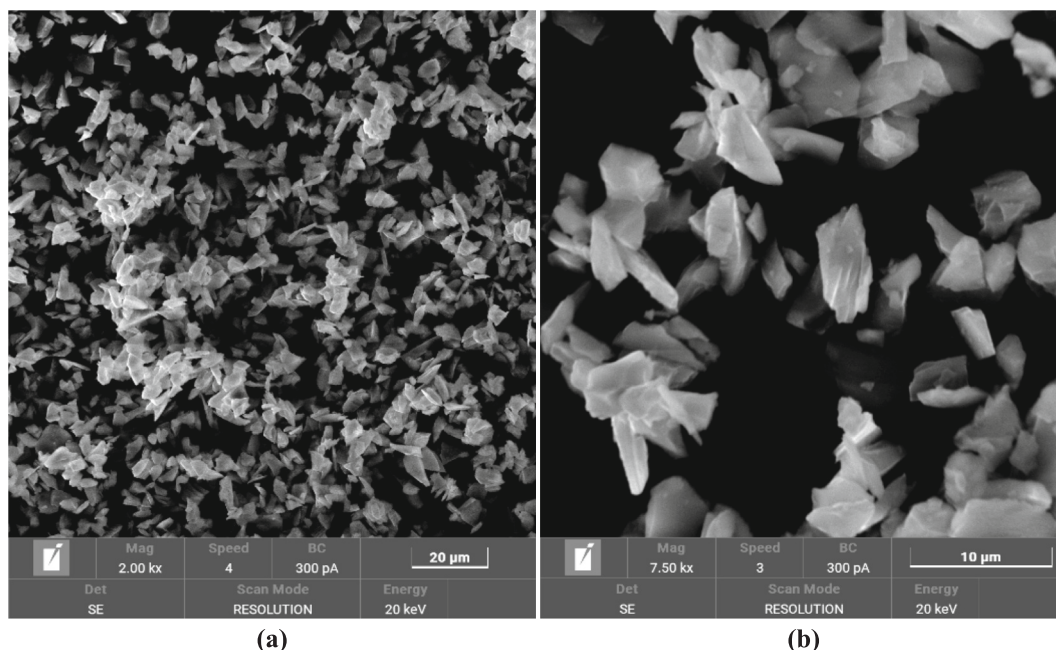


Fig. 2. SEM-SE α -SiC powder: (a) 2000 $\times$, and (b) 7500 $\times$ magnification.

mixture flow, and behavior during sintering, especially when metal powders serve as the binder phase and α -SiC as the dispersed rigid phase. Specifically, Co exhibits a more concentrated, asymmetric distribution, with a well-defined peak at a few micrometers, indicating a predominance of fine particles and less dispersion than in α -SiC. Ni, on the other hand, exhibits the widest distribution, shifting towards larger diameters and a long tail, reflecting greater size variability. WC shows a relatively narrow distribution, centered in the intermediate range (4–10 μ m), with good particle-size uniformity, a desirable characteristic for efficient packing.

α -SiC presents a broad, clearly multimodal distribution, with a significant fraction of fine particles (< 5 μ m) and an extended tail towards

larger diameters, indicating high dimensional heterogeneity and fragmentation/agglomeration. Table 4 presents the results of semi-quantitative chemical analysis of the α -SiC powder obtained by EDS. The chemical composition estimate by EDS (area) was obtained from Fig. 3, with a magnification of 2000 $\times$.

Based on the frequency curves and CPFT (cumulative passing curve) presented in Fig. 3, it can be observed that the fine powders exhibit distinct particle-size distributions consistent with their physical natures, as indicated by the manufacturers' generic information.

Table 4 shows that the material is predominantly composed of α -SiC (96.52%), indicating that the powder is not highly pure. The presence of impurities such as free Si or Si not combined with carbon (1.80 wt% Si)

Table 4

- Chemical composition of the supplied Silicon Carbide (α -SiC) powder.

Composition (wt%)	Carbon (free)	Si	SiO ₂	Fe	Al	α -SiC
	0.25	1.80	0.7	0.48	0.25	96.52

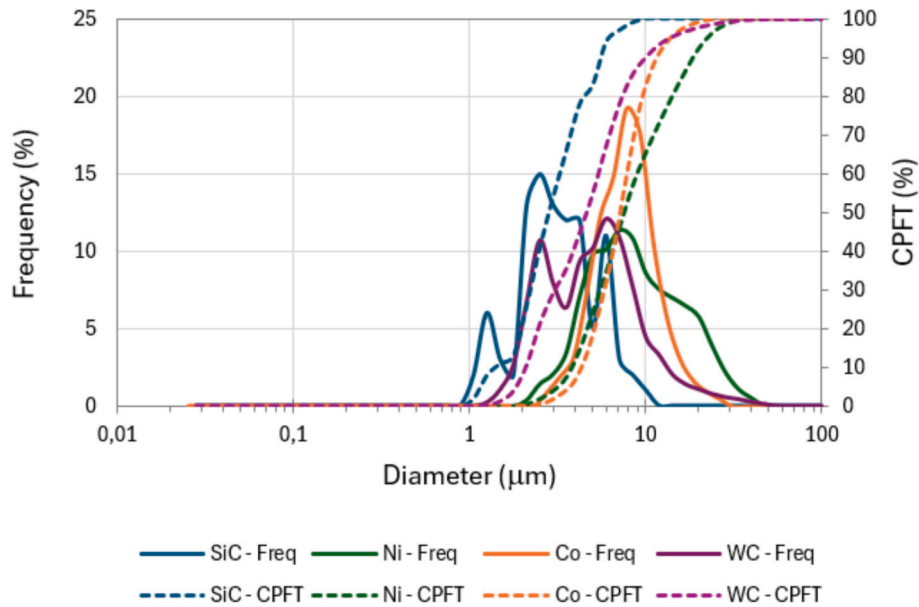


Fig. 3. Particle size distribution of WC, α -SiC, Co, and Ni powders: cumulative frequency and pass-through (CPFT) curves.

and SiO₂ (0.70 wt%) is relevant from a metallurgical point of view, since these species represent an additional load of oxygen and reactive elements, capable of interfering with the carbon-oxygen balance during the thermal processing of WC-Co alloys. SiO₂ can promote carbon consumption and favor the formation of undesirable phases (η phase), while free Si can dissolve in the metallic binder, altering its chemical stability. The residual contents of Fe (0.48 wt%) and Al (0.25 wt%) are attributed to contaminations from the processing route and, although relatively low, can act as inclusions or locally modify the binder chemistry. The small fraction of free carbon (0.25 wt%) tends to play a secondary role, possibly contributing partially to offsetting the carbon consumption associated with the presence of oxides. Still, it can also appear in microstructures as free carbon in the bonding phase.

The actual density values obtained with the helium pycnometer for the virgin raw materials, presented in Table 5, are consistent with the

values reported in their respective technical data sheets. Co powder has the largest specific surface area among the powders. The comparative analysis of the particle size distributions reveals systematic differences among the investigated materials. α -SiC exhibits the smallest mean particle size (3.55 μ m), characteristic of a fine powder with moderate dispersion. WC presents an intermediate mean particle size (6.42 μ m) but the broadest size distribution, as reflected by the highest coefficient of variation (CV = 61.7%). In contrast, Co displays a more homogeneous particle size distribution, with a mean size of 8.38 μ m and the lowest coefficient of variation (CV = 42.8%). Ni exhibits the largest mean particle size (10.58 μ m), associated with a moderately broad distribution (CV = 59.0%).

The WC powder had an average real density of 15.494 g·cm⁻³, slightly lower than the theoretical density. This difference suggests the presence of small fractions of closed porosity and/or residual oxides. The low specific surface area (0.624 m²·g⁻¹) indicates limited surface reactivity, which is favorable for controlling the carbon balance during sintering. The low total pore volume, associated with a relatively high average diameter, indicates a predominance of interparticle pores.

The Co powder had a real density of 8.422 g·cm⁻³, significantly lower than the theoretical value of 8.91 g·cm⁻³. This sharp reduction is associated with greater surface oxidation and/or the presence of closed porosity, in accordance with the high specific surface area measured (4.667 m²·g⁻¹). From a metallurgical point of view, this behavior makes Co powder the most critical component of the WC-Co mixture, since the associated oxygen can negatively impact the carbon balance and microstructural stability of the sintered alloy. Ni powder showed an average real density of 8.952 g·cm⁻³, a value very close to the theoretical density of 8.90 g·cm⁻³, indicating a lower degree of oxidation and closed porosity when compared to Co. The intermediate surface area (1.252 m²·g⁻¹) and the larger average pore diameter suggest a less fine agglomerate structure with lower chemical reactivity.

Using the results from Table 5, the theoretical specific gravity of the alloys was recalculated based on the actual densities of WC, Co, and Ni powders determined by a helium pycnometer. In contrast, for α -SiC, the

Table 5

- Actual density obtained by helium pycnometer, surface area, total pore volume, and average pore diameter of virgin raw materials used in the preparation of hardmetals parts.

Specification	Average grain size $x \pm \sigma$ (CV (%)) (μ m)	Average Real Density (g cm ⁻³)	Surface Area (m ² ·g ⁻¹)	Total Pore Volume (cm ³ ·g ⁻¹)	Average Pore Diameter (nm)
WC	6.42 $\pm$ 3.96 (61.7%)	15.494 $\pm$ 0.040	0.624	0.006	35.770
α -SiC	3.55 $\pm$ 1.79 (50.5%)	3.21 $\pm$ 0.030	5.012	0.010	<10.000
Co	8.38 $\pm$ 3.56 (42.8%)	8.422 $\pm$ 0.068	4.667	0.015	13.126
Ni	10.58 $\pm$ 6.24 (59.0%)	8.952 $\pm$ 0.031	1.252	0.012	38.974

theoretical density value was adopted, as its experimental characterization was not performed. The progressive replacement of WC by α -SiC resulted in a monotonic reduction in the theoretical specific gravity of the alloys, associated with the lower intrinsic density of α -SiC. It is also observed that the recalculated values are systematically higher than those previously obtained with purely theoretical densities, more realistically reflecting the characteristics of the powders used and providing a more consistent estimate of the expected density for the alloys after sintering.

