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## SiC-BASED COMPOSITES MADE WITH SHS DERIVED POWDERS

The applications of silicon carbide-based composites at extremely high temperatures and under high partial pressure of water vapor require some modifications of the silicon carbide structure and microstructure in order to increase the reliability of the composite component. One of the methods of such modification could be to introduce phases containing yttria or chromia compounds into the composite microstructure. The presented paper reports the results of investigations on the SHS of silicon carbide powders enriched with yttrium or chromium precursors. It was experimentally proven that it is possible by the means of the SHS technique to obtain powders containing only silicon carbide and dispersions of yttrium silicate or yttrium silicide. Such powders were consequently compacted by hot-pressing or the U-FAST technique. The level of densification and the phase compositions of the materials were characterized. It was found that the sintering conditions determine the phase compositions of the sintered samples. Consolidation using the hot-pressing technique leads to the decomposition of silicon carbide and reduction of the remaining starting phases. As an effect, free graphite and carbide phases ( $YC_2$  or  $Cr_3C_2$ ) appear in the sintered samples. Applying the U-FAST technique and short sintering times lasting a few minutes allows some yttrium-silicon phases from the SiC-Y system (oxide, carbide, silicide) to be preserved in the sintered material. In the SiC-Cr system after U-FAST consolidation the  $CrSi_2$  silicide phase was preserved, which is not desirable in the final material because of its relatively low melting point of 1470 °C.

**Keywords:** silicon carbide, self-sustaining high-temperature synthesis SHS, upgraded field assisted sintering technique U-FAST, hot-pressing HP

## KOMPOZYTY NA BAZIE SiC WYTWARZANE Z PROSZKÓW OTRZYMANYCH METODĄ SHS

Zastosowania materiałów kompozytowych na bazie węgla krzemu w warunkach ekstremalnie wysokich temperatur i pod wysokim ciśnieniem parcyjnym pary wodnej wymagają pewnej modyfikacji struktury oraz mikrostruktury węgla krzemu, w celu zwiększenia niezawodności kompozytowego komponentu. Jednym ze sposobów takiej modyfikacji może być wprowadzenie do mikrostruktury kompozytowej faz zawierających itr lub chrom. Niniejsza praca prezentuje wyniki badań, otrzymanych syntezą SHS, proszków kompozytowych na podstawie węgla krzemu wzbogaconej prekursorami itru i chromu. Dowiedziono eksperymentalnie, że jest możliwe uzyskanie metodą SHS proszków zawierających tylko węgiel krzemu i wtłoczenia krzemianu itru lub krzemku itru. Wytworzone proszki zostały poddane zagęszczaniu za pomocą dwóch różnych metod, tj. prasowania na gorąco (HP) oraz techniki U-FAST. Scharakteryzowano poziom zagęszczenia otrzymanych spieków kompozytowych oraz ich skład fazowy. Stwierdzono, że warunki spiekania determinują skład fazowy spieków. Zagęszczanie przez hot-pressing prowadzi do rozkładu węgla krzemu i do redukcji pozostałych faz wyjściowych, w wyniku czego w spiekach pojawia się wolny grafit oraz fazy węglkowe ( $YC_2$  lub  $Cr_3C_2$ ). Zastosowanie techniki U-FAST i krótkich, kilkuminutowych czasów spiekania pozwala na zachowanie w spiekach z układu SiC-Y faz itrowo-krzemowych (tlenku, węgla i krzemku). W spiekach z układu SiC-Cr zachowana zostaje faza krzemkowa  $CrSi_2$ , która nie jest pożądana w finalnym materiale ze względu na niską temperaturę topnienia 1470 °C.

**Słowa kluczowe:** węgiel krzemu, samorozwijająca synteza wysokotemperaturowa SHS, spiekanie wspomagane działaniem pola elektrycznego U-FAST, prasowanie na gorąco, HP

## INTRODUCTION

Silicon carbide materials are very profitable in high-temperature applications due their relatively high chemical stability accompanied by very good mechanical properties. Nevertheless, the application of silicon carbide is limited due to the possibility of its degrada-

tion, which is especially destructive when the work environment contains water, even a small amount [1-3].

