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MEHMET BUGDAYCI[1,2*], LEVENT ONCEL[3], MURAT ALKAN[4], AHMET TURAN[5], UMAY CINARLI[5]

A COMPARATIVE STUDY ABOUT PRODUCTION OF VANADIUM CARBIDE VIA SELF PROPAGATING HIGH TEMPERATURE SYNTHESIS AND REDUCTION

Vanadium carbide is important for industrial applications because of its high hardness, high temperature resistance, high chemical, and thermal stability. It is generally obtained from the reaction between V and C powders at a high temperature ranging from 1100 to 1500°C. Investigations on these high strength, high abrasion resistant, hard materials have been intensified in recent years and consequently, significant improvements have been achieved. In this study, VC alloys are produced with low cost processes, by reducing the oxides of their components by SHS methods and ball mill-assisted carbothermal reduction. In the experimental stage, V_2O_5 was used as oxidized Vanadium source, C_{black} as carbon source, magnesium and C_{black} as reductant. In the study, VC powders were synthesized by two different methods and optimum production conditions were determined. Furthermore, the effect of different stoichiometric charge components and the effect of experiment durations were realized by X-ray diffraction, HSC Chemistry, and SEM analyses for different reductants.

Keywords: Vanadium Carbide; SHS; Carbothermal Reduction; Leaching

1. Introduction

Transition metals are any of various chemical elements that have valence electrons in two shells instead of one [1]. Because of these features, transition metals have high hardness, temperature resistance and melting point. The transition metal carbides are a very important class of materials and their properties are similar to transition metals. In addition to the properties previously mentioned for transition metals, transition metal carbides have high thermal and electrical conductivity. Because of their outstanding properties, transition metal carbides are used in various applications including cutting tool materials, wear-resistant parts and high-temperature structural materials [2]. Among transition metal carbides, vanadium carbide (VC) stands out with its physical and mechanical properties such as high hardness, excellent wear resistance, good corrosion resistance, excellent high-temperature resistance, and high chemical and thermal stability even at high temperatures [3-6]. Vanadium carbide's molecular weight is 62.953 g/mol, melting point is 2810°C, the boiling point is 3900°C, density is 5.77 g/cm^3, hardness is 28000 kg/mm^2 and the thermal expansion coefficient is 7.2×10^{-6}/K [7].

Vanadium carbides are generally used to increase the wear resistance and hardness of the metallic materials, and their primary usage area is cutting tools. They can be directly added to the structure of the materials or can be used as a coating material [8]. Recently, environmental regulations regarding the composition of fuels used in transportation have been tightened, and for this reason, removing the harmful components of fuels has become an extremely important issue. Vanadium carbide with a high surface area acts as a catalyst in applications such as the removal of sulfur compounds from the structure [9-11]. Also, vanadium carbide is used in the production of ferrovanadium as a vanadium source [12].

Grain size affects the properties of the materials, and the mechanical properties of vanadium carbide are also significantly affected by the grain size. Hardness, strength, and wear resistance are the main features affected by grain size [13,14]. In metallurgical applications, grain refining is one of the most common processes used to increase the strength of the material. Small concentrations (0.01%) of strong carbide-forming elements such as niobium, titanium, and vanadium are added to the mild steel and ferritic steel structures to increase the strength by the

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[1] YALOVA UNIVERSITY, FACULTY OF ENGINEERING, CHEMICAL ENGINEERING DEPARTMENT, 77200, YALOVA, TURKEY
[2] ISTANBUL MEDIPOL UNIVERSITY, VOCATIONAL SCHOOL, CONSTRUCTION TECHNOLOGY DEPARTMENT, 34810, ISTANBUL, TURKEY
[3] SINOP UNIVERSITY, FACULTY OF ENGINEERING AND ARCHITECTURE, METALLURGICAL AND MATERIALS ENGINEERING DEPARTMENT, 57000, SINOP, TURKEY
[4] DOKUZ EYLUL UNIVERSITY, ENGINEERING FACULTY, DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING, 35390, IZMIR, TURKEY
[5] YEDITEPE UNIVERSITY, ENGINEERING FACULTY, MATERIALS SCIENCE AND NANOTECHNOLOGY ENGINEERING DEPARTMENT, 34755, ISTANBUL, TURKEY

* Corresponding author: mehmet.bugdayci@yalova.edu.tr

grain refining mechanism. The fine dispersion of a particular alloy carbide in the structure further increases the strength of this fine-grained ferrite structure. The fact that carbides form dispersion has made them a popular study topic [15].

