Effect of sintering method on the microstructure of pure Cr_2AlC MAX phase ceramics

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Synthesis and sintering behavior of Cr_2AlC compounds were investigated using two sintering techniques: pressureless sintering and field assisted sintering technology/spark plasma sintering. Both processes—synthesis and sintering—were carried out simultaneously in one or two different steps. Pure Cr_2AlC bulk materials but with relative density below 90% can be obtained by pressureless sintering, whereas highly dense compounds with secondary phases were achieved by FAST/SPS. The optimized processing route to obtain highly pure and dense (98.9%) Cr_2AlC materials is based on the synthesis of the pure phase by pressureless calcination followed by FAST/SPS densification.

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1. Introduction

MAX phases are a relatively new family of materials with general formula of $M_{n+1}AX_n$, where M corresponds to an early transition metal, A is a A-group element (IIIA or IVA element), X is C and/or N, and n is typically equal to 1, 2 or 3.¹⁾ They were discovered by Nowotny et al.²⁾ in 1960's but the interest in them grew in 1996, when Barsoum et al.³⁾ reported on the synthesis of a pure Ti_3SiC_2 phase and its properties. Nowadays, there are more than 70 pure MAX phases and the number of these phases and their solid solutions increases year by year.⁴⁾ The great expectations on these materials are related to the combination of their unique properties, bridging the gap between ceramics and metals.⁵⁾ In general, MAX phases are lightweight, elastically stiff, good thermal conductors and resistant to oxidation and chemical attack at high temperatures as carbides and nitrides ceramics, while they are soft, readily machinable, thermal shock resistant and damage tolerant as metals. This singular behavior is linked to their crystal structure: the $M-X$ bond has a mixed covalent/ionic character, whereas the $M-A$ bond is metallic.

The ternary carbide Cr_2AlC is one of the most promising MAX phases for high temperature applications due to its excellent combination of properties.^{6,7)} Cr_2AlC presents density of 5.23 g/cm³ and it has been reported low hardness (3.5–5.5 GPa), high Young's modulus (288 GPa), intermediate fracture toughness (5.2 MPa·m^{1/2}), good flexural (378 MPa) and compression strengths (1160 MPa).⁶⁾ Furthermore, bulk Cr_2AlC materials are good electrical ($2.3 \cdot 10^6 \Omega^{-1} \text{m}^{-1}$) and thermal (22 W/mK) conductors, show excellent oxidation resistance at high temperature in air ($1.1 \cdot 10^{-11}$ and $3.0 \cdot 10^{-9} \text{kg}^2 \text{m}^{-4} \text{s}^{-1}$ at 1000 and 1300°C, respectively) and exhibit self-healing mechanisms at high temperature.^{8–10)} Nevertheless, the effect of the microstructure on the final properties has not been enough investigated. This lack of information is caused by the novelty of this material but also by

the difficulty to obtain pure and highly dense bulk materials, since second phases—carbides and intermetallic compounds—are commonly observed in the final microstructure, altering the final properties. There are two factors that should be considered prior to obtain the desired pure and dense Cr_2AlC compounds: the synthesis of the Cr_2AlC phase and the densification process. In most of the cases both processes—synthesis and sintering—are simultaneously achieved during heat treatment.