For the WC-11(Co, Ni) alloy, without the addition of α -SiC, a theoretical specific gravity of $14.55 \text{ g}\cdot\text{cm}^{-3}$ was obtained. The progressive addition of α -SiC promoted a systematic reduction in the theoretical specific gravity of the alloys, reaching values of $14.33 \text{ g}\cdot\text{cm}^{-3}$ for the alloy with 0.7 wt% α -SiC, $14.12 \text{ g}\cdot\text{cm}^{-3}$ for 1.3 wt% α -SiC, and $13.46 \text{ g}\cdot\text{cm}^{-3}$ for the composition containing 3.2 wt% α -SiC. It should be noted that, although α -SiC is part of the studied system, the analysis of the actual density, specific surface area, and porosity of the α -SiC powder was not performed in Table 5; therefore, it is not possible to compare it with its theoretical density. It is also observed that the recalculated theoretical specific gravities differ from the values originally estimated based solely on the constituents' theoretical densities, more accurately reflecting the real characteristics of the powders used. In particular, the lower actual density of Co powder significantly influences the final density of the alloys, highlighting the importance of using experimental densities to estimate the theoretical specific gravity of modified WC-Co systems.

3.2. DSC result of the binder based on WC-(Co, Ni)

Fig. 4 shows the DSC of the WC-11(Co, Ni) system. An intense endothermic peak centered at 1200°C is observed [2], attributed to the beginning of liquid phase formation (Co, Ni). The plateau with a slight trend from 1230 to 1380°C is compatible with WC-Co alloys [5], a condition in which part of the binder is already in a liquid state (or highly enriched and with high mobility), and WC dissolution/precipitation in the binder and compositional redistribution occur, typical phenomena during the liquid stage (even when the liquid fraction is still low). After this event, the DSC signal stabilizes up to 1400°C , suggesting a regime dominated by binder redistribution and WC dissolution/precipitation, typical of the liquid stage of sintering. The sintering temperature for all samples was chosen based on this DSC analysis.

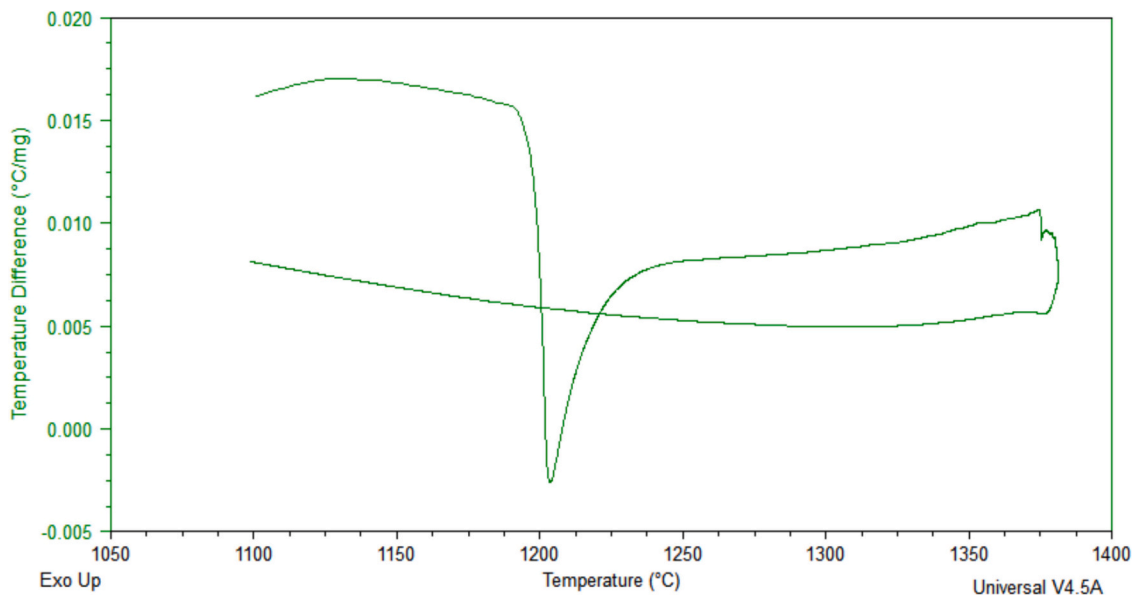


Fig. 4. DSC-TGA of the WC-11(Co, Ni) alloy without the addition of α -SiC.

Formation of a eutectic/ternary liquid composition under real conditions (Co-W-C): in practice, the system is ternary (W-Co-C); there is discussion of a eutectic temperature close to 1340°C and, in the presence of carbon/specific conditions, reports of the formation of a ternary eutectic with a lower effective temperature (on the order of 1280°C). The change from WC-Co to WC-Ni results in a significant increase in the equilibrium temperatures of the eutectic and peritectic points. The partial substitution of Co by Ni induces an increase in equilibrium temperatures, depending on the Co: Ni ratio. However, the prediction of the effects on the solid/liquid equilibrium temperature remains relatively small until the complete substitution of Co by Ni [33].

3.3. Results of the dilatometry of WC-(Co, Ni) and WC-(Co, Ni)-SiC based alloys

Fig. 5 and Fig. 6 shows the thermal expansion curves of the WC-11(Co, Ni) and WC 11(Co, Ni)-1.3SiC alloys, obtained in dilatometry tests with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The tests allowed monitoring the relative dimensional variation ($\Delta L/L_0$) of the specimens throughout the thermal cycle, as well as identifying the different stages of the densification process during heating and the isothermal plateaus.

In Fig. 5, a slight thermal expansion is initially observed for both alloys up to approximately 400 – 500°C , predominantly attributed to the thermal expansion of the solid constituents. From this range, a progressive contraction regime begins, associated with solid-state sintering, as particles rearrange and diffusion in the metallic binder begins. The WC-11(Co, Ni) alloy with the addition of α -SiC exhibits a more abrupt and intense contraction from about 1100 – 1200°C , culminating in a strong dimensional shortening during the isothermal plateau at 1400°C for 60 min. This behavior is characteristic of liquid-phase sintering, resulting from the formation of the liquid metallic binder and the consequent capillary reorganization of the WC binder system, promoting rapid densification.

On the other hand, the WC-11(Co, Ni)-1.3SiC alloy, heated to 1420°C with an isothermal plateau of 60 min, exhibits a distinct behavior. Although shrinkage associated with sintering is also observed, the shrinkage rate is more gradual, and the total shortening is significantly lower than that of the alloy without α -SiC. This effect indicates that the addition of α -SiC acts as a refractory phase and is not wettable by the metallic binder, restricting the mobility of the liquid and reducing the efficiency of the capillary densification mechanism during liquid-phase

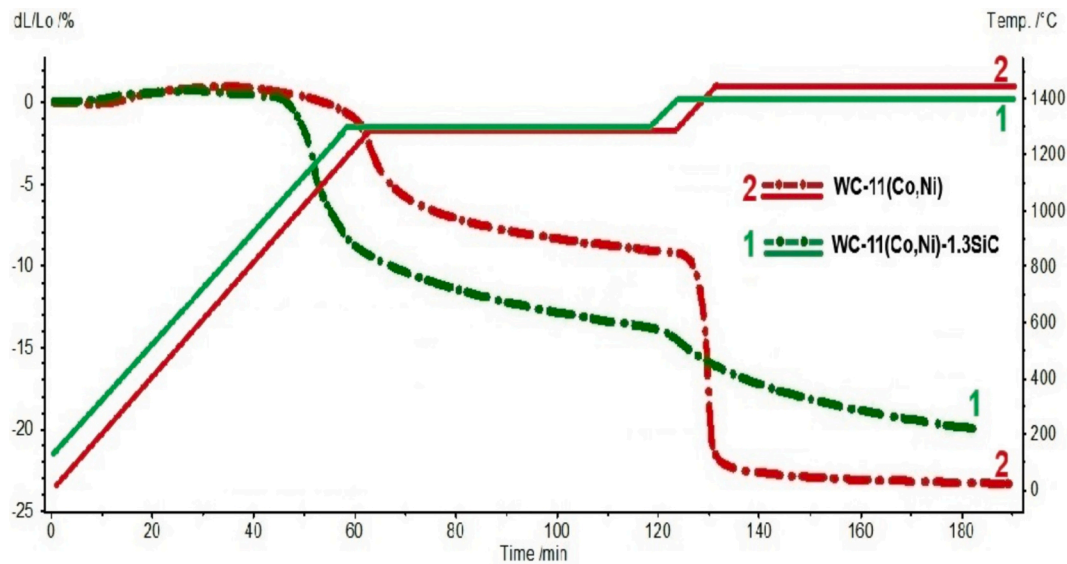


Fig. 5. Dilatometry of the WC-11(Co, Ni) 1.3SiC alloy at a temperature of 1420 °C and of the WC-11(Co, Ni) alloy without α -SiC at a temperature of 1400 °C, with stabilities of 60 min for both.

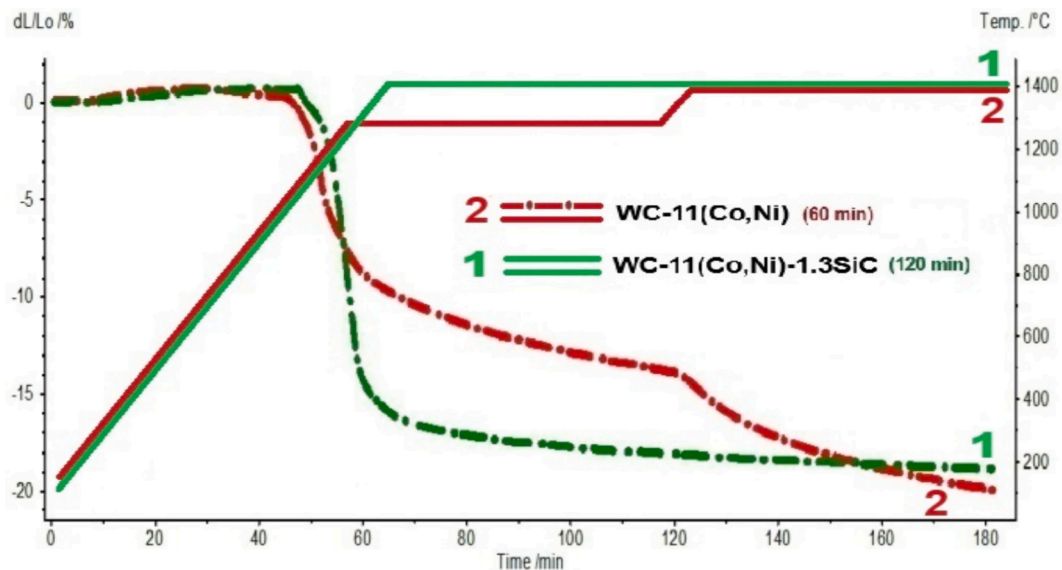


Fig. 6. WC-11(Co, Ni)-1.3SiC dilatometry, for the 60–120 min plateaus at a temperature of 1400 °C.

sintering.