Self-propagating high-temperature synthesis (SHS) is used in the production of various materials including ceramics, conventional metals, intermetallic materials, alloys and composites [16,17]. In SHS, the reaction is triggered with an external heat source and it propagates spontaneously in the reactant mixture because of the reaction's exothermic character [18]. For this reason, SHS is a cost-effective method [19]. In SHS, the metal content of the metal oxide is reduced by a reductant having a higher oxygen affinity. Adiabatic temperature (T_{ad}) and specific heat are two parameters that show if the SHS reaction will complete successfully. T_{ad} of the reaction must be over 1527°C for the reaction to start and propagate spontaneously [20]. Specific heat is obtained by dividing the enthalpy of the reaction at (25°C) by the sum of the molecular weights of the reaction products. If the specific heat is between –2250 and –4500 J/g, the reaction proceeds spontaneously in a controlled manner. It is undesirable if the specific heat of the reaction is less than –2250 J/g or more than –4500 J/g. Specific heat values below –2250 J/g are not enough to melt the charge and separate metal and slag based on density difference. On the other hand, when the specific heat value is more than –4500 J/g, high amount of metal loss occurs [21].

Carbothermic reduction is used in the production of carbides, borides and nitrides that are not in oxide form. In a carbothermic reaction, a metal oxide reacts with a carbon source in a furnace that is working at high temperatures. CO gas is formed as a by-product in the reaction and thus the oxygen in the structure of the metal oxide is removed. Unlike SHS, the carbothermic reduction has an endothermic character, and energy is needed for this reaction to proceed [22].

When SHS and carbothermic reduction were compared, they have advantages and disadvantages over each other. Minimum energy need, simplicity of the operation, short process time, using low-cost equipment and the production of high purity products without carbon are the main advantages of the SHS. There are also disadvantages of the SHS. Reactants may not react completely, and the chemical composition of the products may have slight differences because of the possible different reaction developments [18,23]. Also, it is not possible to control the temperature during the reaction, and as a result, undesirable vanadium carbide compounds could form. In carbothermic reactions, the temperature can be controlled, therefore it is much easier to obtain the product with the desired composition compared to SHS. Alloys obtained in aluminothermic and silicothermic methods contain aluminum and silicon, but this problem does not exist in carbothermic reduction. The time and energy spent during the reaction are the disadvantages of carbothermic reduction[24,25].

Different methods are also used in vanadium carbide production. Some of these methods are mechanochemical synthesis [26,27], molten salt electrolysis [28], and thermal reactive diffusion (TRD) [29,30]. A high-energy ball mill is used in the mechanochemical synthesis method, and VC products are obtained using different raw material ratios, ball-to-powder weight ratios, times, and temperatures [26,27]. In the molten salt electrolysis method, VC is produced by dissolving the $NaVO_3$ compound in a $CaCl_2$-NaCl-based molten salt bath, followed by the electrolysis process [28]. The production of VC coatings with the TRD method can occur in liquid and solid media. The liquid media can contain a mixture of borax, vanadium oxide, and reductant, while in the solid media, a mixture containing boron carbide and ferrovanadium can be used [29,30].

In this study, it is aimed to produce vanadium carbide with carbothermic reduction and self-propagating high-temperature synthesis methods, and to determine the optimum parameters for these methods. The efficiencies and the products obtained in these two methods will be compared.

2. Material method

High grade, V_2O_5 (Nanokar, 99.20%), C (>98.00%) and metallic magnesium powders (99.70%) were used for the SHS experiments. The raw materials prepared in varying stoichiometries were dried in ETUV for 1 hour at 105°C, then homogenization was achieved by mixing in the ball mill for 15 minutes. Self-propagating high temperature synthesis (SHS) reactions are a process that generates its own energy, in need of a trigger. In order to start the reaction, electricity is sent from VARIAC with copper cable, and heat is obtained with the resistance of the CrNi wire at the end and this heat triggers the SHS process.