Chromium, aluminum and graphite powders—the elemental constituents—are commonly used as starting materials for the synthesis process of the Cr_2AlC phase, although intermediate products such as carbides could be also utilized.^{11,12)} Excess of aluminum (<30 at %) is typically incorporated to the starting composition to compensate the loss of Al during the thermal process, since aluminum melts at 661°C and the synthesis temperature ranges from 1000 to 1400°C. As a result, phase formation sequence of Cr_2AlC is produced by solid–liquid and solid–solid reactions, where some intermetallic compounds as Cr_2Al and Al_8Cr_5 , and carbide such as Cr_7C_3 and Cr_3C_2 , are intermediate products during the synthesis process.¹³⁾ These stable secondary phases can be remained in the final compound, so careful control of the reactions is essential. As commented above the synthesis and the densification occurred simultaneously as both processes require a thermal treatment. Pressureless sintering (PS), Hot-Pressing (HP) and Spark Plasma Sintering (SPS)—also known as Field Assisted Sintering Technology (FAST)—are the common sintering techniques to in-situ synthesize and densify the Cr_2AlC materials.^{13–15)} Pressureless sintering leads to a fine control of the purity phase in a range of temperatures between 900 and 1400°C during 1 to 5 h of isothermal holding time.¹²⁾ However, final density of the sintered material is low (<80% theoretical density) as typically observed for other MAX phases. Hot-Pressing is the most used and studied sintering technique to consolidate Cr_2AlC due to the uniaxial pressure applied during the whole heating process promoting the densification of the material. Almost pure Cr_2AlC phase and high densities are obtained using maximal temperature of 1400°C and uniaxial pressure of 20 MPa.¹⁶⁾ However, possible reaction

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between the starting Al and Cr powders and the graphite of the mold could cause inhomogeneous sintering and defects on the edge of the specimens.¹⁷⁾ Finally, FAST/SPS is also used to obtain Cr₂AlC dense specimens, although it presents the same problem of reactivity with the graphite die than HP. In addition, the fast heating rates ($\sim 100^\circ\text{C}/\text{min}$) and short sintering times ($\sim$ minutes) typically used in FAST/SPS lead to incomplete reactions to form the Cr₂AlC phase, so pure phase has not been reported.^{11),18),19)}

The aim of this work was to investigate the synthesis and the densification process of Cr₂AlC using two different techniques: pressureless sintering and Spark Plasma Sintering (FAST/SPS). Synthesis and sintering processes were carried out simultaneously in one step or in separate steps affecting the final density, purity of the Cr₂AlC phase and microstructure. A processing route combining both sintering techniques—first pressureless sintering followed by FAST/SPS—is carried out to obtain high dense and pure Cr₂AlC materials. Reactions during the synthesis process and evolution during the sintering behavior are considered in order to achieve the main goal of this investigation.

2. Experimental procedure

Chromium (-100 mesh, 99.0% pure), aluminum (-325 mesh, 99.5% pure) and graphite ($7-11\ \mu\text{m}$, 99.0% pure) powders (all from Alfa Aesar, Germany) were used as starting materials. Particle size distribution of the starting materials was measured by laser diffraction (Horiba LA950V2, Retsch, Germany) and values are shown in **Table 1**. Particle size of chromium was reduced by planetary milling (PM400, Retsch, Germany) due to its larger size in comparison with aluminum and carbon particles. Chromium powder was poured into the milling jar with Cr-alloy balls (5 mm diameter) under argon atmosphere to avoid oxygen contamination during the milling process, and the powder was milled for 3 h at 400 r.p.m. The final particle size is shown in Table 1. The powders were weighed according to the desired composition (Cr:Al:C = 2:1.1:1) and mixed in a planetary milling for 20 min at 150 r.p.m. under argon atmosphere. An aluminum excess of 10 at. % was added to compensate the Al loss during the thermal treatment. The resultant mixed powder was the starting composition for the consolidation of Cr₂AlC materials. Consolidation of Cr₂AlC was carried out in one step, synthesis and sintering together (*insitu*-Cr₂AlC), or in two steps, first the synthesis and followed by the sintering process (*2steps*-Cr₂AlC). *Insitu*-Cr₂AlC and *2steps*-Cr₂AlC processes were carried out using two different techniques: pressureless sintering and FAST/SPS.

