YERLİ HAMMADDELERDEN HAREKETLE TiB₂ ESASLI İLERİ TEKNOLOJİ SERAMİKLERİN ÜRETİLMESİ

ÖZET

TiB₂ (titanyum diborür), yüksek sertlik, mukavemet, elektriksel iletkenlik, isol iletkenlik ve kimyasallara ve ergimış metallerle karşı yüksek dirence sahip bir geçmiş grubu metal diborürdür. TiB₂'nin egeme sıcaklığı 3225 °C civarındadır, yüksek oranda kovalent bağlı yapısına ve hezkagonal kristal yapısı sahiptir. TiB₂'den üretilmiş farklı şekillerdeki ürünlerin güncel ve başlica kullanım alanları zırh plakaları, kesici takımlar, alüminyum buharlaştırma kayıcıkları, aşınmaya dirençli kaplamalar ve alüminyum elektroliz katotlardır.

Tez çalışması kapsamında, TiB₂'nin SHS ile sentezine, karbotermik olarak sentezlenmiş ticari kalite TiB₂ tozlarının SPS şartlarının araştırılmasına, SHS ile sentezlendirilen TiB₂ tozlarının basınçlar senterleme ve SPS ile sinterlenebilirliğini ve ticari kalite TiB₂ tozlarından SPS ile PVD hedef malzemelerin üretildiğin PVD performans testlerinin yapılmasına yönelik deyisel çalışmaları yürütülmüştür.

SHS deneysel çalışmaları ve takip eden HCl liqi işlemler sonucunda, %100 Mg stokiyometrisi ve argon atmosferi altında yürütülen deneysel çalışmalarda, %0,81 Mg içeriğine, 6,42 m²/g spesifik yüzey alanına ve yaklaşık 200 nm ortalama tane boyutuna sahip TiB₂ tozları sentezlenmiş ve bu parametrelerin TiB₂'nin optimum SHS parametreleri olduğu tespit edilmiştir. SHS çalışmalarda NaCl ve MgSO₄·7H₂O gibi fonksiyonel ilavelerin de SHS ürünlerine olan etkileri irdelenmiştir.

SPS çalışmaları önemli bir şekilde deyisel olarak, 6,24 μm ortalama tane boyutundaki ticari kalite TiB₂ tozlarının sinterlendinden, 30 MPa basınçta 50 MPa sinterleme basıncının uygulandığı ve argon atmosferi altında yürütülen deney setinin 1800 °C sinterleme sıcaklığında sinterlenen numunelerinde elde edilmiştir. En yüksek sertlik değerleri ise 17,46 GPa ile 50 MPa sinterleme basıncının 1500 °C'den sonra uygulandığı ve vakum altında deneysel çalışmaların gerçekleştirilmesi deney setinin 1780 °C sinterleme sıcaklığında sinterlenen numunelerinde elde edilmiştir.

Ticari kalite TiB₂ tozlarına WC-Co bilyali yüksek enerjik atritör ile 60 dakikaya varan proses sürelerinde mekanik aktivasyon işlemi de uygulanmıştır. 60 dakika mekanik olarak aktive edilen numunelerde 5,84 μm ortalama tane boyutu ve %2,15 W, %0,44 C ve %0,26 Co kontaminasyonu tespit edilmiştir. Mekanik olarak aktive edilen TiB₂ tozlarının SPS deneyseleri, WC-Co içeriklerinden dolayı katlı sinterleme çalışmaları kapsamında değerlendirilmiştir. Bu çalışmalarla elde edilen en yüksek bağlı yoğunluk, sertlik ve kurna tokluğunun değerleri sırası ile %99,57, 20,73 GPa ve 3,45 MPa.m⁻¹/² olarak, 50 MPa sinterleme basıncının uygulandığı ve argon atmosferinin kullanım şartlarında, 1700 °C sinterleme sıcaklığında sinterlenen numunede ölçülmüştür. Bu sonuçlardan, ticari kalite TiB₂ tozlarının SPS ile
sinterlenebilirliğin tanı boyutunun düşürülmesi yanı sıra WC-Co katkısı ile önemli ölçüde artırılabileceği anlaşılmuştur.