In SHS experiments, 95%, 100%, 105% and 110% of the amount of Mg that can reduce the reactants were mixed with V_2O_5 and C powders. The weight of the 100% stoichiometric mixture was determined as 50 g, and the other compositions were changed by weight according to the amount of Mg. Experiments were carried out under atmospheric conditions. TABLE 1 presents experimental conditions.

TABLE 1

Amount of Raw Materials in SHS Experiments

	Raw Materials (g.)		
Mg. Stoc. Change %	**V_2O_5**	**Mg**	**C**
95	27,7	17,62	3,66
100		18,55	
105		19,47	
110		20,40	

As a result of SHS experiments, it was determined in XRD analysis that Mg-based products were also included in the structure besides VC phases. Leaching was applied to the products in order to eliminate these phases. Experiments were carried out with 20 grams of SHS products. The products were leached in an HCl medium, and the HCl concentration was 9.3 M. In the experiments, the solid-liquid ratio was chosen as 1/5. Leaching was carried out at 80°C and 320 rpm for 1 hour. Subsequently, the leached samples were characterized and it was found that the Mg based impurities could not be removed. Therefore, a second leaching process was applied to the leached samples under the same conditions.

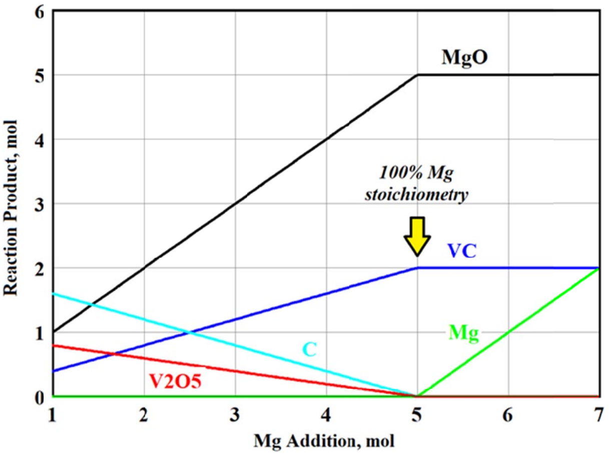
After the SHS and leaching experiments were completed, the production conditions of VC were investigated by carbothermic reduction method. In ball mill experiments, 40 grams of charges were mixed at 350 rpm for the specified test times, with a ball-to-powder ratio of 1/10. At this stage, milling duration was changed and mixtures 0 hours, 3 hours, 6 hours, and 18 hours were prepared. Subsequently, the mixtures were loaded into alumina boats and kept under 0.1 mbar vacuum at 1050°C for 60 min. After the furnace cooled to room temperature, the boats were removed, and then samples were characterized.

3. Characterization techniques

In the characterization studies, X-ray diffraction (XRD) analysis was done with BrukerTM D8 Advanced Series powder diffractometer (operated at 35 kV and 40 mA) with CuKα (k = 1.5406 Å) radiation at 2 h range of 0-90° using a step size of 0.02° and a rate of 4°/min was used for investigations of the VC samples. Microstructure images of the products were taken with Carl Zeiss/Gemini 300 brand-model SEM.

4. Results and discussion

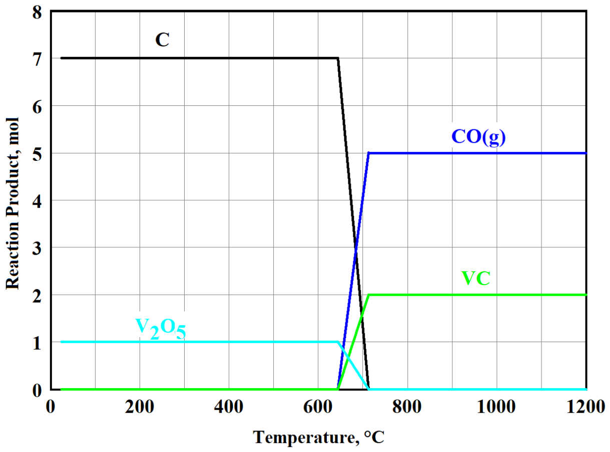
Before starting the experiments for vanadium carbide synthesis, the reduction system was thermodynamically modeled with the HSC 7 program. In the thermodynamic simulation studies, SHS production conditions were first researched and the findings are given in Fig. 1. When Fig. 1 is examined, it is seen that the VC phase can be successfully obtained by adding 5 moles of magnesium. Therefore, the amount of 5 moles of Mg was determined as 100% stoichiometric ratio in the study. It was determined that the VC phase formed stably with increasing Mg amount, so the effect of the change in magnesium stoichiometry on VC formation was investigated in experimental studies.