For pressureless sintering the mixed powder was uniaxially pressed at 200 MPa to obtain the green bodies. These green bodies for *insitu*-Cr₂AlC were heated under argon atmosphere using a heating rate of $5^\circ\text{C}/\text{min}$, maximal temperature between 700 and 1450°C , and isothermal holding time of 3 h. For *2steps*-Cr₂AlC specimens, the optimized *insitu*-Cr₂AlC samples (pure phase, explained in the discussion section) were ground in an

agate mortar and using a vibratory milling (Pulverisette Spartan, Fritsch, Germany). The resulting powder (hereafter *powder*-Cr₂AlC) was uniaxially pressed at 200 MPa, followed by pressureless sintering under argon atmosphere using a heating rate of $5^\circ\text{C}/\text{min}$, maximal temperature from 1150 to 1300°C , and isothermal holding time of 3 h.

Spark plasma sintering process was carried out using a FAST/SPS (FCT-HPD5, FCT Systeme GmbH, Germany) with standard graphite tools of 20 mm inner diameter. For *insitu*-Cr₂AlC, the starting mixed powder was poured into the graphite die and pre-compacted under uniaxial pressure of 50 MPa for 60 s. Graphite foils were previously placed between the powders and the graphite die/punches to ensure the electrical, thermal and mechanical contact during the sintering. Additionally, the graphite die was covered with a carbon felt to reduce the heat loss. Temperature was controlled with a pyrometer that was focused on the bottom of the upper punch at a distance of 5 mm from the sample. Sintering was carried out under vacuum (~ 3 Pa) using a heating rate of $100^\circ\text{C}/\text{min}$ up to the desired temperature, uniaxial pressure of 50 MPa during the whole thermal cycle and isothermal holding time of 10 min. Maximal temperature varied from 1200 to 1400°C . The *2steps*-Cr₂AlC specimens were sintered using the same FAST/SPS configuration but the initial powder was different. Here, *powder*-Cr₂AlC (obtained by pressureless sintering) was poured into the graphite die and densified by FAST/SPS. The maximal temperatures were 1200, 1250 and 1300°C , using same heating rate ($100\ \text{K}/\text{min}$), pressure (50 MPa) and dwell time (10 min) than for *insitu*-Cr₂AlC tests.

Bulk densities of the sintered specimens were measured by the Archimedes principle in water at room temperature, and relative densities were calculated using the theoretical value of Cr₂AlC ($5.23\ \text{g}/\text{cm}^3$, JCPDS 29-0017). For microstructure characterization the samples were ground and polished up to $0.5\ \mu\text{m}$ diamond paste. Polished surfaces were observed using a table top microscope (TM3030, Hitachi, Japan) and a Scanning Electron Microscope (SEM, Zeiss Ultra55, Germany). Furthermore, phase analysis was characterized by X-ray Diffraction (XRD, D8-Discover, Bruker, US) over the polished specimens.

3. Results and discussion

As received chromium, aluminum and graphite commercial powders presented unimodal particle size distributions but large differences in size between them (Table 1). Mean grain size of chromium was $85.54\ \mu\text{m}$, meanwhile aluminum and graphite exhibited 9.05 and $6.85\ \mu\text{m}$, respectively. Mean particle size of chromium powder was reduced by milling up to $26.45\ \mu\text{m}$ (Table 1) and no contamination was detected by X-ray diffraction or observed in SEM micrographs (not shown in this document). After the reduction of the chromium powder all the starting materials were mixed together in dry conditions by planetary ball milling. The final composition presented an aluminum excess of 10 at.%, as typically added by other authors, to compensate the Al loss during the heat treatment. Homogeneous dispersion of the Cr, Al and C powders was attained after the mixing process.

