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Research Article

Shaping of Titanium Dioxide by Slip Casting Technique*

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Abstract

In this study, shaping of titanium dioxide powders using slip casting method was aimed. Experimental work essentially includes three stages. Initially, settling experiments were carried out using 2 vol. % TiO_2 suspensions. In the second stage TiO_2 slip was prepared at dispersion condition (pH = 7.0) and then shaped using plaster mould. The sintering process of shaped samples were carried out at 1300, 1400 and 1500°C. Finally, shrinkage, Archimedes and flexural strength tests, microstructure (SEM) and phase analysis (XRD) were performed. Settling experiments tests for the powder of TiO_2 suspensions showed that the zpc (zero point of charge) is at approximately pH = 1-2. XRD patterns showed only rutile phase peaks for the samples sintered at three different temperatures. There is a small difference between the peak intensities of the sintered samples. Liquid phase formation containing titanium dioxide may have caused a decrease in peak intensities. Consequently, increasing the sintering temperature resulted in a decrease in total porosity, and an increase in firing shrinkage, closed porosity, apparent density, bulk density and bending strength values. Water absorption decreased from 5.24% to 1.96%. Apparent porosity decreased from 18.03% to 7.12%. Firing shrinkage increased from 8.70% to 11.30%. Bulk density increased from 3.24 to 3.64 gr/cm^3. Three point bending strength increased from 399.36 kg/cm^2 to 566.33 kg/cm^2 with the increasing sintering temperature.

Keywords: Titanium Dioxide, Slip Casting, Dispersion, Mechanical Properties.

Titanyum Dioksitin Slip Döküm Tekniği ile Şekillendirilmesi

Öz

Bu çalışmada, titanyum dioksit tozunun slip döküm tekniği ile şekillendirilmesi amaçlanmıştır. Deneysel çalışmalar esas olarak üç aşamadan oluşmaktadır. İlk olarak, hacimce % 2'lik TiO_2 süspansiyonları kullanılarak sedimentasyon deneyleri yapılmıştır. İkinci aşamada, dispersiyon şartlarında TiO_2 slip çamurları hazırlanmıştır ve daha sonra alçı kalıplarda şekillendirilmiştir. Şekillendirilen numunelerin sinterleme işlemi 1300, 1400 ve 1500°C'de 2 saat süre ile yapılmıştır. Son olarak, küçülme, Arşimed ve eğme dayanımı testleri, Mikroyapı (SEM) ve faz (XRD) analizleri uygulanmıştır. TiO_2 tozuna ait süspansiyonların sedimentasyon testleri zpc noktasının (zero point of charge) yaklaşık olarak pH = 1-2'de olduğunu göstermiştir. Üç farklı sıcaklıkta sinterlenen numunelerin XRD paternleri sadece rutil fazına ait pikleri göstermiştir. Sinterlenmiş numunelerin pik şiddetlerinde çok küçük bir fark vardır. Titanyum dioksit içeren sıvı faz oluşumu pik şiddetlerinde bir düşüşe sebep olmuş olabilir. Sonuç olarak, sinterleme sıcaklığının artması toplam gözenek değerlerinde bir düşüşe ve pişme küçülmesi, kapalı porozite, görünür yoğunluk, bulk yoğunluk ve eğme

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dayanımında bir artışa sebep olmuştur. Su emme değeri %5.24'den %1.96'ya düşmüştür. Görünür gözeneklilik %18.03'ten %7.12'ye düşmüştür. Pişme küçülmesi oranı %8.70'den %11.30'a yükselmiştir. Bulk yoğunluk 3.24'ten 3.64 gr/cm^{3}'e yükselmiştir. Üç nokta eğme dayanımı, artan sinterleme sıcaklığı ile 399.36 kg/cm^{2}'den 566.33 kg/cm^{2}'ye yükselmiştir.

Anahtar Kelimeler: Titanyum Dioksit, Slip Döküm, Dispersiyon, Mekanik Özellikler.

1. Introduction

Nowadays the important properties and the critical application of the advanced technology of ceramics has become one of the significant material technologies of this century (Ceramic Industry, 1999).

Titanium dioxide has a great importance due to its photocatalytic activity (Fujishima and Zhan 2006). Titanium dioxide found I nature as rutile, anatase and brookite phases (Wu et al., 2006). Rutile form decomposes at 1640°C.

Production of TiO_2 ceramic parts includes; dry mixing, pressing, extrusion or slip casting followed by firing the parts to vitrification with approximately 2 hr. at 2400-2450°F (Ceramic Industry, 1999; Information Center Battelle, 1981).