Fig. 6 complements this analysis by comparing the dilatometric behavior of the WC-11 (Co, Ni)-1.3SiC alloy subjected to isothermal plateaus of 60 and 120 min at 1400 °C. It can be observed that increasing the plateau time promotes additional contraction, indicating continuity of the densification process over time. However, even after 120 min, the total shrinkage remains lower than that observed for the alloy without α -SiC, confirming that the presence of α -SiC limits densification, even under prolonged exposure times to the sintering temperature.

This DSC and Dilatometry analysis reinforces that the balance between binder fraction, sintering temperature, and thermal plateau time is crucial for obtaining stable microstructures and adequate mechanical performance. Aiming for good optimization of the binder phase, to achieve high densification (relative density above 99%), with control of grain growth, reflecting in improvements in the hardness-toughness combination [5].

In general, the dilatometry results demonstrate that the addition of α -SiC significantly alters the sintering kinetics of WC-11(Co, Ni) alloys,

reducing linear and total dimensional shrinkage and delaying densification associated with liquid-phase formation. These results are consistent with the relative density values obtained after sintering, in which alloys with higher α -SiC content showed greater residual porosity. Thus, dilatometry proved to be an effective tool for predicting dimensional variations in the specimens and correlating thermomechanical behavior with the sintering mechanisms operating in the α -SiC-modified WC-Co-Ni system.

3.4. Apparent porosity of samples via LPS

Micrographs obtained with optical microscopy, Fig. 7, without chemical etching, at 100 $\times$ magnification and with a 200 μ m scale bar, enable qualitative evaluation of the apparent porosity of WC-11(Co, Ni) alloys with varying α -SiC content. Porosity is identified as dark regions distributed in the light matrix, associated with residual voids from the sintering process.

The alloy without α -SiC addition (Fig. 7(a)) showed extremely low

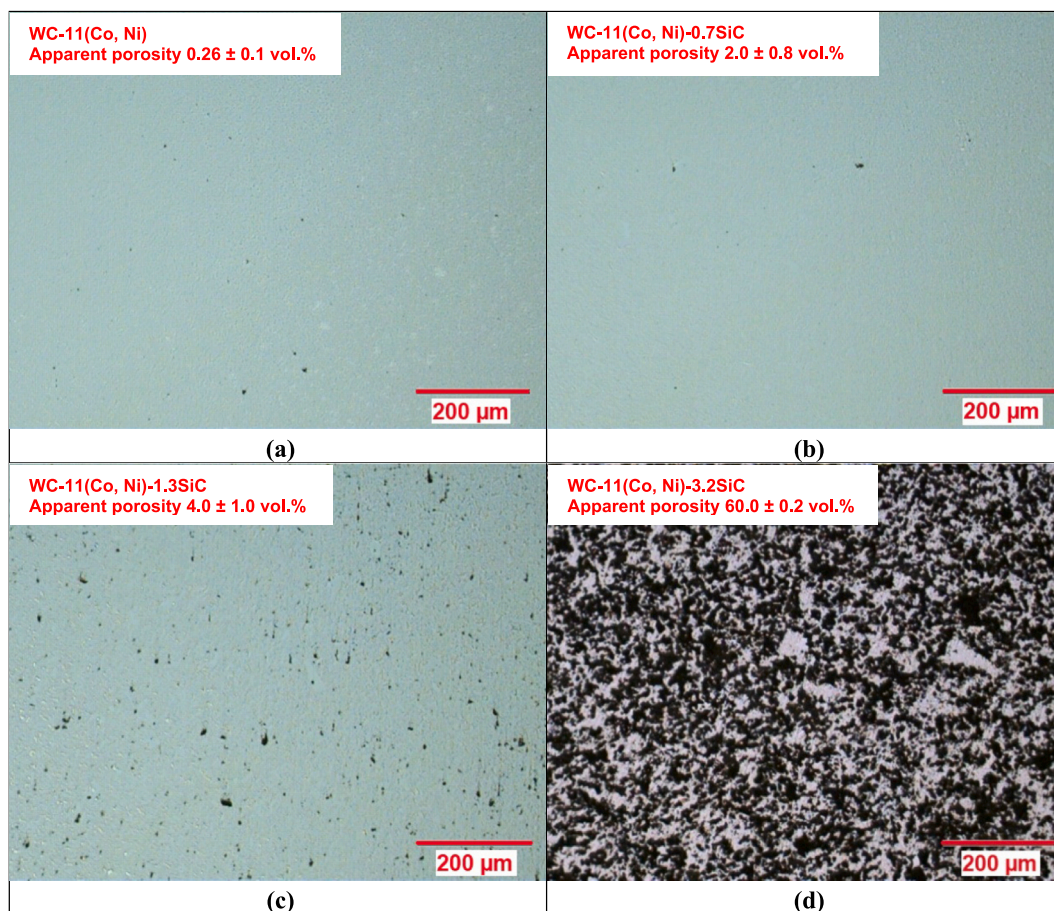


Fig. 7. Optical Micrographs (OM 100 $\times$, 200 μ m scale) for apparent porosity evaluation of WC-11(Co, Ni) alloys with different α -SiC contents: a) sem adiao de α -SiC; b) com 0.7SiC, c) com 1.3SiC; d) com 3.2SiC.

apparent porosity, on the order of 0.1%, indicating high efficiency of the liquid-phase sintering process and excellent mobility of the Co—Ni binder. A similar result was observed for the alloy with 0.7 wt% α -SiC, Fig. 7(b), whose apparent porosity remained below 0.1%, indicating that, at this content, the addition of α -SiC does not significantly compromise the material's densification. For the alloy containing 1.3 wt % α -SiC, Fig. 7(c), a measurable increase in apparent porosity was observed, reaching approximately 1.8%. This increase is associated with the partial dissolution of α -SiC in the metallic binder and the formation of Co_2Si and Ni_2Si silicides, which reduce the effective liquid fraction available during sintering, thereby hindering the complete elimination of voids.

In contrast, the alloy with 3.2 wt% α -SiC, Fig. 7(d), exhibited an extremely high apparent porosity of nearly 60%, confirming that the material did not sinter adequately under the conditions employed. The high fraction of interconnected pores is attributed to excessive consumption of the metallic binder by extensive silicide formation and the presence of residual α -SiC, which prevented the formation of a continuous liquid phase and resulted in incomplete sintering. (c) (d)

The presence of 0.25 wt% of free carbon in the α -SiC powder plays a relevant role in the observed microstructural evolution. At low α -SiC contents (0.7–1.3%), this additional carbon can help maintain the system's carbon-oxygen balance, preventing the formation of η phases (M_6C or M_{12}C) and favoring the stability of WC [25], as confirmed by XRD analysis. In general, the micrographs confirm that increasing the α -SiC content promotes a progressive increase in apparent porosity, which is strongly correlated with reductions in volumetric shrinkage and sintered density. The presence of free carbon in the α -SiC powder contributes to phase stability but does not prevent the degradation of sinterability at

high addition contents. These results directly corroborate the low values of volumetric shrinkage and sintered density previously discussed.

3.5. Microstructural characterization via SEM

Figs. 8(a), 8(b), and 8(c) present the Optical Microscopy (OM) micrographs of the WC-11(Co,Ni), WC-11(Co,Ni)–0.7SiC, and WC-11(Co, Ni)–1.3SiC alloys, respectively. Electrolytic etching at 5 V enabled phase identification through grayscale contrast, clearly revealing the WC grain boundaries. The α -SiC-free alloy exhibits a relatively homogeneous microstructure, whereas the α -SiC-containing compositions show a progressive increase in microstructural heterogeneity, with the presence of coarser WC grains dispersed within a fine-grained matrix, indicating the occurrence of abnormal grain growth.

Considering the occurrence of abnormal grain growth, the analysis was complemented by a qualitative assessment of the microstructural distribution, revealing the presence of significantly coarser WC grains dispersed within a fine-grained matrix, characterizing a heterogeneous distribution typical of abnormal grain growth. Although the intercept method provides a representative estimate of the mean grain size, the identification of this phenomenon requires a combined analysis of quantitative metrics and direct microstructural evidence.

A comparison of the microstructures reveals a clear evolution with increasing α -SiC content: the WC-11(Co,Ni) alloy exhibits a relatively homogeneous grain size distribution, whereas the addition of 0.7 wt% α -SiC already promotes the formation of isolated coarse grains. This effect is further intensified at 1.3 wt% α -SiC, where pronounced grain growth and loss of microstructural uniformity are observed. This behavior is directly associated with the partial dissolution of α -SiC