Incorporating phases containing yttrium or chromium could be an effective way of increasing of the high temperature stability of silicon carbide materials in

a humid environment [4-6]. However, the homogeneous dispersion of yttrium or chromium enriched particles at the submicrometric level is a complex process. Some authors have investigated the possibility of depositing a yttrium silicate phase on SiC using the chemical vapour method [5]. Such an idea was also applied for coating SiC particles by depositing chromium vapours and producing chromium silicides [6]. These methods did not provide uniform distribution of the incorporated phases. Some authors developed a method which employed the electrophoretic deposition of yttrium silicates [7-9]. Such an approach is more effective but complicated. Another method of incorporating well dispersed minority phases into a polycrystalline matrix could be self-propagation high-temperature synthesis (SHS). The synthesis of SiC or SiC based composites by means of SHS has been intensively elaborated for many decades [10, 11]. The aim of the presented studies was to check the possibility of incorporating phases containing yttrium or chromium into silicon carbide sinterable powders and preserving the yttrium-silicon or chromium-silicon rich phases in the polycrystalline material during sintering. Two methods of sintering were selected: typical hot-pressing and the upgraded field assisted sintering technique. Such a choice was driven by the possibility of significant differentiation of the sintering process intensity, which could be realised when comparing the two mentioned techniques of densification.

## EXPERIMENTAL PROCEDURE

### Preparation of composite powders

The scheme of the experimental procedure was as follows: in the first step, the SHS of silicon carbide was conducted starting from stoichiometric proportions of elemental silicon and graphite. The silicon source was the slag from operations of cutting and screwing silicon monocrystals. The total content of metallic impurities in this slag was lower than 0.5%. Its specific surface area was  $5.8 \pm 0.3 \text{ m}^2/\text{g}$ . 50% of the carbon used for the reaction came from the decomposition of phenol-formaldehyde resin (Nowolak, Organika Nowa Sarzyna, Poland) and the other 50% from carbon lignin (Carbomed, Poland).

The powders of the raw materials were mixed with a suitable oxide additive ( $\text{Y}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$  - Sigma Aldrich, Germany). The amount of each additive was 5 wt.%. The substrates were mixed together in a rotation mill, using SiC milling balls, for 2 hours, then compacted by uniaxial pressing and heated up to  $1550^\circ\text{C}$  in argon atmosphere when the SHS reaction started. To check the proper stoichiometry of the mixture, the phase composition of the products obtained during synthesis were examined by the XRD method. The results showed the presence of free elemental silicon in both cases (Figs. 1 and 2).

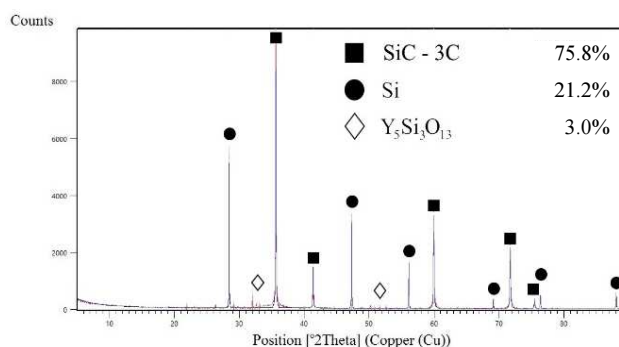


Fig. 1. Phase composition of SiC-(Y) powder after SHS of stoichiometric proportions of substrates ( $1500^\circ\text{C}$ , Ar)

Rys. 1. Skład fazowy proszku SiC-(Y) po syntezie SHS reagentów w proporcji stechiometrycznej ( $1500^\circ\text{C}$ , Ar)

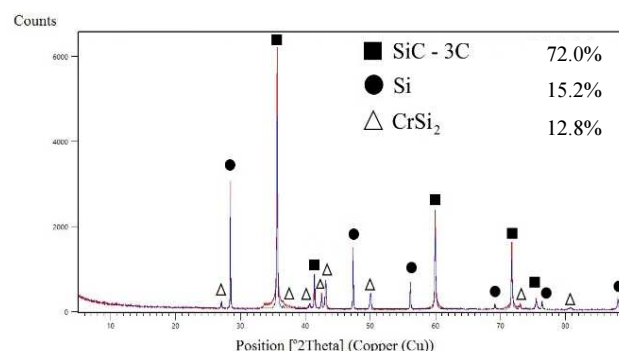


Fig. 2. Phase composition of SiC-(Cr) powder after SHS of stoichiometric proportions of substrates ( $1500^\circ\text{C}$ , Ar)