Dutta et al. investigated the adsorption of arsenate (As(V)) and arsenite (As(III)) to two commercially available titania slips. The zeta potential value of tatania was measured to evaluate the differences in slip behaviors. The points of zero charges (zpc) for two dispersants were at pH 6.2 and 6.9, respectively (Dutta et al., 2004).

Jingxian et al. studied the dispersion properties of titanium dioxide slips via rheological measurements and sedimentation tests (Jingxian et al., 2004).

Cesarano and Aksay studied the flocculation and dispersion mechanisms of aluminum oxide suspensions with (PMMA-Na) at different pH values. Settling experiments were carried out using 2 vol. % alumina suspensions. For the sample of α-alumina the zpc was at about pH = 8.7 (Cesarano and Aksay, 1988-1; 1988-2).

In our study we investigated the stability of aqueous TiO_2 suspensions using sedimentation tests and determined the zpc of TiO_2 suspensions as pH=1-2.

2. Material and Method

2.1. Materials

The raw material used in this study was anatase TiO_2 (Kronos Titania, 99.8 % pure, d_{50}=1.5 µm). Deionized water was used for suspension preperation. The pH was calibrated by standardized HCl and NaOH solutions.

2.2. Settling Tests

Settling tests were carried out using 2 vol. % TiO_2 suspensions. 10 suspensions were prepared at different pH changing from 1 to 10, then stirred for 4 hours 70 ml of each suspension was then poured into glass tubes and after a few days, the final sedimentation heights were noted.

2.3. Shaping

TiO_2 slip was prepared at dispersion condition (pH = 7.0) and then shaped using plaster mould.

2.4. Sintering

The shaped samples were sintered at 1300°C, 1400°C and 1500°C for 2 h. in a labaratory furnace ($MoSi_2$ resistance) with a heating rate of 5 °C/min.

2.5. Characterization of the Samples

Shrinkage, Archimedes, density, porosity and flexural strength tests were applied to the powder and sintered samples. The samples were characterized by XRD using Cu-Kα radiation (Shimadzu). Leo 1430VP electron microscopy was used for performing SEM image analysis of the sintered samples.

3. Conclusions and Recommendations

3.1. Settling Test Results

Settling experiments results of titanium dioxide powder are given in Figure 1. As shown in Fig.1 flocculation and large sedimentation volumes are at pH =1, 2 and 3. The point of zero charge (zpc) for Kronos titania was obtained as pH = 1-2. Dispersion and small sedimentation volumes are at pH ≥ 4. All slip suspensions used in this study were prepared at pH =7.

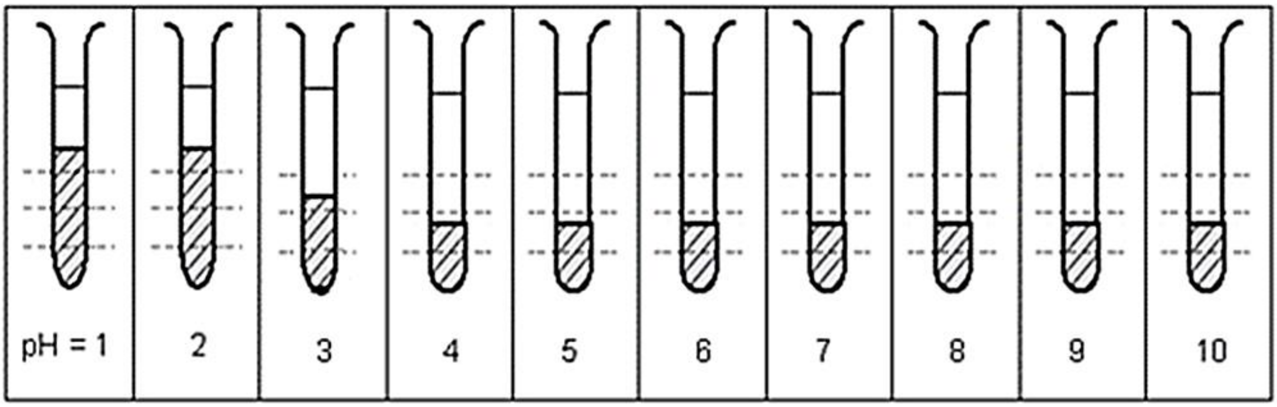


Fig. 1. Shematic representation of settling experiments

The charge at the surface of particles is controlled by pH of the liquid and by addition of chemicals that give monovalent cations (Na^+, $NH4^+$, Li^+).