$V_2O_5 + 2C + 5Mg = 2VC + 5MgO$

Fig. 1. Probable phases in the V_2O_5-C system that will occur with increasing Mg stoichiometry

The carbothermic reduction conditions of vanadium carbide synthesis simulated with the HSC 7 program, the findings are shown in Fig. 2. According to Fig. 2, it is seen that the Boduard reaction takes place at 600°C to form the CO phase and it is possible to reduce vanadium penta oxide around 650°C. Zaki et al. modeled the same system with the Fact Sage program in their study and found that the system was activated kinetically at 1050°C [25]. Accordingly, the operating temperature was determined as 1050°C in carbothermic reduction experiments.

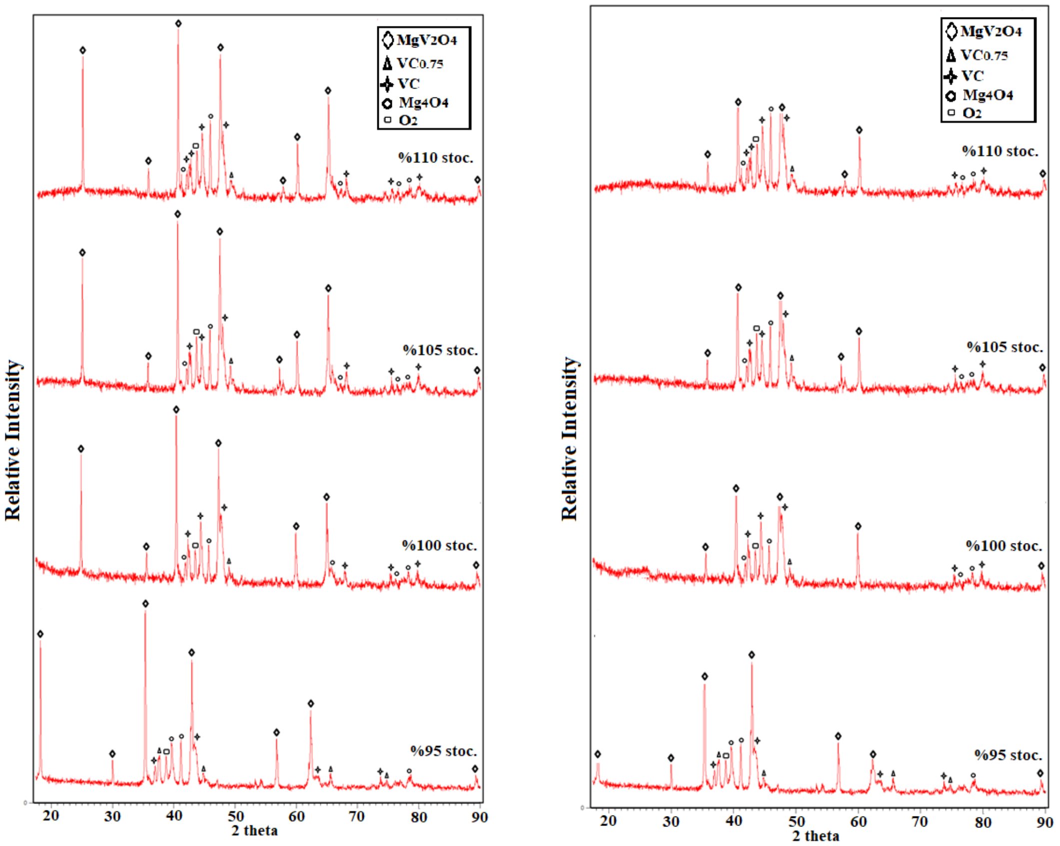


$V_2O_5 + 7C = 2VC + 5CO$

Fig. 2. Probable phases in the V_2O_5-C system that will occur with increasing C stoichiometry