3.1 Pressureless sintering

Pellets of the homogeneous mixture of Cr, Al and C powders were heated between 700 and 1450°C under argon atmosphere to synthesize the Cr₂AlC phase and sinter the samples in one step (*insitu*-Cr₂AlC). XRD patterns of the samples at each temperature are shown in **Fig. 1**, using the intensity peaks to estimate the variation of phase contents as a function of temperature (**Table 2**) and to predict the synthesis reactions of Cr₂AlC. In

Table 1. Particle size distribution of the as received, milled and synthesized powders

Compound	D10 (μm)	D50 (μm)	D90 (μm)
Cr	43.64	85.54	142.40
Cr-milled	9.91	26.45	64.66
Al	5.66	9.05	13.64
C	4.43	6.85	10.29
powder-Cr ₂ AlC	4.64	9.21	16.80

Fig. 1. XRD patterns of *insitu*-Cr₂AlC samples sintered by pressureless sintering at 700–1450°C for 3 h.

Table 2. Variation of phase content of the samples as a function of temperature. s = strong, m = medium, w = weak and vw = very weak

Temperature (°C)	Phase content*							
	Cr	Al	C	Al ₈ Cr ₅	AlCr ₂	Cr ₇ C ₃	Al ₄ C ₃	Cr ₂ AlC
700	s	w	s	s	w	—	—	—
800	m	—	s	s	m	—	vw	—
900	vw	—	s	s	s	vw	vw	vw
1000	—	—	s	s	s	m	w	w
1100	—	—	s	s	s	s	w	m
1200	—	—	w	w	w	m	w	s
1250	—	—	—	vw	w	w	—	s
1300	—	—	—	—	vw	—	—	s
1350	—	—	—	—	—	—	—	s
1400	—	—	—	—	—	—	—	s
1450	—	—	—	—	—	—	vw	s

* Based on XRD.

Table 3. Method, sintering technique, maximal temperature, density and theoretical density of all the sintered specimens

Method	Sintering	Temperature (°C)	Density (g/cm ³)	Theo. Density (%)
in situ-Cr ₂ AlC	Pressureless	1250	1.72	32.9
in situ-Cr ₂ AlC	Pressureless	1300	2.37	45.3
in situ-Cr ₂ AlC	Pressureless	1350	3.17	60.6
in situ-Cr ₂ AlC	Pressureless	1400	3.35	64.1
in situ-Cr ₂ AlC	Pressureless	1450	3.83	73.2
2step-Cr ₂ AlC	Pressureless	1150	4.16	79.5
2step-Cr ₂ AlC	Pressureless	1200	4.44	84.9
2step-Cr ₂ AlC	Pressureless	1250	4.61	88.1
2step-Cr ₂ AlC	Pressureless	1300	4.61	88.1
in situ-Cr ₂ AlC	FAST/SPS	1200	4.13	79.0
in situ-Cr ₂ AlC	FAST/SPS	1300	5.06	96.8
in situ-Cr ₂ AlC	FAST/SPS	1400	5.08	97.1
2step-Cr ₂ AlC	FAST/SPS	1200	5.03	96.2
2step-Cr ₂ AlC	FAST/SPS	1250	5.17	98.9
2step-Cr ₂ AlC	FAST/SPS	1300	5.21	99.6

addition, final densities of the sintered specimens from 1250°C are presented in Table 3. The synthesis process of the Cr₂AlC phase started with the melting of the aluminum at 661°C (Reaction 1). From this temperature aluminum reacted with the solid chromium producing Cr–Al intermetallic compounds, mainly Cr₅Al₈ and Cr₂Al (Reactions 2 and 3). These intermetallic

Fig. 2. Scanning electron micrograph of *insitu*-Cr₂AlC sintered by pressureless at 1400°C for 3 h.

phases and large contents of unreacted graphite and chromium were detected at 700°C, as well as small amounts of aluminum phase (Fig. 1).