Flocculation and large sedimentation volumes are at pH =1, 2 and 3. As van der Waals attraction force between particles is higher than the repulsion force at these pH, particle-particle attraction results in the formation of agglomerates and in a decrease in viscosity.

The zpc results of Kronos Titania in our study is at pH= 1, 2 and 3. These results contrast with appreciations of Dutta et al. (2004), who reported that the zpc of Degussa P25 is at pH 6.8 ± 0.2 (Dutta et al., 2004).

At pH ≥ 4 repulsion force between particles is higher than van der Waals attraction force. Similar charges repel each other, and the particles are held apart in the suspension by electrostatic forces. As the charge of surface increases, the degree of dispersion increases and agglomeration decreases.

3.2. Physical and Mechanical Test Results

Archimedes and flexural strength results are given in Table 1. Table 1 shows that the higher the temperature the higher the shrinkage, closed porosity, apparent density, bulk density and flexural strength values but the smaller the water absorption and porosity percentage. It was reached 14.75% minimum total porosity at 1500°C sintering temperature.

Table 1. Archimedes and Flexural Strength Test Results

Sintering temperature (°C)	**1300**	**1400**	**1500**
Firing shrinkage (%)	8.70	10.10	11.30
Water absorption (%)	5.74	3.05	1.96
Apparent porosity (%)	18.03	10.73	7.12
Closed porosity (%)	6.09	6.83	7.63
Total porosity (%)	24.12	17.56	14.75
Apparent density (gr/cm^3)	3.50	3.81	3.97
Bulk density (gr/cm^3)	3.24	3.52	3.64
Flexural strength (kg/cm^2)	399.36	566.33	>600

Along with the increase in sintering temperature, an increase in firing shrinkage, closed porosity, apparent density, bulk density and flexural strength values is expected. As a result of diffusion mechanisms proceeding with sintering at high temperatures, the grains get closer to each other and the spaces between them are closed, while some of the open pores are lost, some of them become closed pores. For these reasons, an increase in density is achieved and an increase occurs in the flexural strength of samples with higher density.

3.3. XRD Analysis

X-ray diffraction patterns of unsintered TiO_2 powder and sintered samples were presented in Fig.2. XRD analysis of the unsintered powder showed only anatase peaks whereas sintered samples showed only rutile phase peaks. There is a small difference between the peak intensities of the samples sintered at three different temperatures.