SHS ile sentezlenen TiB\textsubscript{2} tozlarının basınçsız sinterleme ve SPS ile sinterlenebilirliğe yönelik deneySEL çalışmalar da gerçekleştirilmiştir. SHS ile sentezlenen ve ticari kalite TiB\textsubscript{2} tozları, öncelikle argon atmosferi altında ve 1500 °C sinterleme sıcaklığında 60 dakika süre ile sinterlenmiştir. Basınçsız sinterleme sonucu, SHS ile sentezlenen ve ticari kalite TiB\textsubscript{2} tozlarından ölçülen bağlı yoğunluk ve sertlik değerleri sırası ile %69,67, %70,86 ve 7,26 GPa, 10,01 GPa olarak ölçülmüştür. Daha sonra SHS ile sentezlenen TiB\textsubscript{2} tozları ağırlıkça %25 ve %50 oranlarında ticari kalite TiB\textsubscript{2} tozlarına katılmış ve SPS ile sinterlenebilirlikleri araştırılmıştır. Deneysel çalışmalar başlangıçta 50 MPa sinterleme basıncı uygulayarak, argon atmosferi altında ve 1600 °C sinterleme sıcaklığında yürütülmüştür. %50 SHS ile sentezlenen TiB\textsubscript{2} ilavesi ile sinterlenen numunede, %96,34 bağlı yoğunluk ve 21,48 GPa sertlik değeri ölçülmüştür ki bu değerler, monolitik TiB\textsubscript{2} tozlarının SPS ile sinterlenmesinde ulaşılan en yüksek yoğunluk ve sertlik değerleridir. Bu sonuçlardan hareketle, SHS ile sentezlenen TiB\textsubscript{2} tozlarının, karbotermik olarak sentezlenmiş tozlara göre monolitik olarak SPS ile sinterlenmeye daha uygun olduklarını anlaşılmatadır.

Son olarak, ticari kalite TiB\textsubscript{2} tozlarının SPS ile sinterlenmesi ile 150 mm çapında bir PVD hedef malzeme de üretiliştir. Üretilen PVD hedef malzeme ile silisyum, cam ve yüksek hız çeligi altlık malzemeler üzerine 80,6 nm'den 600,0 nm'ye kadar değişen kalınlıklarda TiB\textsubscript{2} kaplamalar başarı ile uygulanmıştır.
PRODUCTION OF TiB$_2$ BASED ADVANCED TECHNOLOGY CERAMICS
BY UTILIZING DOMESTIC RAW MATERIALS

SUMMARY

TiB$_2$ (titanium diboride) is characterized with its unique properties such as high hardness, strength, melting point, wear resistance, thermal and electrical conductivity and it also has high durability against chemical substances and molten metals. It is a transition metal boride and it has hexagonal crystal structure with space group of P6/mmm. The melting point of TiB$_2$ is about 3225 °C. Its covalently bonded atomic structure provides the hardness values as high as 45 GPa.

Impact resistant armors, cutting tools, aluminum evaporation crucibles, wear resistant coatings and aluminum electrolysis cathodes are between the main applications areas of TiB$_2$.

Synthesis of TiB$_2$ is conducted via several methods in laboratory or in industrial scale. Carbothermic synthesis of TiB$_2$ from the oxides of titanium and boron by a reducing agent such as carbon or B$_2$C at high temperatures, metallothermic reduction of oxides of titanium and boron by a reducing agent such as magnesium or aluminum, mechanical alloying of titanium and boron oxides by using metallothermic route or mechanical alloying of elemental forms of titanium and boron, sol-gel method and aluminum melt reaction process of titanium and boron oxides following leaching of aluminum matrix to recover synthesized TiB$_2$ powders are among the most important techniques to synthesize TiB$_2$.

Self-propagating high temperature synthesis (SHS) is one of the important methods to synthesize advanced materials such as ceramics (e.g. TiB$_2$, B$_4$C, Si$_3$N$_4$); abrasives, cutting tools and polishing powders (e.g. TiC, cemented carbides); resistive heating elements (e.g. MoSi$_2$), shape-memory alloys (e.g. TiNi); high-temperature structural alloys (e.g. nickel aluminides); master alloys (e.g. AlTiB); neutron attenuators (e.g. refractory metal hydrides) as well as conventional metals and their alloys. Although the discovery of metallothermic reactions (Beketov 1865; Goldschmidt 1895) is earlier, combining with flame propagation theories and the first gasless metallothermic combustion experiments were conducted by Merzhanov et al. in the middle of 1960s. SHS reactions are highly exothermic. Thus, the propagation of reactions and the yield of reaction products continue in self-sustaining mode without requiring additional heat or energy.

SPS is one of the newest approaches for the sintering of ceramics and metallic powders. It provides an internal heating by the formation of spark plasma, which is generated from direct current electricity discharge, between powders. Shorter sintering times at relatively lower temperatures are the most important features of the process. An SPS system is roughly the combination of graphite die system, electrodes, pressure mechanism, chamber to work under vacuum or gas atmosphere, pyrometers, water cooling unit, DC generator and a control unit.

In the present study, SHS of TiB$_2$ ceramic powders, SPS of commercial grade (carbothermically synthesized) and synthesized by SHS TiB$_2$ powders and
production of TiB₂ PVD target materials by the SPS of commercial grade TiB₂ powders were investigated.

In the SHS stage, TiO₂ and B₂O₃ powders were mixed with 90%, 100% and 110% of stoichiometrically required amount of Mg powders. SHS experiments were conducted under both air and argon atmospheres to determine the optimum process atmosphere. The effects of some functional additives (NaCl and MgSO₄·7H₂O) were also carried out with the various addition ratios. SHS products were leached in HCl media to purify their TiB₂ contents.