When the temperature was increased up to 800°C aluminum reacted with graphite to form Al₄C₃ (Reaction 4) and the content of pure chromium was reduced due to the formation of Cr₅Al₈ and Cr₂Al compounds by reactions (2) and (3). At this temperature, pure aluminum was vanished and the content of unreacted graphite was still high. At 900°C, almost all of the pure chromium was reacted by reaction (2) and (3) and through reaction (5) to form Cr₇C₃. Interestingly, from this temperature Cr₂AlC phase started to be formed by reactions 6–8. Similar temperature for the onset of the formation of Cr₂AlC phase has been detected by other authors using hot press and spark plasma sintering.^{16,19)}

Nevertheless, at 900°C the major phases were still Cr₅Al₈, Cr₂Al and graphite. These phases were predominant up to 1100°C, although in this temperature range formation of Cr₇C₃, Al₄C₃ and Cr₂AlC was encouraged. At 1200°C content of all the secondary compounds—Cr–Al intermetallics and carbides—strongly decreased due to reactions 6–8 to form Cr₂AlC. As a consequence, Cr₂AlC phase was the majority phase. At 1250°C practically all the secondary phases were consumed and only Cr₂AlC and traces of Cr₂Al were detected. Finally, pure Cr₂AlC phase was obtained at 1350 and 1400°C. However, small contents of Al₄C₃ were detected when the temperature was increased above 1400°C, indicating a small degradation of the Cr₂AlC phase. As a result, 1400°C is the highest sintering temperature for *insitu*-Cr₂AlC with respect to keep the pure phase. Pure phase was successfully attained under these conditions, although density of the specimen was low, 3.35 g/cm³ that corresponds with a theoretical density of 64.1%. As expected, high dense and pure Cr₂AlC cannot be achieved by pressureless sintering from the elemental constituents in one step. Figure 2 shows the polished surface of this specimen, where gray areas correspond with the Cr₂AlC grains and black areas with the porosity. Some grains were not properly formed and they presented several defects. Delamination of the grains were observed, which could be generated during the synthesis process of the phase. Cr₂AlC

Fig. 3. Scanning electron micrographs of *powder-Cr₂AlC*. Fig. 4. a) Scanning electron micrograph and b) XRD of 2step-Cr₂AlC obtained by pressureless sintering at 1250°C for 3 h.

grains, as all the MAX phases, are composed by layered structures and some delamination might be occurred.

In order to increase the density while maintaining the pure Cr₂AlC phase, the 2 step method was introduced as a new processing route. Here, the pure Cr₂AlC sample obtained at 1400°C was ground and milled to produce pure powder. **Figure 3** presents this milled powder (*powder-Cr₂AlC*) and the particle size distribution is shown in Table 1. No hard agglomeration was observed and the powder presented a unimodal particle size distribution with a mean particle size of 9.21 µm. Cr₂AlC particles were surrounded by their own debris from the milling and other impurities were not detected. The typical layered structure of the Cr₂AlC particles can be observed, suggesting a possible delamination during the milling process [Fig. 3(b)]. This powder was uniaxially pressed at 200 MPa and the pellets were sintered by pressureless sintering under argon atmosphere at different temperatures, between 1150 and 1300°C. Table 3 shows the relative and the theoretical density of the specimens at each temperature. At the lowest temperature of 1150°C the final density was 4.16 g/cm³, which is already higher than obtained by the *insitu-Cr₂AlC* method at 1400°C. Increase of the sintering temperature up to 1250°C entailed a raise in the final density, achieving a value of 4.61 g/cm³, which corresponds with 88.1% theoretical density. An increment of the sintering temperature did not further increase the density. The increase of the final density achieved by the *2step-Cr₂AlC* method (88.1%) in comparison with the *insitu-Cr₂AlC* (64.1%) process could be related with a volume change. The overall reaction of the synthesis in the *insitu-Cr₂AlC* process is:

so, 2 unit cell volume of Cr (62.1 Å) + 1 unit cell volume of Al (66.2 Å) + 1 unit cell volume of C (35.3 Å) → 1 unit cell volume of Cr₂AlC (90.6 Å).

Therefore, synthesis of Cr₂AlC from the elemental constituents triggers 2.5 times reduction of the unit volume of the reaction product. This effect generated large pores (Fig. 2) during the

synthesis process due to the lack of assisted pressure to close them, hindering the densification of the sample. This hindering effect is avoided through the *2step-Cr₂AlC* method since the phase was already formed.