Rys. 2. Skład fazowy proszku SiC-(Cr) po syntezie SHS reagentów w proporcji stechiometrycznej ( $1500^\circ\text{C}$ , Ar)

Based on that, the SHS of silicon carbide from elemental powders with a proper oxide additive was conducted once again, but with an excess of elemental graphite. All the steps of the synthesis were repeated. The phase composition of the products obtained during renewed synthesis were again examined by the XRD method. The results confirmed the proper stoichiometry of the obtained mixture. The whole amounts of silicon and carbon reacted and there was no free elemental silicon or carbon detected in the products (Figs. 3 and 4).

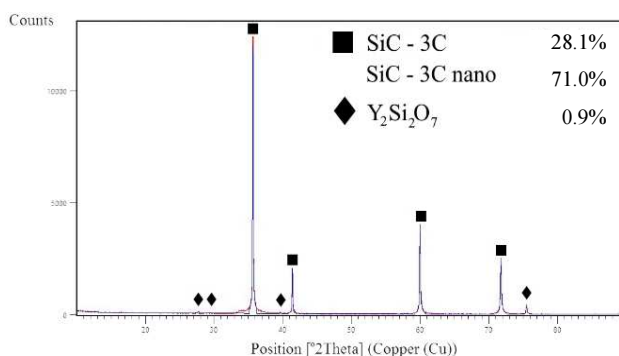


Fig. 3. Phase composition of SiC-(Y) powder after SHS of substrates with carbon excess ( $1500^\circ\text{C}$ , Ar)

Rys. 3. Skład fazowy proszku SiC-(Y) po syntezie SHS reagentów z nadmiarem węgla ( $1500^\circ\text{C}$ , Ar)

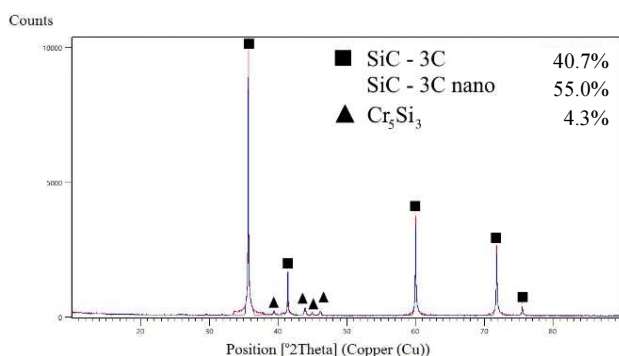


Fig. 4. Phase composition of SiC-(Cr) powder after SHS of substrates with carbon excess (1500°C, Ar)

Rys. 4. Skład fazowy proszku SiC-(Cr) po syntezie SHS reagentów z nadmiarem węgla (1500°C, Ar)

Powders with a proper phase composition were also examined by combined SEM/EDS techniques using a NovaNano SEM 200 (FEI, UK) device. Analyses were performed using a BSE (back-scattered electron) detector and Everhart-Thornley detector (ETD - secondary and back-scattered electron detector). Comparison of both the detection systems allowed us to visualize places where the yttrium or chromium compounds were located (see Figs. 5 and 6).