The optimum SHS parameters were determined as stoichiometrically 100% Mg addition and Ar process atmosphere. Mg content of the experiment which was conducted with the optimum parameters was measured as 0.81%. Besides, its specific surface area was measured as 6.42 m²/g and its average grain size was about 200 nm. The experiment, which was conducted with 90% Mg addition under atmospheric conditions, also provided the purest TiB₂ powders having a Mg content as 0.77%. But this experiment had lower leaching cake weight as 3.9 g and lower specific surface area value as 5.77 m²/g than the experiment which was conducted with stoichiometrically 100% Mg addition and under Ar process atmosphere.

Addition of NaCl and MgSO₄·7H₂O increased the amounts of impurities in the synthesized powders and in the leached TiB₂ powders. The mentioned impurities were TiO₂ for NaCl addition and Mg based oxides for MgSO₄·7H₂O. But, specific surface area values of the leached powders were remarkably increased with the addition of NaCl. Measured values were 11.50 m²/g for 2.5% NaCl addition ratio and 11.78 m²/g for 5.0% NaCl addition ratio. It showed that if leaching step is modified to remove remaining TiO₂ phase, NaCl addition can be utilized to synthesize TiB₂ powders with superior specific surface area values. On the contrary, MgSO₄·7H₂O addition dropped the specific surface area values.

In the SPS stage, determination of the optimum SPS sintering parameters of commercial grade monolithic TiB₂ was the first objective of the present study. TiB₂ powders were sintered at various temperatures both under vacuum and argon atmospheres with different pressure values for this purpose. XRD, SEM, micro hardness and Archimedes density measurement techniques were applied to the sintered compacts for the characterization.

Sintering parameters of monolithic TiB₂ ceramics which have an average grain size of 6.240 µm were investigated by using SPS. Effects of sintering temperature between 1600 °C and 1800 °C, sintering pressure of 50 MPa and 70 MPa and sintering pressure mode as initial and after 1500 °C were among the parameters to be investigated. The constant parameters of SPS were heating rate of 150 °C·min⁻¹ and 5 minutes of soaking time.

It was clearly observed that increase in sintering pressure from 50 MPa to 70 MPa, the application of sintering pressure after 1500 °C (to prevent the negative effects of the oxide films surrounding ceramic grains) and the use of argon sintering atmosphere beneficially influenced the density and hardness values. The highest hardness values were obtained in the experiments as 17.46 GPa at 1780 °C under 50 MPa pressure applied after 1500 °C and as 16.59 GPa at 1780 °C under initially applied pressure of 70 MPa under both vacuum atmosphere. Relative density values of the compacts which were produced in these experiments were 79.44% and 80.17% respectively. The highest relative density value was achieved as 94.22% from the sample which was sintered under argon atmosphere with an initial pressure of 50
MPa at 1800 °C. Also the increase in the average grain sizes of sintered samples was determined in accordance with higher hardness and relative density values due to the increase in diffusion between the grains.

Another experimental set was designed for the SPS of mechanically activated commercial grade TiB$_2$ powders. Commercial grade TiB$_2$ powders were mechanically activated by using high energetic attritor with increasing process durations till 60 minutes. The powders which were milled for 60 minutes had an average grain size of 5.842 µm and 2.150% W, 0.443% C and 0.260% Co content due to WC-Co milling balls. So, the SPS experiments of mechanically activated TiB$_2$ powders were evaluated as WC-Co added experimental studies. Sintering experiments were conducted under argon atmosphere with an initial sintering pressure of 50 MPa and at 1600 °C, 1700 °C and 1800 °C. The soaking time of the experiments at 1600 °C and 1700 °C was 5 minutes and 3 minutes for the experiment at 1800 °C due to the beginning of melting. The highest density, hardness and fracture toughness values were measured as 99.57%, 20.73 GPa and 3.45 MPa-m$^{1/2}$ from the sample sintered at 1700 °C. It was clear that the addition of WC-Co to TiB$_2$ increases the mechanical properties of sintered TiB$_2$ samples.

TiB$_2$ powders which synthesized by SHS were also sintered by pressureless sintering and SPS. Pressureless sintering was conducted under argon atmosphere for 60 minutes at 1500 °C. The relative density and hardness values of pressureless sintered SHS synthesized and commercial grade TiB$_2$ powders were 69.67%, 70.86% and 7.26 GPa, 10.01 GPa, respectively. TiB$_2$ powders which were synthesized SHS were added to commercial grade TiB$_2$ powders 25% and 50% by weight respectively. SPS experiments were conducted under argon atmosphere with an initial pressure of 50 MPa at 1600 °C. The highest relative density and hardness values were measured as 96.34% and 21.48 GPa from the experiment conducted with 50% SHS synthesized TiB$_2$ addition. These values are also higher than measured results from the sintered samples of commercial grade TiB$_2$ powders. It is clear to understand that TiB$_2$ powders synthesized by SHS are more suitable to monolithically sinter by using SPS.

Also commercial grade TiB$_2$ powders were synthesized in the form of PVD target material. PVD thin film coatings were successfully produced on the surfaces of silicon, glass and high speed steel substrates with various thicknesses varying from 80.6 nm to 600.0 nm.