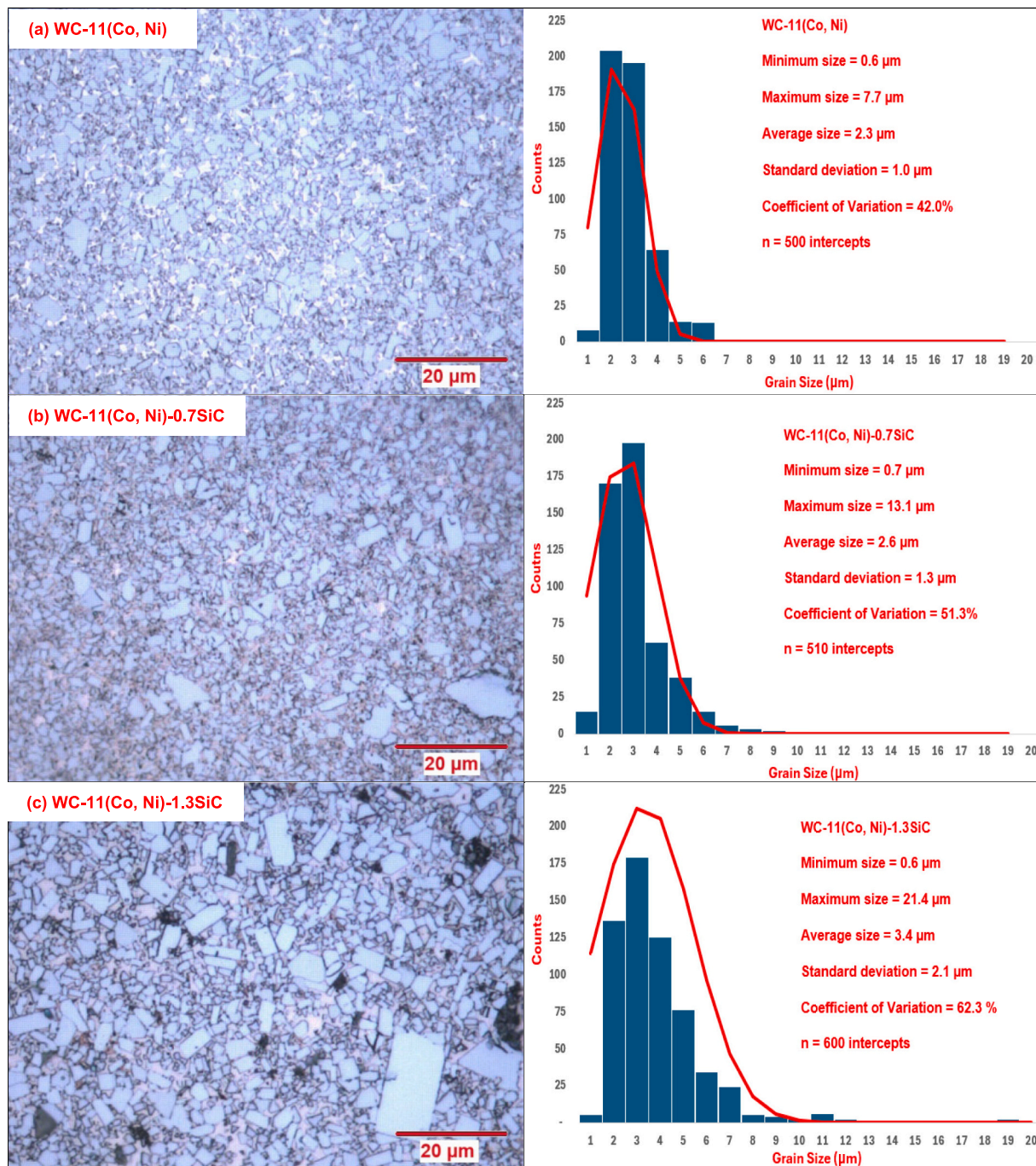


Fig. 8. Optical Micrographs (OM 1000 $\times$, 20 μm scale) used for WC grain size evaluation in WC-11(Co,Ni) alloys with different α -SiC: (a) without α -SiC; (b) 0.7 wt% α -SiC; (c) 1.3 wt% α -SiC. The mean WC grain size and corresponding standard deviation were determined using the linear intercept method in accordance with ASTM E112.

during sintering, leading to Si enrichment of the binder phase and the formation of silicides, which alters the dissolution–reprecipitation kinetics of WC and reduces grain boundary stability.

Additionally, the free carbon generated from α -SiC decomposition may locally modify the carbon balance of the WC–C system, promoting supersaturation conditions and liquid-phase instability, which contribute to the preferential growth of specific grains. As a result, the system evolves from a homogeneous microstructure to a regime dominated by abnormal grain growth, with direct implications for the degradation of mechanical properties.

For the composition containing 3.2 wt% α -SiC, microstructural characterization by optical microscopy (OM) and scanning electron

microscopy (SEM) was not feasible due to the lack of adequate consolidation after sintering. The samples exhibited high porosity and low structural cohesion, resembling green-state behavior, indicating severe limitations in densification. This result suggests that high α -SiC contents significantly impair liquid phase formation and wettability in the WC-(Co,Ni) system, preventing the development of a representative microstructure.

The statistical analysis of WC grain size (Fig. 8) reveals a clear evolution with increasing α -SiC content, even under identical sintering conditions (1400 $^{\circ}\text{C}$ for 30 min). The WC-11(Co,Ni) alloy exhibited a mean grain size of $2.3 \pm 1.0 \mu\text{m}$ (CV = 42.0%; $n = 500$), whereas the addition of 0.7 wt% α -SiC increased the mean size to $2.6 \pm 1.3 \mu\text{m}$ (CV =

51.3%; $n = 510$), accompanied by an increase in maximum grain size ($13.1 \mu\text{m}$). For 1.3 wt% $\alpha\text{-SiC}$, a more pronounced grain growth was observed, with a mean grain size of $3.4 \pm 2.1 \mu\text{m}$ ($\text{CV} = 62.3\%$; $n = 600$) and a maximum size of $21.4 \mu\text{m}$. The progressive increase not only in the mean grain size but, more importantly, in the standard deviation and coefficient of variation indicates a significant broadening of the grain size distribution, characterizing a transition from a relatively homogeneous microstructure to a regime dominated by abnormal grain growth. As all samples were processed simultaneously, these differences can be directly attributed to the effect of $\alpha\text{-SiC}$ addition, which promotes microstructural instability and preferential growth of WC grains.

Fig. 9, Fig. 10 and Fig. 11 shows, respectively, the EDS or EDX (Energy Dispersive X-ray Detector) analyses of the WC-11(Co, Ni), WC-11(Co, Ni)-0.7SiC and WC-11(Co, Ni)-1.3SiC alloy inserts, sintered at 1400°C ; performed on an EMU - Scanning Electron Microscope (SEM) Vega LMU, TESCAN, high vacuum mode (9×10^{-3} Pa) SEI = 3.0 nm at an acceleration voltage of 20 kV , electron gun – heated tungsten cathode, sample current 300 to 670 pA, with scan speeds ranging from 6 to 7 ms per pixel, magnifications of $10,000\times$. Using an electrolytic attack at 5 V , it was possible to identify the phases present in the gray scale, revealing the grain boundaries of WC. This method allows the distinction between WC (gray) hexagonal and irregular particulates and the binding phase around the WC (light), Fig. 9 and Fig. 10. In Fig. 11, solid solutions or W—Si and Ni—Si precipitates in the binding phase (Co, Ni).

Considering the elements detected by EDS (SEI), presented in Table 6, the elements Si, Co, Ni, and W are highlighted. The chemical element carbon is not considered, as this is a qualitative and semi-quantitative evaluation. The presence of W and Si in the EDS spectrum, Fig. 10, of the metallic matrix and EDS Fig. 11, indicates the possibility that dissolutions of $\alpha\text{-SiC}$ particles occurred in the binder phase (Co, Ni).

The results show that the addition of $\alpha\text{-SiC}$ intensifies the abnormal growth of WC grains, especially at higher temperatures, due to dissolution and reprecipitation during liquid-phase sintering. Although hardness increases slightly with $\alpha\text{-SiC}$, the reduction in TRS is significant, attributed to increased porosity, poor interfacial adhesion, and coarse grain growth.

3.6. XRD - diffractograms of samples, via LPS

In Fig. 12, the XRD shows a wide angular range ($25^\circ\text{--}125^\circ$) combined

with a fine step size (0.025°), enabling reliable phase discrimination among WC, the metallic binder (FCC/HCP), and silicide phases. Phase identification was performed by cross-correlating ICDD PDF files and calculated patterns from the ICSD, AMCSO, and COD databases using Match! and Crystallographica Search-Match software, ensuring robust analysis of this multicomponent system. The absence of η -phase reflections further indicates that carbon released from partial $\alpha\text{-SiC}$ dissolution did not induce critical decarburization of the WC phase.

The reference WC-11(Co, Ni) alloy sintered at 1400°C exhibited WC as the dominant phase with hexagonal structure, together with a Co—Ni metallic binder presenting the coexistence of Co-HCP and Co/Ni-FCC structures. The absence of η phase-type carbides indicates an adequate carbon balance during liquid-phase sintering, confirming the intrinsic phase stability of the WC—Co—Ni system [33]. This condition provides a reliable baseline for assessing the phase evolution induced by the addition of $\alpha\text{-SiC}$. With the addition of $0.7 \text{ wt}\%$ $\alpha\text{-SiC}$, additional diffraction peaks corresponding to $\text{Co}_{0.85}\text{Si}_{0.15}$, Co_2Si and Ni_2Si phases were detected, along with weak reflections associated with residual $\alpha\text{-SiC}$. These results indicate partial dissolution of $\alpha\text{-SiC}$ into the metallic binder during sintering, followed by preferential reaction of Si with Co and Ni in the liquid phase. At this composition, silicide formation is limited, and the metallic binder remains predominantly in the Co—Ni solid solution state.

Increasing the $\alpha\text{-SiC}$ content to approximately $1.3 \text{ wt}\%$ led to a marked intensification of the $\text{Co}_{0.85}\text{Si}_{0.15}$, Co_2Si and Ni_2Si diffraction peaks, accompanied by a relative reduction in the intensity of the Co—Ni FCC phase. This behavior suggests that this composition approaches the effective solubility limit of Si in the metallic binder, promoting the precipitation of thermodynamically stable silicides. Throughout this compositional range, the WC phase remains structurally stable, with no evidence of decomposition or formation of η -phases.

At the highest $\alpha\text{-SiC}$ content ($3.2 \text{ wt}\%$), Co_2Si and Ni_2Si phases become well defined and prominent, indicating substantial consumption of the metallic binder. The simultaneous presence of residual $\alpha\text{-SiC}$ suggests saturation of the binder's dissolution and reaction capacity at the sintering temperature of 1400°C . Across all compositions, the persistence of WC and the absence of η -phases indicate that $\alpha\text{-SiC}$ additions primarily modify the chemistry and phase constitution of the binder, which is expected to influence the balance between hardness and toughness of the hardmetals system.