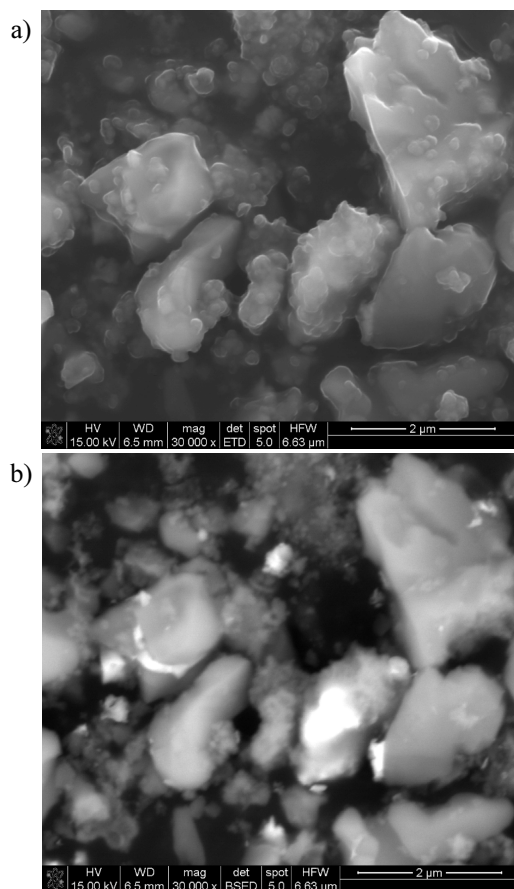


Fig. 5. SEM micrographs of same area of SiC-(Y) powder after SHS collected using ETD (a) or BSE (b) detectors - light areas show location of yttrium rich regions

Rys. 5. Obrazy SEM tego samego obszaru proszku SiC-(Y) po syntezie SHS uzyskane poprzez systemy detekcji ETD (a) i BSE (b) - jasne obszary pokazują położenie obszarów bogatych w Yttrium

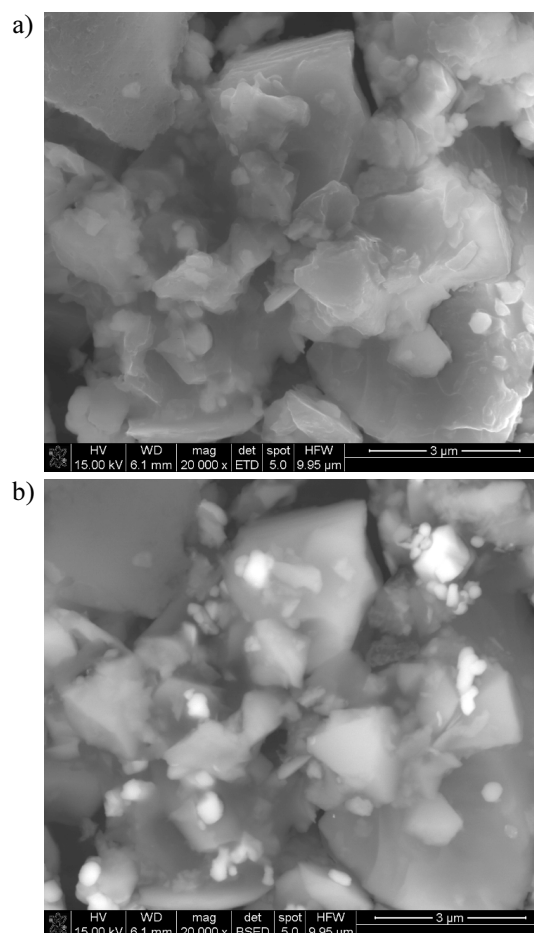


Fig. 6. SEM micrographs of same area of SiC-(Cr) powder after SHS collected using ETD (a) or BSE (b) detectors - light areas show location of chromium rich regions

Rys. 6. Obrazy SEM tego samego obszaru proszku SiC-(Cr) po syntezie SHS uzyskane poprzez systemy detekcji ETD (a) i BSE (b) - jasne obszary pokazują położenie obszarów bogatych w chrom

### Sintering of composite powders

The powders obtained from the renewed SHS procedure (SiC-(Y) and SiC-(Cr)) were consequently milled in a rotation-vibration mill, using SiC milling balls, for 2 hours and then consolidated by two techniques: hot-pressing (HP) and U-FAST. The processes were conducted employing devices produced by the National Forge Company (hot-pressing) or Genicore (U-FAST). The conditions of the HP procedure were as follows, the same for both the SiC-(Y) and SiC-(Cr) samples: graphite stamps and die, argon atmosphere, 2150°C maximum temperature with a 45-minute soaking time. The heating rate was 15°C/min and applied pressure was 25 MPa. The conditions of the U-FAST procedure were different for each powder. For the SiC-(Y) sample the conditions were as follows: graphite stamps and die, argon atmosphere, 2000°C maximum temperature with a 20-minute soaking time. The heating rate was 15°C/min and maximum applied pressure was 63 MPa. For the SiC-(Cr) samples the conditions were as follows: graphite stamps, argon atmosphere, 1750 and 1800°C maximum temperature with a 10- and 20-minute soaking time, respectively. The heating rate

was 15°C/min and the maximum applied pressure was 63 MPa for both samples. All the obtained samples were then grinded and polished to prepare them for further investigations.