According to the data obtained from thermodynamic simulation studies, SHS experiments were carried out and the effects of the change in Mg stoichiometry were determined. The powders synthesized as a result of the experiment were analyzed by XRD and it was determined that there were phases containing Mg in the structure. Leaching process was applied to the samples to remove these phases. Fig. 3a shows the XRD patterns of the mixtures containing 95%, 100%, 105%, and 110% stoichiometric Mg before the leaching process. Fig. 3b presents these mixtures' XRD patterns after leaching. Fig. 3 clearly shows that all SHS experiments give similar results. In addition, as a result of the leaching process, when the samples were compared with each other, similar results were obtained. Therefore, the 100% stoichiometric mixture was determined as the appropriate condition for VC, and the reductant stoichiometry was not changed in further leaching processes.

Fig. 3a shows the XRD patterns of the mixtures containing 95%, 100%, 105%, and 110% stoichiometric Mg before the leaching process. It was determined that the VC with $VC_{0.75}$ crystalline structure was formed, but undesirable phases such as MgV_2O_4, Mg_4O_4, and O_2 appeared intensely. According to the diffraction patterns, SHS experiments using 100% and more Mg reducing agent give similar phase formation. However, when 95% stoichiometric amount Mg was used, the other Mg-based phases were observed. In order to eliminate these undesirable



(a) (b)

Fig. 3. (a) XRD Results of SHS Experiments, (b) XRD Results of Leaching Experiments

phases, leaching was applied, and Fig. 3b presents the XRD patterns after leaching. As a result of the leaching process, when the samples were compared with each other, similar results were obtained. A decrease was observed in the aforementioned structures, but the structure could not be completely freed from undesired phases. In all samples, the main observed phase, MgV_2O_4 structure, also reduced its intensity. It was determined that the strong peak seen at 25°C in the graph disappeared. Although the highest number and intensity of VC peaks were observed in the mixture containing 110% Mg in SHS experiments, the 100% stoichiometric mixture did not show a very different composition. Therefore, the 100% stoichiometric mixture was determined as the appropriate condition for VC, and the reductive stoichiometry was not changed in further leaching processes.

Acceptable results could not be obtained for VC recovery after leaching. Although the VC phase was successfully formed after both SHS and leaching processes, the structure could not be obtained with the desired purity. When the results of SHS and leaching tests were examined, it was seen that the most vanadium carbide composition was obtained in a mixture of 100% at least. Therefore, the second leaching process was applied to these mixtures.

The sample exposed to the second leaching process was compared with the SHS product and the first leach product, the results are given in Fig. 4.

According to Fig. 4, it was seen that after the second leaching process, the MgV_2O_4 phase in the structure removed and the VC containing structure obtained with $VC_{0.75}$. In addition to XRD characterizations, microstructure investigation of the same samples were also made, and the findings are presented in Fig. 5.