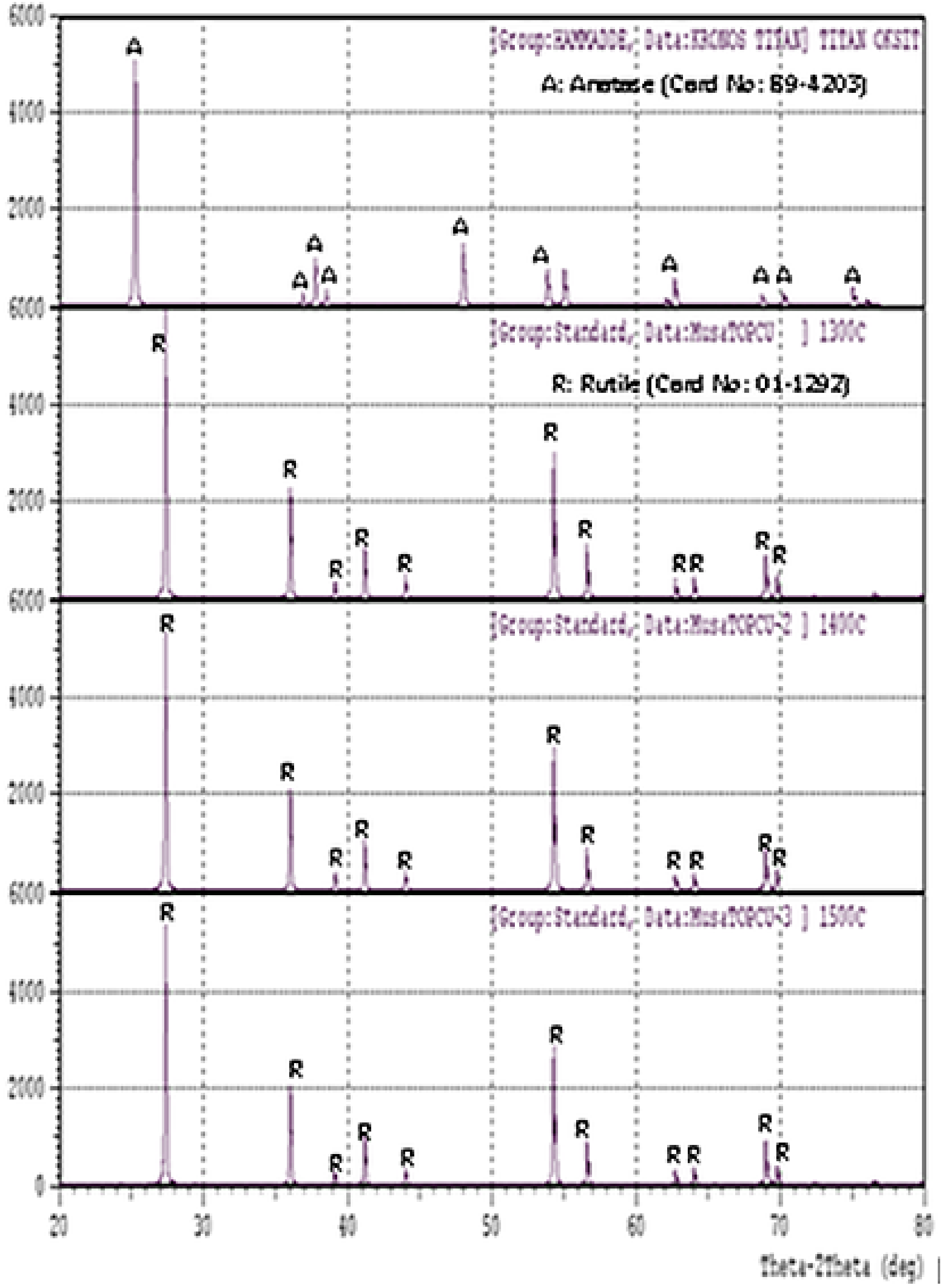
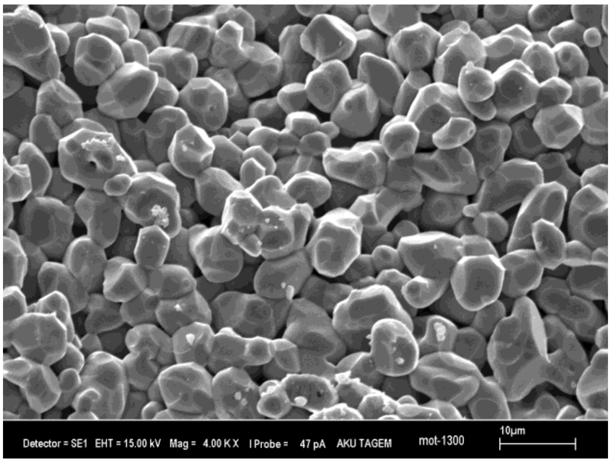


Fig. 2. XRD patterns of the sintered samples

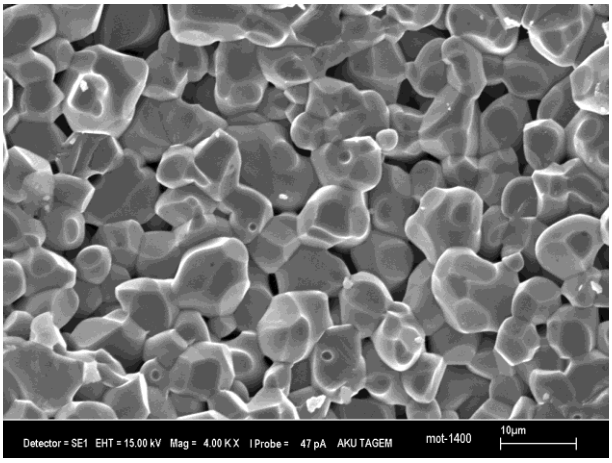
When the XRD patterns given in Fig. 2 are examined, it is seen that changes in the peak intensities occur by increasing the temperature. The reason for this is thought to be the decrease in crystallinity with the formation of liquid phase containing TiO_2, by increasing the temperature.

3.4. SEM Analysis

Scanning Electron Microscopy (SEM) images of the samples were presented in Fig. 3. The images showed that the higher the sintering temperature the larger the particle size.