The analysis of the X-ray diffraction (XRD) patterns of WC-11(Co, Ni)

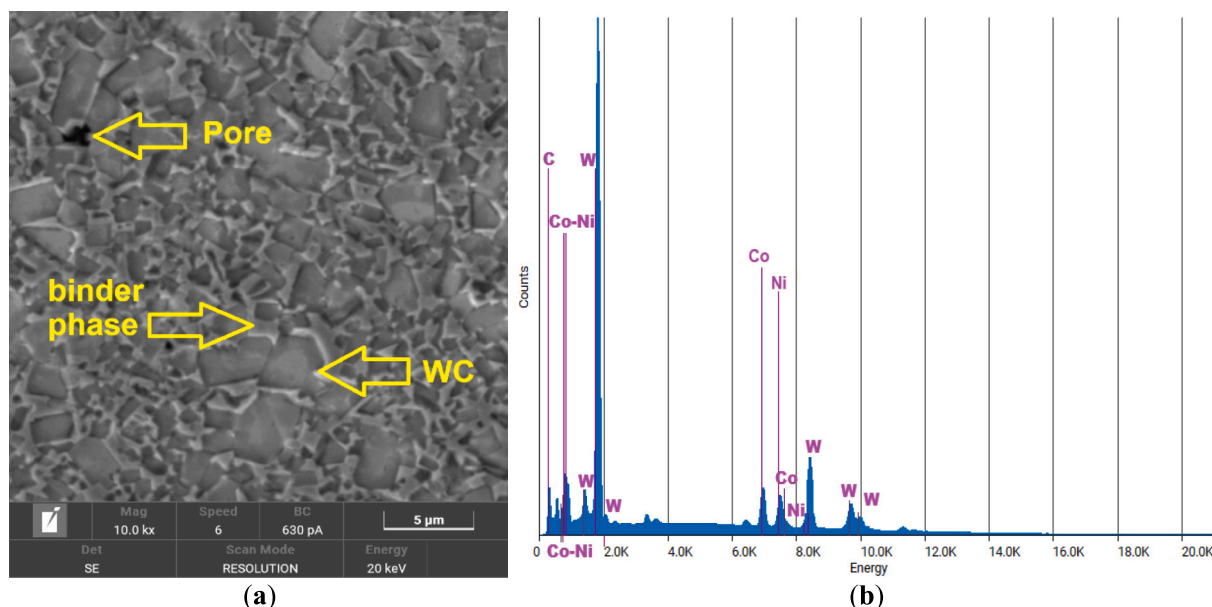


Fig. 9. SEM-EDS of a polished cross-section: (a) SEM, and (b) EDS of the WC-11(Co, Ni) alloy without $\alpha\text{-SiC}$.

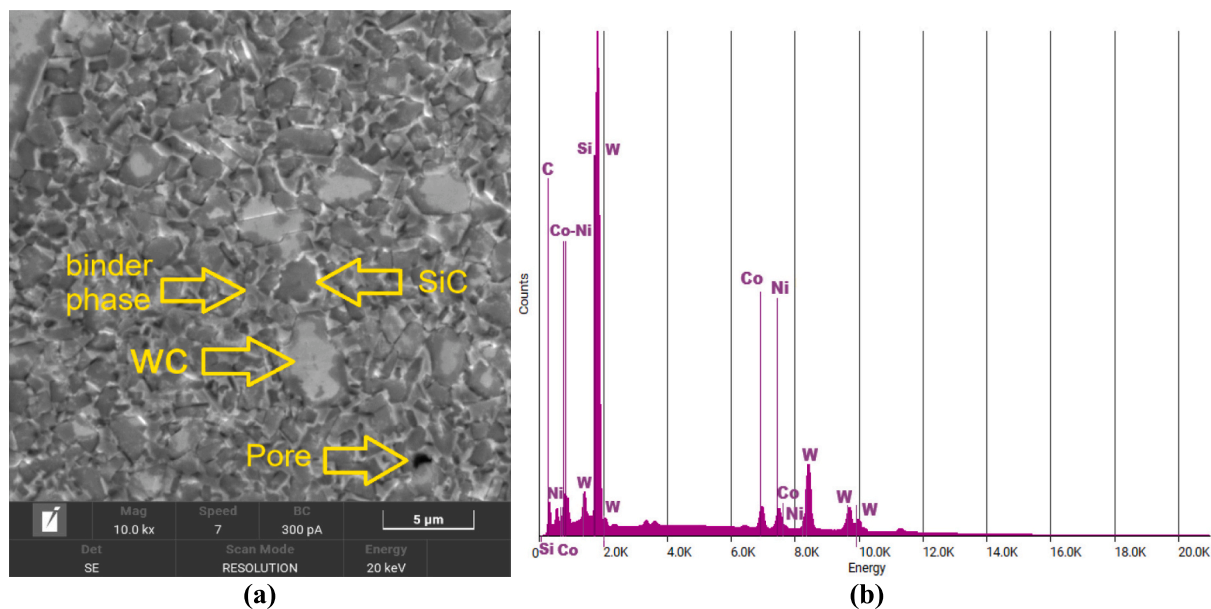


Fig. 10. SEM-EDS of a polished cross-section: (a) SEM, and (b) EDS of the WC-11(Co, Ni)-0.7SiC alloy.

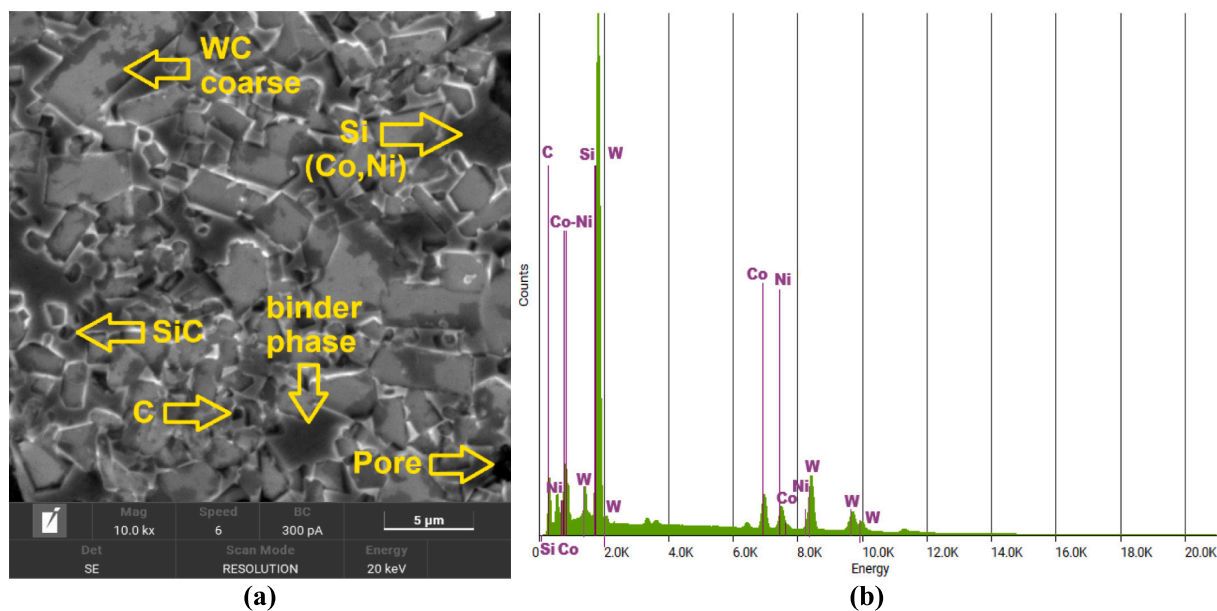


Fig. 11. SEM-EDS of a polished cross-section: (a) SEM, and (b) EDS of the WC-11(Co, Ni)-1.3SiC alloy.

Table 6

Chemical composition of the regions (EDS), Fig. 8 (a), 9(a), and 10(a), of the mixtures.

Sample	Si (wt %)	Co (wt %)	Ni (wt %)	W (wt %)
EDS Fig. 8 (a) WC-11(Co, Ni)	0.0	8.93	7.5	52.15
EDS Fig. 9 (a) WC-11(Co, Ni)-0.7SiC	2.54	6.92	6.0	56.71
EDS Fig. 10 (a) WC-11(Co, Ni)-1.3SiC	3.29	7.52	6.43	45.76

alloys with different α -SiC contents (0, 0.7, 1.3, and 3.2 wt%) reveals the predominance of the WC phase (hexagonal, P-6 m2; ICDD PDF N°. 96–150-1517) under all conditions, confirming its stability during processing. The binder phases were identified as ϵ -Co (HCP, P6₃/mmc; ICDD

PDF N°. 96–900-8492), α -Co (FCC, Fm-3 m; ICDD PDF N°. 96–900-8493), and Ni (FCC, Fm-3 m; ICDD PDF N°. 96–900-8476), whose coexistence is associated with thermal conditions and the role of Ni in stabilizing the FCC structure.

With the addition of α -SiC, the formation of α -SiC (hexagonal, P6₃/mmc; ICDD PDF N°. 96–900-8840) and silicide phases, mainly Ni₂Si (orthorhombic, Pnma; ICDD PDF N°. 96–900-9657), Co_{0.85}Si_{0.15} (cubic, Fm-3 m; ICDD PDF N°. 96–152-4832), and Co₂Si (orthorhombic, Pnma; ICDD PDF N°. 96–901-2575), is observed, with increasing peak intensity at higher α -SiC contents, indicating silicon diffusion into the binder phase and interfacial reactions during sintering. Peaks corresponding to free Si (cubic, Fd-3 m; ICDD PDF N°. 96–900-8577) were also detected at low intensity, possibly associated with incomplete reactions.

These results indicate modifications in the phase composition of the WC-(Co, Ni) system, in agreement with recent studies reporting phase evolution and silicide formation in WC-Co-Ni composites containing

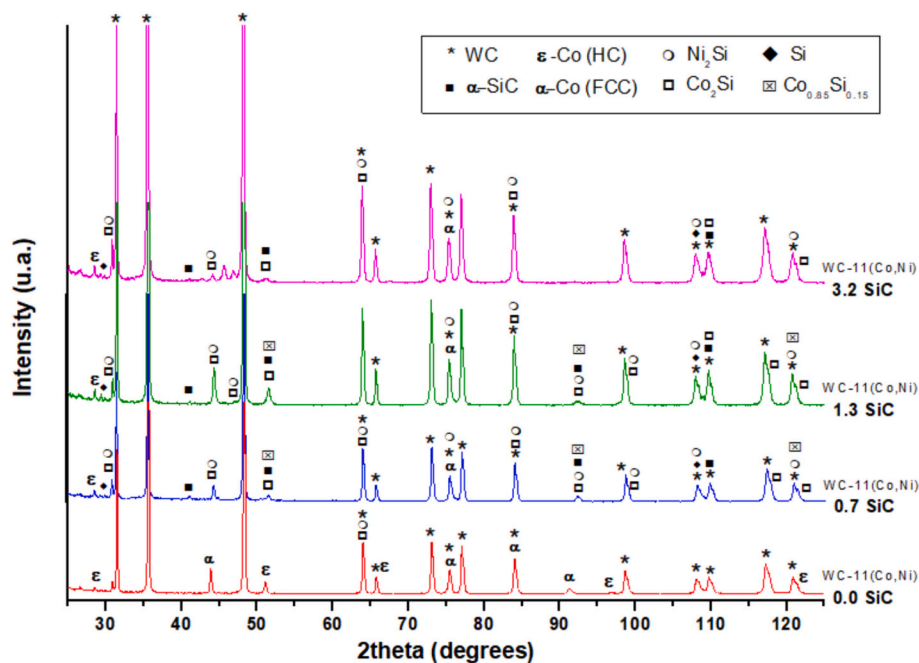


Fig. 12. XRD patterns of WC-11(Co, Ni) alloys with different SiC contents sintered at 1400 °C.