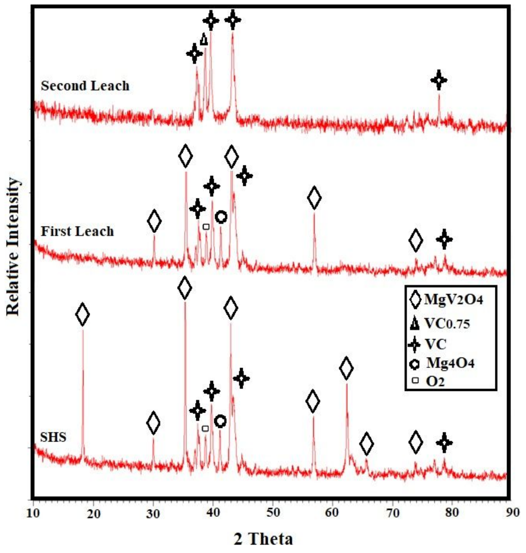
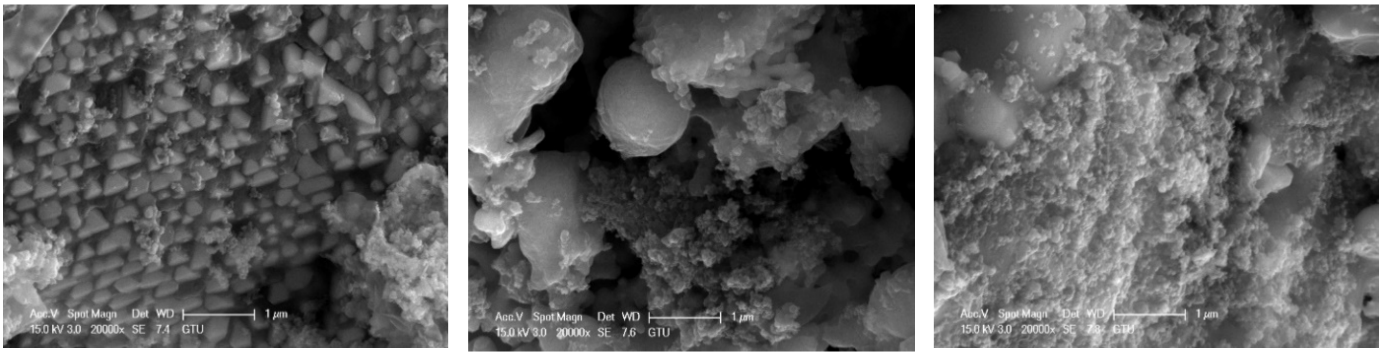


Fig. 4. Comparison of XRD results for 100% stoc. sample produced by SHS and after leaching stages (SHS, First Leach, Second Leach)

It was determined that the Mg-containing structures (assumed according to XRD data) seen in Fig. 5(a) lost their sharp morphology in Fig. 5(b) as a result of the leaching process. In addition, when Fig. 5(a) and (b) are compared, it was observed



(a) Before leach (b) First leach (c) Second leach

Fig. 5. SEM images of 110% stoichiometric mixtures; (a) before leach, (b) after first leach, (c) after second leach

that the Mg-containing structures seen in Fig. 4 decomposed and disappeared. When Fig. 5(c) was examined, it was determined that by removing the impurities from the composition at a higher rate, structures with a higher surface area were formed.

After the SHS studies were completed, the carbothermal production conditions were examined.

In the study of Zaki et al., VC production parameters were investigated by the carbothermal method and it was observed that the vanadium oxide phases were significantly removed at 1050°C [25]. Accordingly, 1050°C was chosen as the reduction temperature, and the samples were treated at varying mechanical alloying times (0 h, 3 h, 6 h, 18 h), and the results were compared with the XRD method. Fig. 6 presents XRD results of the samples.