(a)



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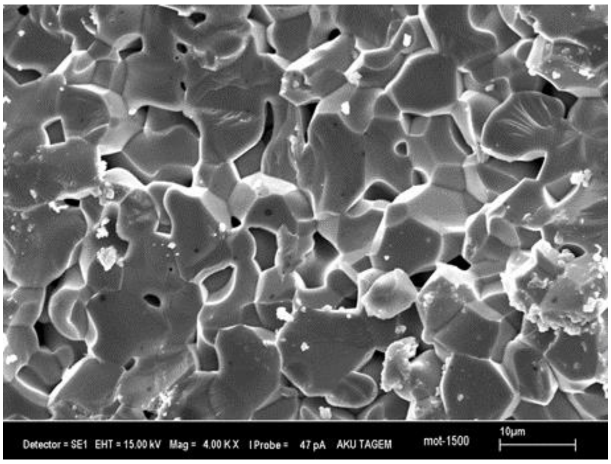
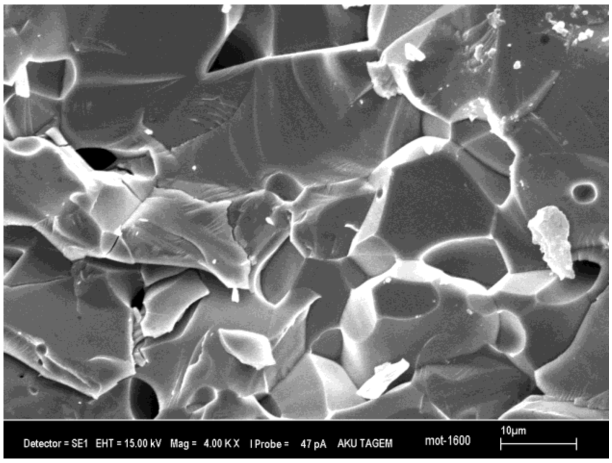
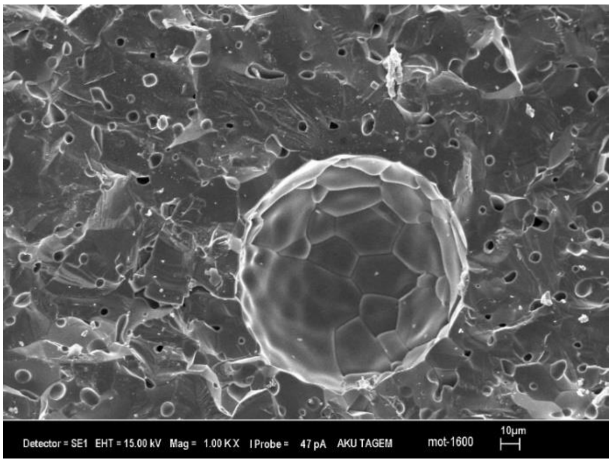


(c)



(d)



(e)

Fig. 3. SEM micrographs of the samples (a.1300°C, b.1400°C, c.1500°C, d.1600°C and e.1600°C)

When SEM images are examined, relatively equaxial grains of approximately 10 µm in size are seen at 1300°C. With the sintering temperature rising to 1400°C, there was a slight increase in grain size. However, intergranular and intragranular pores are also noteworthy.

The formation of closed pores, which are also noticeable in SEM images, is consistent with the increase in the closed pore percentage given in the physical test results. With the sintering temperature rising to 1500°C, relatively equaxial spherical grains were replaced by larger irregularly shaped grains. At this temperature, closed pores are observed. At 1600°C, an abnormal growth occurred in the grains and grain sizes reached almost 20-30 µm.

4. Conclusion

Optimum conditions were determined by sedimentation experiments in order to shape Kronos Titania by slip casting method. Physical and mechanical tests, as well as phase analysis and SEM analysis, of the samples obtained by sintering the TiO_2 slip cast samples prepared under these optimum conditions were performed. The results obtained from this study are summarized below:

- Flocculation and large sedimentation volumes are at pH =1, 2, 3 and the point of zero charge for Kronos Titania was obtained as pH = 1-2. Optimum dispersion conditions are at pH ≥ 4 where repulsion force between particles is higher than Van der Waals attraction force.

- The higher the sintering temperature the higher the firing shrinkage, closed porosity, apparent density, bulk density and flexural strength values of the sintered samples while the smaller the water absorption, and porosity.

- XRD analysis of the sintered samples showed only rutile phase peaks at three different temperatures while unsintered powder was in the anatase form.

- With the sintering temperature rising especially to 1500°C and 1600°C, the equaxial grains in the microstructure have grown excessively and turned into irregular shaped grains.

Acknowledgment

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