α -SiC, directly related to diffusion and interfacial interaction phenomena [34]. Phase identification was performed by comparison with standard ICDD (PDF) database cards, widely used for XRD characterization (ICDD), while the formation and stability of silicides are consistent with phase equilibria in the Co—Si and Ni—Si systems [35,36].

3.7. Residual thermal stresses of WC-11(Co, Ni) based samples, via LPS

XRD analysis of thermal residual stresses reveals that all WC-11(Co, Ni) alloys, with and without α -SiC addition, in Fig. 13, exhibit compressive residual stresses, regardless of the surface condition (rough or polished) and the position analyzed (compaction direction or lateral). This behavior is typical of hardmetals and is mainly associated with the mismatch of the coefficients of thermal expansion (CTE) between WC

and the Co—Ni binder phase during cooling after sintering, resulting in residual compression in the WC phase.

In the alloy without α -SiC addition, the compressive stresses exhibit moderate, relatively dispersed values that vary with measurement orientation and surface finish. It is observed that the lateral and polished surfaces tend to exhibit higher compression values, which can be attributed to local stress redistribution induced by both the part geometry and the partial relief of surface stresses during polishing. The dispersion of the data suggests a microstructure dominated by a continuous metallic binder, capable of partially accommodating thermal incompatibilities.

With the addition of 0.7 wt% of α -SiC, there is a significant increase in the magnitude of compressive stresses, especially in measurements taken on the lateral surfaces of the sample. This behavior is directly related to the partial dissolution of α -SiC in the metallic binder and the

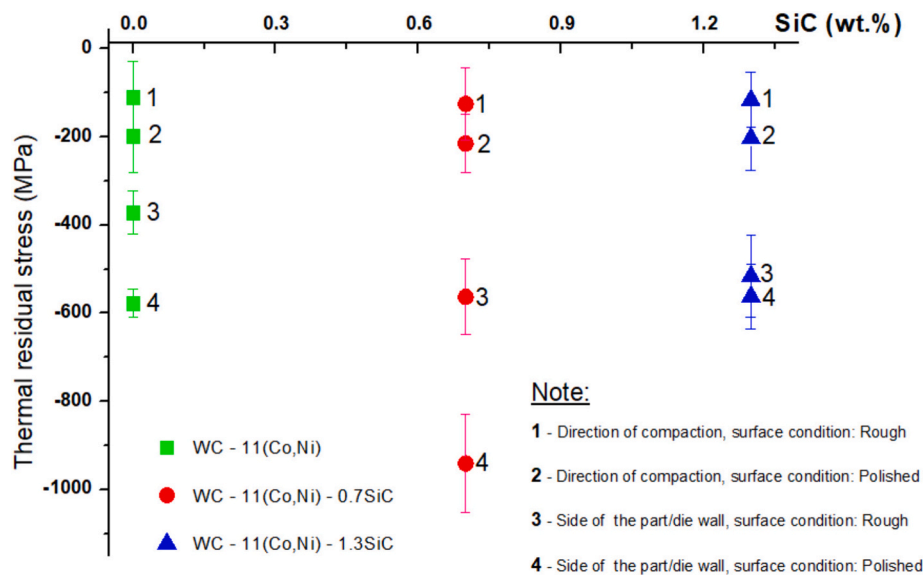


Fig. 13. Thermal residual stresses measured by XRD in WC-11(Co, Ni) alloys with varying α -SiC contents, considering compaction direction and lateral surfaces under rough and polished conditions.

incipient formation of Co_2Si and Ni_2Si silicides, as evidenced by XRD analysis. The formation of these phases reduces the effective fraction of the ductile Co—Ni binder, limiting its plastic relaxation capacity during cooling and intensifying the transfer of thermal stresses to the WC phase.

In the sample containing approximately 1.3 wt% $\alpha\text{-SiC}$, the compressive residual stresses reach the highest absolute values, with less dispersion between the different measurement conditions. This result indicates a more homogeneous stress state, associated with the precipitation of more extensive amounts of Co_2Si and Ni_2Si silicides, which increases the overall stiffness of the binder system. The reduction in binder ductility, combined with the greater contrast of thermal energy concentrations (TEC) between WC, silicides, and the remaining metallic phase, promotes the accumulation of more intense and stable compressive stresses.

In Fig. 13, the sample containing 0.7 wt% SiC shows a higher individual peak of residual compressive stress, while the condition with 1.3 wt% SiC shows higher average compressive stress values with less dispersion, indicating a more homogeneous and representative stress state. This interpretation is corroborated by the XRD results, which reveal a more pronounced formation of silicides (Co_2Si and Ni_2Si) with 1.3 wt% SiC, contributing to binder modification and a more uniform distribution of compressive stress. Furthermore, the hardness results (HV1 and HV30) reinforce this analysis: greater consistency in residual stresses correlates with a more homogeneous macroscopic mechanical response (HV30), while local variations (HV1) reflect underlying microstructural heterogeneity, particularly in the condition with lower $\alpha\text{-SiC}$ content. Therefore, the interpretation is based on an integrated analysis of residual stresses, X-ray diffraction, and mechanical properties, rather than isolated extreme values.

In general, the results demonstrate that the addition of $\alpha\text{-SiC}$ plays a determining role in the evolution of thermal residual stresses in the WC—(Co, Ni) system. The progressive increase in $\alpha\text{-SiC}$ content intensifies the compressive stresses by modifying the chemistry and stiffness of the binder phase, without altering the compressive nature of the stress state. This effect is particularly relevant from a functional point of view, since high compressive stresses tend to favor resistance to wear and crack initiation. However, they can negatively impact fracture toughness if the binder becomes excessively stiff. All WC—11(Co, Ni) alloys, with and without $\alpha\text{-SiC}$ addition, exhibited Residual Stress of a compressive nature, regardless of the measurement orientation and surface condition. This behavior is typical of hardmetals and is associated with the mismatch in thermal expansion coefficients between WC and the Co—Ni binder phase during post-sintering cooling. The measured values depend strongly on the crystallographic orientation of the WC grain, demonstrating that the crystallographic anisotropy of WC translates into differences in stresses and in the local hardness measured in the composite [37].

Although it was expected that the as-sintered surface would exhibit higher compression than polished surfaces, due to the stress relief promoted by metallographic preparation, comparable or even higher values were observed after polishing (R_a 0.1 μm). This result suggests the introduction of additional stresses during embedding in bakelite and abrasive wear, which can induce surface plastic deformation and reintroduce residual compression. Differences between measurements in the compaction direction and on the side of the part indicate anisotropy induced by the forming process, which remains detectable after surface finishing and is progressively intensified with the addition of $\alpha\text{-SiC}$, due to the reduction in the plastic relaxation capacity of the metallic binder caused by the formation of Co_2Si and Ni_2Si silicides.

The increase in compressive residual stresses from approximately -150 MPa (without $\alpha\text{-SiC}$) to values close to -1000 MPa with the addition of $\alpha\text{-SiC}$ shows an intensification of thermal and chemical incompatibility in the WC—Co—Ni system. The XRD diffractogram confirms the formation of Ni—Si and Co—Si intermetallics, indicating depletion of the binder phase in ductile Co/Ni and consequent reduction in its plastic accommodation capacity during cooling. The modification of the

liquid phase composition, possibly enriched in Si, alters the solution-precipitation kinetics of WC and generates microstructural heterogeneity, with abnormal grain growth and residual porosity.

3.8. Effect of $\alpha\text{-SiC}$ addition on densification and mechanical properties

Table 7 presents the results for sintered density, linear and volumetric shrinkage, hardness, and transverse rupture strength (TRS) of WC—(Co, Ni) alloys sintered at 1400°C and compacted at 100 MPa, highlighting the progressive effect of $\alpha\text{-SiC}$ addition on densification behavior and mechanical properties. The alloy without $\alpha\text{-SiC}$ addition showed high sintered density (14.5 g/cm^3) and high volumetric shrinkage (approximately 48%), indicating efficient liquid-phase sintering and good coalescence of the metallic binder, which was reflected in high hardness (12.86 HV_1 ; 12.64 HV_{30}) and TRS (1220 MPa) values.

For the WC-11(Co, Ni) alloy with the addition of 0.7 wt% $\alpha\text{-SiC}$, a moderate reduction in sintered density and volumetric shrinkage was observed, accompanied by an increase in hardness and a sharp drop in TRS. This behavior is associated with partial dissolution of $\alpha\text{-SiC}$ in the metallic binder and the incipient formation of Co_2Si and Ni_2Si silicides, which increase the system's stiffness and hinder complete densification, while reducing the binder's plastic deformation capacity and negatively affecting mechanical strength. For the alloy containing 1.3 wt% $\alpha\text{-SiC}$, the trend is even more pronounced, with a further reduction in density and volumetric shrinkage, concomitant with an additional increase in hardness and significantly lower TRS values. These results indicate that the higher fraction of silicides formed compromises the continuity and ductility of the Co—Ni binder, thereby increasing hardness but at the cost of substantial loss of flexural strength.

Finally, the alloy with approximately 3.2 wt% $\alpha\text{-SiC}$ showed very low density and volumetric shrinkage (5%), indicating that the material did not sinter adequately under the conditions employed. The low volumetric shrinkage indicates the absence of an effective liquid phase capable of promoting densification, possibly due to excessive consumption of the metallic binder by silicide formation and the presence of residual $\alpha\text{-SiC}$. Consequently, it was not possible to reliably determine hardness and TRS, reinforcing that this $\alpha\text{-SiC}$ content exceeds the processable limit of the system under the adopted sintering conditions.

The combined use of HV1 and HV30 is not redundant but complementary, enabling multi-scale microstructure-property correlation in WC—(Co, Ni) hardmetals. HV1 (1 kgf) assesses local microhardness, being sensitive to microstructural heterogeneity such as binder distribution, WC-rich regions, grain boundaries, secondary phases, and porosity—particularly useful for detecting localized effects induced by $\alpha\text{-SiC}$ addition and silicide formation. In contrast, HV30 (30 kgf) reflects macroscopic hardness, integrating a larger plastically deformed volume and capturing the global microstructural response, including porosity and binder continuity; it is also required for reliable fracture toughness (K_{IC}) evaluation via indentation. The discrepancy observed in the figure highlights such heterogeneity: while HV1 remained within levels typical of ISO K30/K40 grades ($>1300\text{ HV}$), HV30 decreased progressively ($\sim 11\%$) with increasing $\alpha\text{-SiC}$ content, indicating that the ceramic addition did not translate into effective bulk strengthening. This multi-scale approach is especially relevant in reactive systems like WC—11(Co, Ni)— $\alpha\text{-SiC}$, where chemical modifications of the binder and microstructural heterogeneities affect local and global mechanical responses differently.