Final microstructure of the Cr₂AlC sample sintered at 1250°C under argon atmosphere is shown in **Fig. 4(a)**. Grays areas correspond with the Cr₂AlC grains while black dots are the pores, which were located at grain boundaries and inside the grains. Both pore positions are commonly observed in Cr₂AlC specimens.^{12),20)} Furthermore, the sintered specimen maintained the purity of the phase, as it was corroborated by XRD [Fig. 4(b)]. Thus, the density of Cr₂AlC compounds can be enhanced using the two steps method up to 88.1% of density, where the pure phase is first formed and the densification process is carried out in a further separate step. Nevertheless, full densification of Cr₂AlC cannot be just obtained by pressureless sintering, as it commonly occurs with other MAX phases.⁴⁾ Therefore, the only alternative to promote the full densification without using ultrafine powders is to assist the sintering process by mechanical pressure, such as HP, FAST/SPS or HIP.

3.2 Field assisted sintering technology/spark plasma sintering (FAST/SPS)

The *insitu-Cr₂AlC* by FAST/SPS was performed using the homogeneous starting composition of Cr, Al and C powders. Pressure (50 MPa), heating rate (100 K/min) and dwell time (10 min) were equal for all the tests, modifying only the maximal temperature, which was 1200, 1300 and 1400°C. **Figure 5** shows the XRD of the sintered specimens at these temperatures. Cr₂AlC phase was the main phase at 1200°C, although Cr₇C₃ and Cr₅Al₈ were also detected. These secondary phases were reduced when the temperature was increased up to 1300°C, identifying only small peaks of Cr₇C₃. However, when the temperature was increased up to 1400°C in order to obtain the pure phase, as by pressureless sintering, more secondary phases were detected, mainly Cr₇C₃. These phases are formed due to the degradation of the Cr₂AlC phase. These XRD results are confirmed by the SEM

micrographs of the polished sample surfaces (**Fig. 6**). The gray areas correspond with the Cr_2AlC grains, while the white zones are Cr_7C_3 . In addition, black “craters” are observed, especially in Figs. 6(a) and 6(c), which are correlated with completely reacted areas. Therefore, pure Cr_2AlC phase were not obtained by FAST/SPS under these conditions using the elemental constituents. Similar results have been observed in the literature, where the pure Cr_2AlC phase was not obtained, and small contents of carbides were always present.¹⁹⁾ One of the explanation can be related with the fast heating rate (100 K/min) and short isothermal holding time (10 min) used in these experiments and by other authors. The fast heating and the short time limited the reaction kinetics to form Cr_2AlC —or other intermediate specimens—, hindering the formation of the pure phase. This effect also can be observed when the resultant phases at an equal temperature are compared between pressureless sintering and FAST/SPS. More Cr_2AlC phase and less carbides and intermetallic compounds were observed using FAST/SPS instead pressureless sintering at 1200°C. On the other hand, less degradation of the Cr_2AlC phase was detected by pressureless sintering at 1400°C despite the larger time at high temperature in comparison with FAST/SPS (hours versus minutes). In this case, applied current by FAST/SPS can play a determinant role as Cr_2AlC materials are electrical conductor and current flows during the sintering of these compounds.²¹⁾ The current can increase the temperature by Joule heating and promote electrochemical reactions during the synthesis process.²²⁾ Several experiments are currently investigating the effect of the current during the FAST/SPS process as it is not completely understood. In the specific case of the MAX phase, and in particular in Cr_2AlC , the current effect has not been investigated yet. Nevertheless, a detailed understanding is required to ensure the

promotion of electrochemical reactions.