### Sample characterization

The phase composition of the powders and sintered samples was analysed by means of the XRD method using a diffractometer (Empyrean system, Panalytical) and the measurements were performed in Bragg-Brentano geometry in the stepwise mode. CuK $\alpha$ 1 radiation, a Johansson monochromator and a strip detector (X'Celerator) were used. The apparent densities of the sintered bodies were determined by the Archimedes method in water at 21°C.

The relative density was determined by reference of the measured density to the theoretical value of the composite density, calculated on the basis of the rule of mixtures. These values could be treated only as an approximation due to the complicated phase composition of the sintered samples. For the calculations we assumed that the densities of the sintered sample compounds were as follows: SiC = 3.21 g/cm<sup>3</sup>; Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> = 4.00 g/cm<sup>3</sup>; Y<sub>3</sub>Si<sub>2</sub>C<sub>2</sub> = 4.55 g/cm<sup>3</sup>; Si = 2.32 g/cm<sup>3</sup>; C (graphite) = 1.90 g/cm<sup>3</sup>; YC<sub>2</sub> = 4.13 g/cm<sup>3</sup>; YSi = 4.23 g/cm<sup>3</sup>; Cr<sub>3</sub>C<sub>2</sub> = 6.68 g/cm<sup>3</sup>; CrSi<sub>2</sub> 4.39 g/cm<sup>3</sup>.

## RESULTS AND DISCUSSION

All the obtained samples, regardless of the sintering technique, were porous, which was confirmed by the density examination (Table 1). None the values of the relative densities were high. The most probable reasons for such an effect was the low sintering activity of the powders which were too coarse for intensive sintering (the microscopic observations showed the average grain size of the dominant grains population significantly exceeded one micrometer (see Figs. 5 and 6). Another reason, probably more important, was that in fact the sintering process was accompanied by intensive chemical reactions in solid state. Such a process usually limits effective working of the diffusional sintering mechanisms and finally limits the level of densification.

TABLE 1. Densities of sintered bodies

TABELA 1. Gęstości otrzymanych spieków

Type of material	Consolidation conditions		Apparent density [g/cm <sup>3</sup> ]	Approximate theoretical density [g/cm <sup>3</sup> ]	Relative density [%]
	Sintering technique	Temperature [°C]			
SiC - (Y)	HP	2150	2.78	3.209	86.63
	FAST	2000	2.86	3.208	89.15
SiC - (Cr)	HP	2150	2.67	3.289	81.18
	FAST	1750	2.69	3.306	81.37
		1800	2.63	3.315	79.33

The analyses of the phase composition of the SiC-(Y) powder, after renewed SHS (Fig. 3), also indicated the fact, which is worth noting, that the silicon carbide produced in that reaction was composed of a moissanite phase in two forms: coarse grains and nanometric ones. The Rietveld procedure applied for the calculations distinctly indicated that the majority of the grains were 3C phase nanometric ones. Yttria introduced into the reacting mixture transformed into a yttrium silicate phase (Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>). The powder obtained in the presence of chromia SiC-(Cr) (Fig. 4) also was composed of two SiC 3C type crystallites differing in size. The amount of the nanometric one was slightly less than in the powder containing the yttria additive. All the oxygen was removed from the system and chromium was present only in the Cr<sub>3</sub>Si<sub>3</sub> phase.