$\alpha\text{-SiC}$ is widely employed in high-temperature applications, where interactions with metallic phases can induce diffusion and solid-state interfacial reactions. Under such conditions, its chemical stability becomes dependent on the adjacent metallic system and the thermal processing parameters [38].

The reactivity of $\alpha\text{-SiC}$ with Ni- and Co-based binders during liquid-phase sintering can be interpreted using the Ni—Si—C and Co—Si—C phase diagrams, in which silicon exhibits high solubility and chemical affinity, favoring the formation of stable silicides. The partial decomposition of

Table 7

Results obtained from WC-11(Co, Ni) mixtures at a temperature of 1400 °C and compacted at 100 MPa.

Alloy	Sintered density (g cm ⁻³)	Shrinkage (%)		Vickers Hardness		TRS (MPa)
		Linear	Volumetric	HV ₁ (GPa)	HV ₃₀ (GPa)	
WC-11(Co, Ni)	14.5 ± 0.1	21.5 ± 0.5	47.8 ± 1.2	12.86 ± 0.03	12.64 ± 0.21	1219 ± 114
WC-11(Co, Ni)-0.7SiC	14.3 ± 0.1	24.5 ± 0.3	40.1 ± 1.4	13.26 ± 0.07	13.24 ± 0.23	571 ± 166
WC-11(Co, Ni)-1.3SiC	14.0 ± 0.2	25.9 ± 0.9	31.6 ± 1.9	13.51 ± 0.11	12.36 ± 0.12	355 ± 87
WC-11(Co, Ni)-3.2SiC	10.1 ± 0.1	15.3 ± 0.2	5.4 ± 0.1	N.A.	N.A.	N.A.

α -SiC (SiC $\rightarrow$ Si + C) promotes enrichment of the liquid phase in Si, as confirmed by XRD results, which reveal the progressive formation of Co₃Si and Ni₂Si, while WC remains structurally stable. This transformation implies consumption of the metallic binder phase and changes in the liquid phase's viscosity and composition, thereby modifying solution–reprecipitation kinetics and promoting abnormal grain growth. Simultaneously, the released carbon may not be fully reincorporated into the WC–C equilibrium, contributing to the formation of residual porosity [38,39].

From a mechanical standpoint, the formation of intermetallic silicides and compositional heterogeneity reduces binder ductility and intensifies thermal expansion mismatch during cooling, resulting in increased compressive residual stresses (–150 to –1000 MPa). This stress state, combined with microstructural instability, is directly associated with a significant reduction in transverse rupture strength (TRS) and fracture toughness (K_{IC}), a transition to a radial–median fracture regime, and reduced energy dissipation capacity [39].

Additionally, the α -SiC–Ni/Co interaction is not limited to the liquid regime, as solid-state interfacial reactions also occur, followed by partial dissolution and diffusion of Si into the metallic phase. This process results in the formation of silicides such as Ni₃Si and Ni₃Si₁₂. At the same time, residual carbon may precipitate as graphite (free carbon), altering the carbon balance of the system and contributing to the microstructural and chemical evolution of the binder [38]. Overall, the literature demonstrates that α -SiC is not thermodynamically stable in contact with Ni- and Co-based binders at elevated temperatures, acting as a reactive phase that modifies binder composition through silicide formation and carbon release. The diffusion of Si in Ni-rich alloys further reinforces this mechanism, directly affecting the microstructural integrity and mechanical properties of the composites [38,39,40].

3.9. Fracture toughness (K_{IC})

Regarding fracture toughness (K_{IC}), calculated using the Palmqvist, Shetty/Radial-Median, and Niihara methods, an inverse trend to hardness is observed. The alloy without α -SiC presented the highest average values (Palmqvist = 28 MPa·m^{1/2}), followed by the alloy with 0.7 wt% α -SiC (16.9 MPa·m^{1/2}) and the alloy with 1.3 wt% α -SiC (8.6 MPa·m^{1/2}). This progressive reduction in toughness with increasing α -SiC content is consistent with the decrease in the effective fraction of ductile binder phase available for energy dissipation through pitting and crack deflection mechanisms. Furthermore, the increase in the c/a ratio was 1.11 (0 wt% α -SiC) compared to 1.28 (0.7 wt% α -SiC) and 1.96 (1.3 wt% α -SiC), indicating a transition from a clearly Palmqvist regime to a condition close to the radial–median regime in the alloy with 1.3 wt% α -SiC, justifying the greater dispersion observed in the K_{IC} values (CV from 16% to 17% by the radial and Niihara models). Table 8 provides more details of the values obtained.

The effect of α -SiC addition on the mechanical behavior of the WC-11 (Co, Ni) alloy was evaluated through Vickers hardness (HV₃₀) and fracture toughness (K_{IC}) tests determined by indentation, considering the Palmqvist [23], Shetty (radial–median) [30], and Niihara models [29]. The revised results indicate that the influence of α -SiC on hardness is not monotonic; it promotes a progressive, marked reduction in fracture resistance. The effect becomes significantly more pronounced for K_{IC} as the α -SiC content increases. For WC-Co-based alloys, Palmqvist-

Table 8

Results obtained in the indentation test.

Alloy	K_{IC} (MPa·m ^{1/2})					
	Palmqvist / CV (%)		Shetty/Radial-Median / CV (%)		Niihara / CV (%)	
WC-11(Co, Ni)	28.0 ± 5.6	20.0	26.0 ± 5.6	5.2	20.0 ± 5.6	5.2
WC-11(Co, Ni)-0.7SiC	16.9 ± 2.3	13.3	21.2 ± 1.7	7.9	16.3 ± 1.3	7.8
WC-11(Co, Ni)-1.3SiC	8.6 ± 1.1	12.1	11.2 ± 1.9	16.8	8.6 ± 1.4	16.8

based models are more reliable than radial–median models [41].

Unlike these additives, α -SiC has limited wettability by the Co–Ni binder phase and can induce interfacial reactions during liquid phase sintering. In WC-Co-Ni systems, alterations in the continuity of the metallic phase or the formation of brittle phases (such as η phase) negatively impact the load transfer between WC grains [17,24,28]. The reduction in hardness observed for 1.3 wt% α -SiC suggests possible combined mechanisms, such as increased residual porosity, reduced continuity of the binder phase, WC/binder/ α -SiC interfacial embrittlement, and imbalance in the carbon balance with the formation of secondary phases. These factors compromise the efficiency of the classic ductile matrix reinforcement mechanism characteristic of hardmetals. The impact of α -SiC addition was substantially more severe on fracture toughness. Considering the Palmqvist model, the average K_{IC} values decreased from 27.3 MPa·m^{1/2} (0 wt% α -SiC) to 16.9 MPa·m^{1/2} (0.7 wt% α -SiC) and 8.6 MPa·m^{1/2} (1.3 wt% α -SiC), corresponding to a total reduction of approximately 68%. A similar trend was observed by the Shetty model, with reductions from 26.0 to 21.2 and to 11.2 MPa·m^{1/2}, and by the Niihara model, with reductions from 20.0 to 16.3 and to 8.6 MPa·m^{1/2}. Although the absolute values depend on the model adopted, the relative reduction is unequivocal and consistent across the methodologies. Classic studies report typical K_{IC} values for WC-10Co of 9–12 MPa·m^{1/2} when determined using standardized mechanical methods [17,18,24,28]. It is observed that the alloy without α -SiC exhibits toughness superior to the typical WC-10Co range. In contrast, the alloy with 1.3 wt% α -SiC falls close to or below these values, evidencing a significant loss of fracture energy absorption capacity.

The increase in the c/a ratio from approximately 1.11 (0 wt% α -SiC) to 1.28 (0.7 wt% α -SiC), Fig. 14(a), and 1.96 (1.3 wt% α -SiC), Fig. 14(b), indicates a progressive transition from the Palmqvist regime to a condition close to the radial–median regime in the alloy with the higher α -SiC content, typical of materials with more brittle behavior, as described by Shetty et al. [30].

This transition is consistent with the sharp reduction in K_{IC} and the increase in the material's ceramic character. Regarding crack propagation resistance, evaluated through fracture toughness obtained by indentation, a consistent reduction was observed with the addition of α -SiC, in line with the previously discussed results, evidenced by the increase in the length of radial cracks, comparison of Fig. 13(a) and Fig. 13(b); and the consequent decrease in the material's fracture resistance (TRS). The progressive reduction in K_{IC} can be attributed to a decrease in the effective ductile binder fraction, an increase in elastic interfacial incompatibility, suppression of crack-stripping and deflection