In order to dismiss the problem of the limited reaction kinetics but using the fast heating rate and short dwell time of the FAST/SPS, *2step-Cr2AlC* method was used. Pure Cr_2AlC powder was not obtained by FAST/SPS so pressureless sintering was used for the synthesis process. As in the previous *2step-Cr2AlC* process by pressureless sintering, we used the *powder-Cr2AlC* (Fig. 3) as starting material. All the FAST/SPS parameters were maintained equal and only the maximal temperatures were modified. For *2step-Cr2AlC*, maximal temperatures were 1200, 1250 and 1300°C. Highly dense bulk Cr_2AlC samples were obtained, achieving densities of 5.17 and 5.21 g/cm³ at 1250 and 1300°C, respectively (Table 3). The attained densities by *2step-Cr2AlC* method are higher than for *insitu-Cr2AlC* process, as already observed for pressureless sintering. However, pure Cr_2AlC phase is just detected by XRD for maximal temperatures of 1200 and 1250°C due to small impurities of Cr_2Al were detected at 1300°C (**Fig. 7**). As a result, the maximal density maintaining the pure Cr_2AlC phase is 5.17 g/cm³, which corresponds with 98.9% of relative density. Similar values were firstly obtained by Duan et al. using the two step sintering method after the FAST/SPS densification of pure coarse and fine Cr_2AlC powder.¹⁷⁾ Microstructure of the sintered specimens was characterized, and polished surfaces of the sintered specimens are shown in **Fig. 8**. The gray areas correspond with the polycrystalline Cr_2AlC , whereas black dots are pores. Pores are mainly located at grain boundaries although they were also observed into the grains. XRD reveals the presence of Cr_2Al in the specimen sintered at 1300°C and this phase can be also observed in Fig. 8(c). Nevertheless, its identification is rather difficult on the polished surfaces since Cr_2Al particles and pores cannot be differentiated. Thus, fracture surfaces of the specimens sintered at

Fig. 5. XRD patterns of *insitu-Cr2AlC* sintered by FAST/SPS at 1200–1400°C for 10 min.

Fig. 7. XRD patterns of *2step-Cr2AlC* sintered by FAST/SPS at 1200–1300°C for 10 min.

Fig. 6. SEM microstructures of polished *insitu-Cr2AlC* sintered by FAST/SPS at a) 1200°C, b) 1300°C and c) 1400°C.

Fig. 8. SEM micrographs of 2step-Cr₂AlC sintered by FAST/SPS at a) 1200°C, b) 1250°C and c) 1300°C.

Fig. 9. Fracture surfaces of 2step-Cr₂AlC sintered by FAST/SPS at a) and b) 1250°C, c) and d) 1300°C.

1250 and 1300°C were observed to detect this phase (Fig. 9). Specimen sintered at 1250°C shows equiaxial Cr₂AlC grains with pores into the grains, but also small particles of a secondary phase is detected [Fig. 9(a)]. These particles were Cr₂Al and were not detected by XRD, indicating a low concentration of this phase. Interestingly, inter- and transgranular fracture grains can be observed. A detailed analysis of one of the fractured grains reveals the characteristic layered structure of the MAX phases [Fig. 9(b)]. On the other hand, fracture surface of the specimen sintered at 1300°C presented two different grains. The gray and black grains correspond with Cr₂AlC and Cr₂Al phases, respectively [Figs. 9(c) and 9(d)]. In addition, inter- and trans-granular fracture grains can be also observed. As a result, synthesis of the pure Cr₂AlC phase by pressureless sintering followed by densification of the pure phase by FAST/SPS (2step-Cr₂AlC method) leads to almost fully dense with highly purity Cr₂AlC materials.

4. Conclusions

Synthesis and densification of Cr₂AlC compounds have been investigated using pressureless sintering and FAST/SPS in order to obtain high dense and pure bulk materials. Pressureless sintering at 1350–1400°C under argon atmosphere of the elemental constituents of Cr₂AlC leads to obtain pure phase materials with low density (64,1%), which can be increased up to 88,1% by a second thermal treatment of the ground pure Cr₂AlC powder. On the other hand, spark plasma sintering of the elemental constituents of Cr₂AlC entails high dense materials (up to 97,1%) but with presence of secondary phases in the final microstructure. The optimized conditions to obtain high dense

and pure Cr₂AlC materials is to perform the synthesis process by pressureless calcination followed by the densification by spark plasma sintering of the pure phase powder.