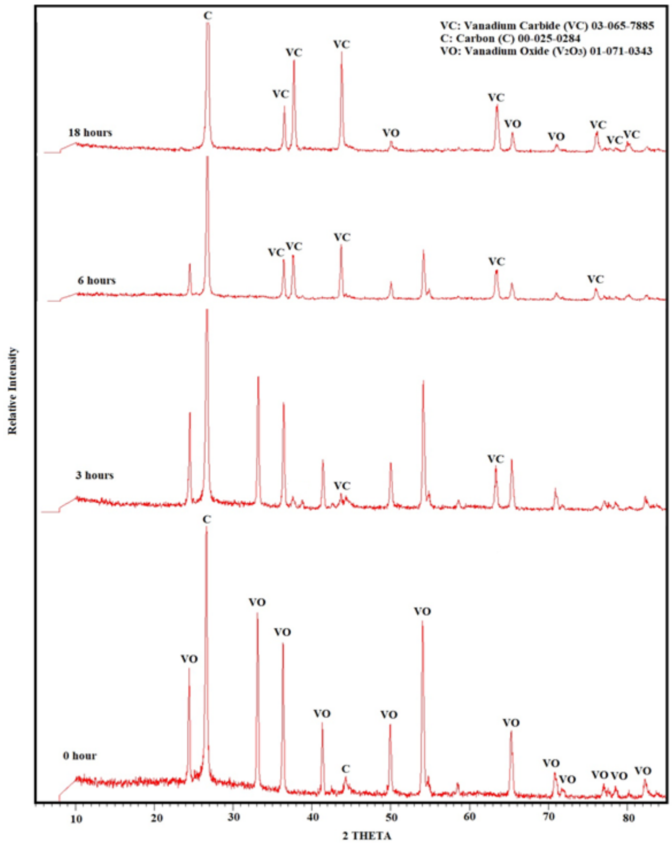


Fig. 6. XRD pattern of ball mill assisted (0 h, 3 h, 6 h, 18 h) carbothermal reduction products, 1050°C, 0.1 bar

According to XRD results, only vanadium oxide (VO) and carbon (C) phases were seen in the structure as a result of the reduction process without mechanical activation. As a result of mechanical activation of the same mixture for 3 hours, it was observed that 3 vanadium carbide (VC) peaks of small intensity were formed, and it was determined that the intensity of both C and VO phases decreased. It is understood from Fig. 6 that this situation continues as the mechanical activation time increases. When the mechanical activation time was increased to 6 hours, the amount of VC formed increased from 3 peaks to 5, and this number increased to 7 at the end of 18 hours. In the experiment, which was carried out with 18 hours of activation, although only one C phase remained, the intensity of the structures containing VO was greatly reduced and the structures containing VC were formed at a high rate. Accordingly, it has been observed that VC can be produced under 0.1 mbar vacuum at 1050°C by mechanical activation

The microstructure of the carbothermal reduction sample activated for 18 hours, in which the best results were seen according to the XRD graph, is shown in Fig. 7. Comparing Fig. 7 with the leached samples (Fig. 5(b), (c)) it is seen that it has a morphology consisting of coarser grains. Accordingly, submicron powders can be obtained by the leaching added SHS method, while micron-sized powders can be produced by the carbothermal method.

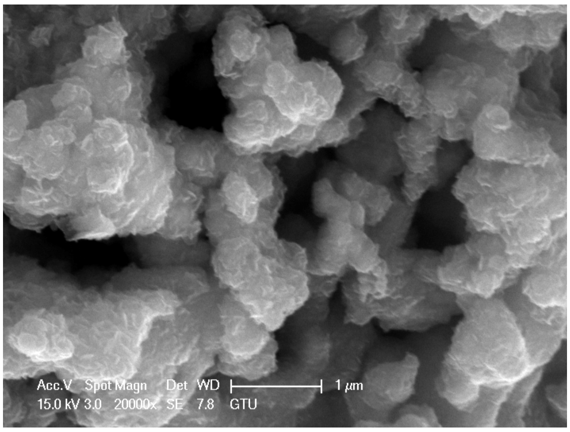


Fig. 7. SEM images of 18 h mechanical activated carbothermal product, 1050°C, 0.1 bar

5. Conclusion

In this study, VC production parameters were investigated by SHS and carbothermal reduction methods. As a result of the SHS experiments analyzes, it was determined that Mg-based impurities remained in the structure, and leaching experiments were carried out to remove them. In the SHS experiments, the effect of the reductant stoichiometry change on the formed products was investigated, and according to the XRD results, the highest number and intensity of peaks were observed in the mixture containing 110% Mg. A second leaching process was applied to increase the amount of VC-based structures here, and the structure completely freed from impurities. In addition, the structure formed in the second leaching process is in the form of $VC_{0.75}$, with VC. Accordingly, the desired VC structure is formed with the SHS method. In the carbothermal reduction experiments, powders with 100% stoichiometric composition were treated with varying mechanical activation times (0 h, 3 h, 6 h, 18 h) and then reduced under vacuum at 1050°C for 60 minutes. According to XRD results, it was seen that the VC phase started to form in the mixture activated for 3 hours, and the amount and intensity of the phase increased as the time increased. A high amount of VC phase could be obtained in the experiment carried out in 18 hours. In the SEM characterization of the samples, it was observed that coarser grains were formed as a result of carbothermal production, while submicron structures were obtained in the leached SHS samples. When the experiments performed in this study were compared, it was determined that the %100 stochiometric SHS mixture with double leach gave the most optimum result for VC production.

Declaration Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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