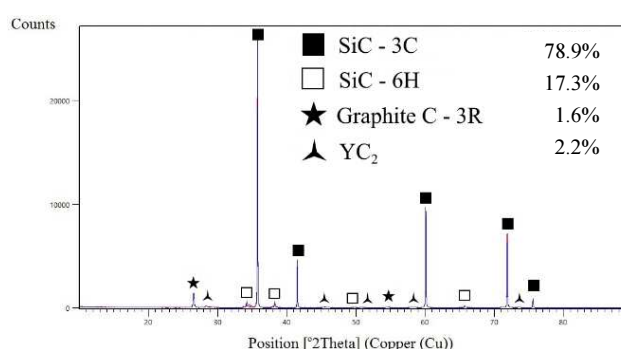


Fig. 7. Phase composition of SiC-(Y) sintered body after HP process (2150°C, Ar)

Rys. 7. Skład fazowy spieku SiC-(Y) otrzymanego przez prasowanie na gorąco HP (2150°C, Ar)

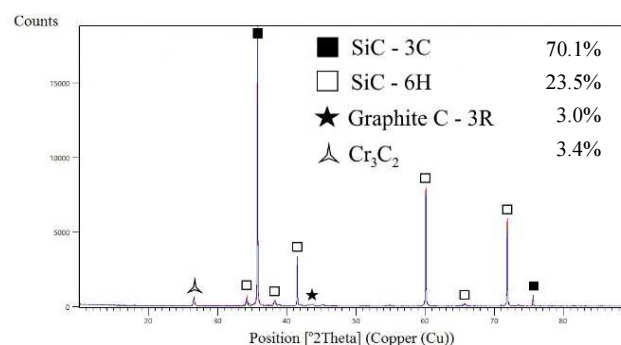


Fig. 8. Phase composition of SiC-(Cr) sintered body after HP process (2150°C, Ar)

Rys. 8. Skład fazowy spieku SiC-(Cr) otrzymanego przez prasowanie na gorąco HP (2150°C, Ar)

The results of the phase composition analyses of the sintered materials obtained by the HP process are shown in Figures 7 and 8. In both cases this process caused significant changes in the SiC phase composition. In both cases the nano SiC phase disappeared, which is obvious because of the higher diffusional activity of the nano grains during sintering. Surprisingly, the structure of the 3C type was detected as a dominant phase, not a 6H structure type usually typical for sintered SiC bodies. Such a phase composition of the sintered bodies could be caused by the presence

of external pressure during sintering and by the presence of nano grains of phases containing yttrium or chromium in the starting powder. The most important statements were that finally both yttrium and chromium were present in the sintered bodies as carbide phases and that the reduction conditions during the HP process led to the appearance of free carbon.

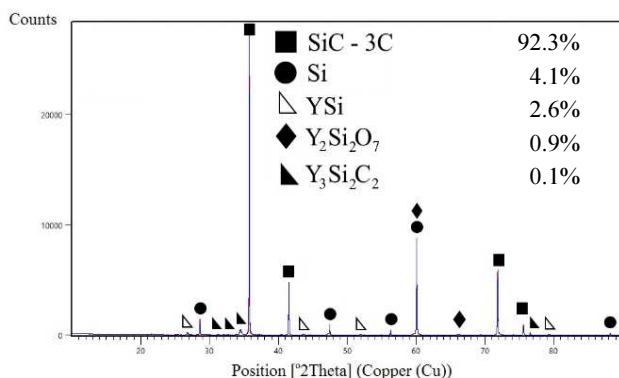


Fig. 9. Phase composition of SiC-(Y) sintered body after U-FAST process (2000°C, Ar)

Rys. 9. Skład fazowy spieku SiC-(Y) otrzymanego techniką U-FAST (2000°C, Ar)

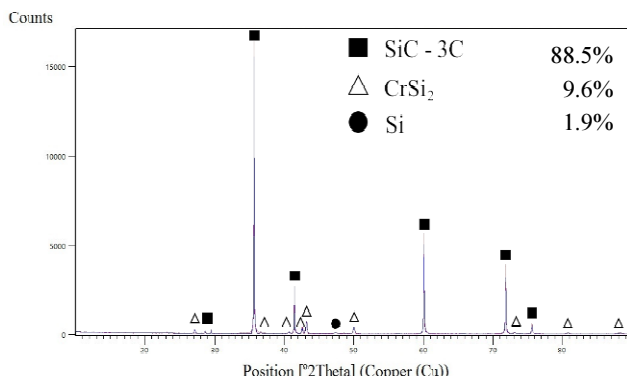


Fig. 10. Phase composition of SiC-(Cr) sintered body after U-FAST process (1750°C, Ar)