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References

- 1) Z. M. Sun, *Int. Mater. Rev.*, **56**, 143–166 (2011).
- 2) H. Nowotny, *Prog. Solid State Chem.*, **5**, 27–70 (1971).
- 3) M. W. Barsoum and T. El-raghy, *J. Am. Ceram. Soc.*, **79**, 1953–1956 (1996).
- 4) M. W. Barsoum, MAX Phases. Properties of Machinable Ternary Carbides and Nitrides. Wiley VCH (2013).
- 5) B. M. Radovic and M. W. Barsoum, *Am. Ceram. Soc. Bull.*, **92**, 20–27 (2013).
- 6) M. W. Barsoum and M. Radovic, *Annu. Rev. Mater. Res.*, **41**, 195–227 (2011).
- 7) Z. J. Lin, M. S. Li, J. Y. Wang and Y. C. Zhou, *Acta Mater.*, **55**, 6182–6191 (2007).
- 8) W. Tian, P. Wang, G. Zhang, Y. Kan, Y. Li and D. Yan, *Scr. Mater.*, **54**, 841–846 (2006).
- 9) H. Li, S. Li and Y. Zhou, *Mater. Sci. Eng., A*, **607**, 525–529 (2014).
- 10) S. Li, H. Li, Y. Zhou and H. Zhai, *J. Eur. Ceram. Soc.*, **34**, 1083–1088 (2014).
- 11) W. Tian, Z. Sun, Y. Du and H. Hashimoto, *Mater. Lett.*, **62**, 3852–3855 (2008).
- 12) B. B. Panigrahi, M.-C. Chu, Y.-I. Kim, S.-J. Cho and J. J. Gracio, *J. Am. Ceram. Soc.*, **1533**, 1530–1533 (2010).
- 13) W. Tian, P. Wang, G. Zhang, Y. Kan, Y. Li and D. Yan, *Mater. Sci. Eng., A*, **454–455**, 132–138 (2007).
- 14) J. Zhu, H. Jiang, F. Wang, C. Yang and D. Xiao, *J. Eur. Ceram. Soc.*, **34**, 4137–4144 (2014).
- 15) W. Tian, Z. Sun, Y. Du and H. Hashimoto, *Mater. Lett.*, **63**, 670–672 (2009).
- 16) W.-B. Tian, P.-L. Wang, Y.-M. Kan, G.-J. Zhang, Y.-X. Li and D.-S. Yan, *Mater. Sci. Eng., A*, **443**, 229–234 (2007).
- 17) X. Duan, L. Shen, D. Jia, Y. Zhou, S. van der Zwaag and W. G. Sloof, *J. Eur. Ceram. Soc.*, **35**, 1393–1400 (2015).
- 18) Z. Sun, H. Hashimoto, W. Tian and Y. Zou, *Int. J. Appl. Ceram. Technol.*, **7**, 704–718 (2010).
- 19) W. Tian, K. Vanmeensel, P. Wang, G. Zhang, Y. Li, J. Vleugels and O. Van der Biest, *Mater. Lett.*, **61**, 4442–4445 (2007).
- 20) G. Ying, X. He, M. Li, W. Han, F. He and S. Du, *Mater. Sci. Eng., A*, **528**, 2635–2640 (2011).
- 21) O. Guillon, J. Gonzalez-Julian, B. Dargatz, T. Kessel, G. Schierning, J. Räthel and M. Herrmann, *Adv. Eng. Mater.*, **16**, 830–849 (2014).
- 22) Z. A. Munir, U. Anselmi-Tamburini and M. Ohyanagi, *J. Mater. Sci.*, **41**, 763–777 (2006).