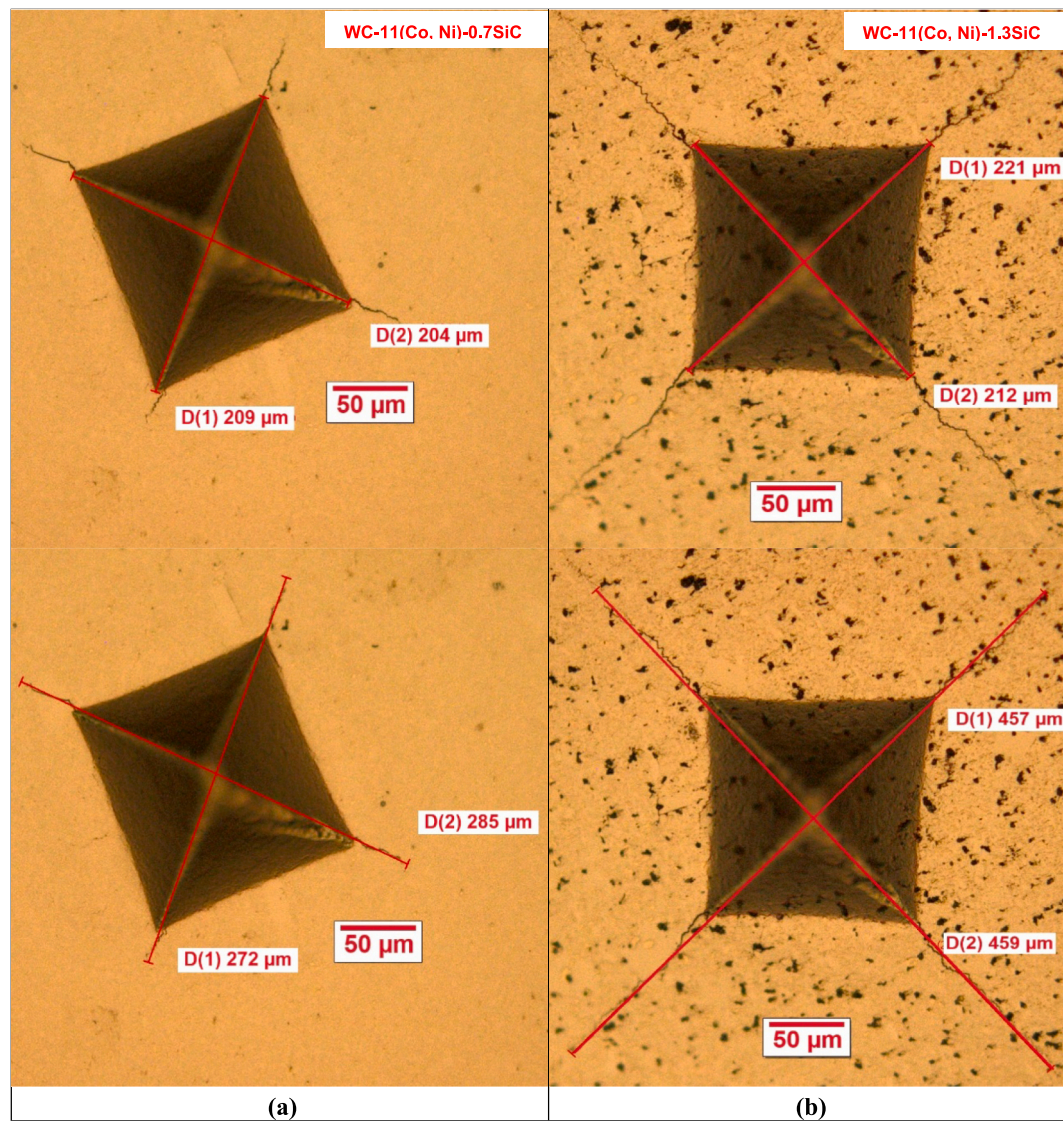


Fig. 14. Optical micrograph of Vickers indentation (30 kgf) and induced radial surface cracking for the specimens of the alloys: (a) WC-11(Co, Ni)-0.7SiC, and (b) WC-11(Co, Ni)-1.3SiC.

mechanisms, and a lower plastic deformation capacity in the plastic zone under indentation. These mechanisms are fundamental to the performance of hardmetals, whose toughness critically depends on the continuity and ductility of the binder phase [17,18,24,28].

It is important to emphasize that fracture toughness (K_{IC}) increases with Co content and WC grain size. Larger grains favor crack deflection, increasing toughness. Conversely, ultrafine grains provide greater hardness, but with reduced toughness [42]. For alloys with 0.7 wt% and 1.3 wt% α -SiC, Fig. 14(a) and Fig. 14(b), abnormal growth of WC grains and the formation of intermetallics in the binder phase occurred, as shown in Fig. 13. The Co phase acts in stress distribution, energy absorption, and crack pitting. Without it, the material behaves like a brittle ceramic [43].

Residual porosity significantly affects indentation-derived hardness (HV) and fracture toughness (K_{IC}). In this study, measurements were performed on polished regions free of visible macropores, using multiple indents ($n \geq 10$) to ensure statistical representativeness, with outliers critically assessed. Thus, the reported values should be interpreted as effective properties of the real (porous) microstructure rather than intrinsic values of fully dense materials. The effects of α -SiC addition, silicide formation, binder depletion, and porosity are strongly coupled, with porosity acting as a dominant factor that amplifies embrittlement

alongside microstructural heterogeneity and abnormal grain growth. Although the statistical dispersion of K_{IC} depends on the adopted model, higher α -SiC contents show a more deterministic response associated with brittle fracture. Accordingly, the α -SiC-free alloy exhibits greater plastic accommodation and higher crack-growth resistance, whereas α -SiC-containing alloys—particularly at 1.3 wt%—display a more brittle response, lower damage tolerance, and more uniform fracture. Mechanistically, the mismatch in thermal expansion between WC and the modified binder, combined with reduced matrix ductility, promotes internal stress concentration and facilitates crack nucleation and coalescence under flexural loading. Consequently, the increase in residual stresses correlates directly with the significant reduction in TRS and K_{IC} , indicating that α -SiC addition disrupts the internal mechanical balance and compromises structural integrity.

In comparison with WC-10Co hardmetals reported in the literature, which typically exhibit hardness between 1400 and 1800 HV and fracture toughness between 9 and 12 $\text{MPa}\cdot\text{m}^{1/2}$ [17,18,24,28], the values obtained in this study show differences consistent with the composition and the binder system employed (Co—Ni instead of pure Co). It was expected that with the addition of α -SiC, the same efficiency as VC, which is more effective in inhibiting WC grain growth than (Ta, Nb)C, would result in finer and more uniform grains [44]. The WC-11(Co, Ni)

alloy without α -SiC presented an average hardness of 1288 HV30, therefore lower than the typical range of WC-10Co. This difference is expected, since the total binder fraction (11%) is higher than that of a conventional WC-Co (10 wt% Co) and, additionally, the presence of Ni tends to slightly reduce the hardness when compared to pure Co, due to the lower intrinsic resistance of the binder phase. On the other hand, the fracture toughness of this alloy ($28 \text{ MPa}\cdot\text{m}^{1/2}$ by the Palmqvist model) is significantly higher than the classical values of $9\text{--}12 \text{ MPa}\cdot\text{m}^{1/2}$ reported for WC-10Co, which may be associated with the higher effective content of ductile phase and the predominant Palmqvist crack regime ($c/a = 1.1$), which tends to result in higher K_{IC} values when compared to the radial-median regime.

For the alloy with 0.7 wt% α -SiC, the hardness increased to 1350 HV30, approaching the lower limit of the typical WC-10Co range from the literature, while the toughness decreased to about $17 \text{ MPa}\cdot\text{m}^{1/2}$ (Palmqvist). Still, this value remains above the conventional WC-10Co range, indicating that the WC-Co-Ni system retains greater energy dissipation capacity, even with a moderate addition of α -SiC. The alloy with 1.3 wt% α -SiC showed a hardness of 1260 HV30, below the typical values of WC-10Co, and a toughness of approximately $8\text{--}9 \text{ MPa}\cdot\text{m}^{1/2}$, placing it within or slightly below the lower range reported for WC-10Co. This behavior suggests that excess α -SiC significantly compromises the toughening mechanisms associated with the binder phase, promoting a transition to a crack regime closer to the radial-median ($c/a = 1.96$) and, consequently, a marked reduction in K_{IC} .

In general, the results indicate that the studied WC-11(Co, Ni) system exhibits higher fracture toughness and lower hardness than conventional WC-10Co, a behavior consistent with the higher total binder content and the presence of Ni. The controlled addition of 0.7 wt% α -SiC brings the hardness closer to the typical range of WC-10Co without drastically reducing toughness. In contrast, 1.3 wt% α -SiC leads the material to a brittleness regime comparable to or lower than that observed in traditional WC-Co alloys.

Although α -SiC was predicted as a potential inhibitor of WC grain growth, the results obtained show the opposite effect, with abnormal WC growth, reduced densification, and a sharp drop in mechanical strength. The analyses indicate partial dissolution of α -SiC in the Co-Ni binder phase, which provides reinforcement and hardening [4], due to the formation of Ni-Si and Co-Si intermetallics, thereby altering the composition and dynamics of the liquid phase during sintering. The potential formation of a Si-enriched liquid phase could intensify the solution-reprecipitation mechanisms of WC, favoring preferential grain growth. Additionally, free carbon from α -SiC can modify the thermodynamic balance of the WC-Co-Ni-C system, contributing to residual porosity and microstructural instability. This scenario is corroborated by the increase in compressive residual stresses observed with the addition of α -SiC, indicating thermal and chemical heterogeneity during cooling, which exacerbates structural integrity loss and explains the significant reductions in TRS and K_{IC} .

4. Conclusions

This study evaluates the effect of α -SiC addition on the microstructure and mechanical properties of LPS WC-11(Co, Ni) alloys. The main conclusions are:

- I. Densification: High relative density ($>99\%$) was achieved for compositions up to 1.3 wt% α -SiC, whereas 3.2 wt% resulted in significantly reduced densification ($\sim 75\%$).
- II. Microstructure: The addition of 0.7–1.3 wt% α -SiC promoted abnormal WC grain growth, broadening the grain size distribution, and increased residual porosity (up to $\sim 0.6 \text{ vol}\%$).
- III. Phases: XRD analysis identified the formation of Co₃Si and Ni₃Si with increasing α -SiC content, while WC remained stable.
- IV. Hardness: HV1 values remained above 1300 HV, while HV30 decreased by $\sim 11\%$ with increasing α -SiC content.

V. Mechanical behavior: TRS and fracture toughness decreased significantly (K_{IC} reduction $\sim 72\%$), accompanied by increased crack length, reduced K_{IC} variability, and a transition towards radial-median cracking behavior.

VI. Residual stresses: Compressive residual stresses increased in magnitude (-150 to -1000 MPa) with α -SiC addition.

VII. Overall effect: The addition of α -SiC is associated with increased porosity, phase formation, and degradation of mechanical performance.

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CRediT authorship contribution statement

Fabio Miranda: Writing – original draft, Validation, Software, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Marcelo Otavio dos Santos:** Writing – review & editing, Validation, Software, Methodology, Formal analysis. **Luis Gallego Martinez:** Writing – review & editing, Validation, Software, Methodology, Formal analysis. **Rene Ramos de Oliveira:** Writing – review & editing, Visualization, Validation, Software, Methodology, Formal analysis. **Gilmar Ferreira Batalha:** Writing – review & editing, Visualization, Validation, Supervision, Project administration. **Jesualdo Luiz Rossi:** Writing – review & editing, Visualization, Validation, Supervision, Project administration.

Institutional review board statement

This study does not require review or approval by an Ethics Committee, as it did not involve human subjects or the collection of personal, clinical, or identifiable information.

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Declaration of competing interest

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Data availability

Data will be provided upon request.

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