Rys. 10. Skład fazowy spieku SiC-(Cr) otrzymanego techniką U-FAST (1750°C, Ar)

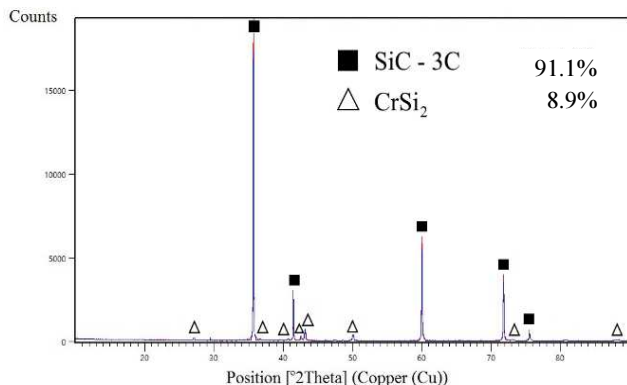


Fig. 11. Phase composition of SiC-(Cr) sintered body after U-FAST process (1800°C, Ar)

Rys. 11. Skład fazowy spieku SiC-(Cr) otrzymanego techniką U-FAST (1800°C, Ar)

The results of the phase composition analyses of the sintered materials obtained by the U-FAST process are shown in Figures 9-11. In both cases, for the SiC-(Y) and SiC-(Cr) systems, this process also caused changes in the SiC phase composition. Similar to the HP process, after U-FAST sintering the nano SiC phase disappeared and the structure of the 3C type was detected as the dominant phase. The 6H structure type was not found in the SiC-(Y) system, nor in the SiC-(Cr) system, in contrast to the HP process. Moreover, after the U-FAST sintering of SiC-(Y) the yttrium silicon oxide phase was preserved and other phases containing yttrium and silicon (intermetallic YSi and yttrium silicon carbide  $Y_3Si_2C_2$ ) were detected. It is worth underlining that the presence of the yttrium silicon carbide phase which has a MAX-phase structure [12] could be profitable to improve the mechanical properties of the composite. In the case of the SiC-(Cr) samples, chromium was present only in the  $CrSi_2$  phase, which was created during  $Cr_5Si_3$  phase transformation. In the SiC-(Cr) sample sintered by U-FAST at 1750°C the presence of free silicon was detected, but in the SiC-(Cr) sample consolidated at 1800°C it was not found. Free silicon was also detected in the SiC-(Y) sample, after U-FAST sintering at 2000°C.

## SUMMARY AND CONCLUSIONS

The incorporation of phases containing yttrium or chromium into silicon carbide polycrystalline material was carried out successfully using SHS, but proper synthesis of SiC demands carbon excess during that process. Oxide additives like yttria and chromia easily transformed during SHS to phases containing silicon -  $Y_2Si_2O_7$  or  $Cr_5Si_3$ .

During the HP densification of SiC-(Y) the reduction process lead to the appearance of  $YC_2$  and pure carbon, whereas phases containing silicon disappeared. During the HP densification of SiC-(Cr) the reduction process lead to the appearance of  $Cr_3C_2$  and pure carbon, while phases containing silicon disappeared.

Densification by means of the U-FAST method allowed the preservation of phases containing yttrium and silicon in the SiC-(Y) material, like  $Y_2Si_2O_7$ , YSi and  $Y_3Si_2C_2$ . This is a profitable effect because these phases have relatively high melting temperatures (1775, 1760 and 1650°C, respectively) and could play the role of SiC oxidation inhibitors at temperatures up to 1600°C. In the case of the SiC-(Cr) material, the U-FAST process lead to material containing chromium-silicon phases rich in  $CrSi_2$  or pure silicon. The presence of the  $CrSi_2$  phase is not acceptable because of its relatively low melting point 1470°C. It means that this material cannot limit SiC water corrosion degradation at high temperatures.

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