

PREFACE

This was a long road walked on bare foot. During this walk, the suffer was permanent. But the success is the sum of the losses and failures we lived through this journey and the real men don't talk about their losses.

ACKNOWLEDGMENT

This work was financially supported by The Marmara University Scientific Research Committee (FEN-C-031210-0288). I express sincere appreciation to Prof. Dr. Ziya Engin ERKMEN for his guidance and insight throughout the research , Prof.Dr. Faik OKTAR for allowing using his lab facilities and Assoc. Prof.Dr. Bora DERİN, for his consistent help for making FACT SAGE analysis. Also, we would like to thank Prof.Dr. Mustafa ÖKSÜZ and Res. Ass. S. Serdar PAZARLIOĞLU for their incredible support to measure the materials' mechanical properties, Prof.Dr. Gürçan ORALTAY and Dr.Eng. Mustafa İLHAN for their kindly help to monitorize the microstructure of the materials, Assoc. Prof. Dr. S. Sinan KESKİN and Res. Ass. Özgür ÇINAR for their sustained assistance to analyze our specimens. Thermal spray processing of the specimens were carried out in the surface engineering application company, Yüzey Muhendislik San. Tic. Ltd. Sti., without considering commercial interest, i also appreciate their contribution to scientific research.

This thesis can not be terminated without sustainable support of my family. But over all, this master thesis is dedicated to my beloved sister, Müberra Burçin ÇETİNER who passed away in 2009, at the age of 23.

TABLE of CONTENTS

	PAGE
PREFACE	i
ACKNOWLEDGMENT	ii
TABLE of CONTENTS	iii
ÖZET	v
ABSTRACT	vi
SYMBOLS	vii
ABBREVIATIONS	viii
LIST of FIGURES	ix
LIST of TABLES	xiv
1-INTRODUCTION	1
2-GENERAL BACKGROUND	2
II.1.1. Alumina	2
II.1.2. Seydişehir Alumina	5
II.2. Titania	6
II.3. Aluminum Titanate	8
II.4. Hydroxyapatite	17
II.5. Thermal Spray Coating Processes	22
II.6. Instruments Used in this Research	23
3. MATERIAL and METHOD	25
III.1. Experimental Setup	25
III.1.1. Materials Used in the Experiment	25
III.1.2. Experimental Setup of Each Procedure	25
4. RESULTS and DISCUSSION	38
IV.1. Results and Discussion of Beneficiation of Seydişehir Alumina	38
IV.1.1. Differential Thermal Analysis Results and Discussion	38
IV.1.2. XRF Analysis Results and Discussion	39
IV.1.3. XRD Analysis Results and Discussion	40
IV.1.4. SEM Analysis Results and Discussion	41
IV.1.5. Laser Particle Size Results and Discussion	41

IV.2. Results and Discussion of Production of Alumina-Titania Biocomposite	42
IV.2.1. Archimèdes Density Measurement Results and Discussion	42
IV.2.2. XRD Analysis Results and Discussion	43
IV.2.3. SEM and EDS Analysis Results and Discussion	45
IV.2.4. Microhardness Testing Results and Discussion	55
IV.2.5. Compressive Strength Testing Results and Discussion	57
IV.3. Results and Discussion of Coating with HA the Alumina-Titania Substrate using Flame Spray Process	58
IV.3.1. Microhardness Testing Results and Discussion	58
IV.3.2. SEM and EDS Analysis Results and Discussion	60
5. CONCLUSION	72
REFERENCES	75
CURRICULUM VITAE	

ÖZET

Alümina 20 yıldan daha uzun bir süredir yüksek sertliğine eşlik eden düşük sürtünme, aşınma ve in vivo ortamda tepkimesizliği nedeni ile seçilen bir biyomalzemedir. Okside olan titanyumun rutil fazının biyouyumlu olduğu belirtilmiştir. Bu, biyocam ve sinterlenmiş hidroksilapatit (HA) gibi bazı seramiklerde keşfedilen bir özelliktir. Fakat alümina ve titanyanın meydana getirdiği tialit karışımı (Alüminyum titanat- 50 % mol Al_2O_3 ve 50 % mol TiO_2 yeni bir meydan okumadır. Bu çalışmada, ilk olarak Seydişehir alüminasını “Kral Suyu” asidik çözeltisinin içinde yıkayıp ıslahını, akabinde % ağı. 2.5, % ağı. 3.5, % ağı. 4.5 MgO ve % ağı. 1 SiO_2 ve kalanı alümina ve titania karışımı (1:1 mol) olacak şekilde harmanların hazırlanması sağlandı. 1600 °C ‘de 12 sa bu harmanları sinterledikten sonra, mekanik özellikleri (basma ve sertlik testi) ve faz oranları (XRD analizi) analiz edildi ve Seydişehir alüminası yerine laboratuvar ölçeğindeki alümina –analitik saflık- içeren kontrol grubu ile karşılaştırıldı. Altlık malzemesinin karakterizasyonun ardından (SEM ve EDS analizi), iki farklı tür malzemenin karşılaştırılması gerçekleştirildi. Alümina-titanya biyokompozitinin üretimini takiben, alev sprej prosesi kullanılarak sığır hidraoksiapatiti ile ısıl püskürtme kaplaması uygulandı ve kaplama tabakalarının karakterizasyonu (SEM ve EDS analizi ve mikrosertlik ölçümleri) yapıldı.

ABSTRACT

Alumina is a biomaterial of choice for more than 20 years due to its high hardness accompanied by low friction, wear and inertness to in vivo environment. It has been reported that titanium oxidized to the rutile phase is bioactive. This is a property discovered for certain ceramics such as Bioglass and sintered hydroxylapatite (HA). But the combination of alumina and titania forming tialite (Aluminium titanate-50 mol % Al_2O_3 and 50 mol % TiO_2) is a new challenge. In this work we made firstly the beneficiation of the Seydişehir alumina by leaching it in the acidic solution “the Aqua Regia” followed by preparation of batches containing 2,5 wt %, 3,5 wt % and 4,5 wt % of MgO as the sintering aid, 1 wt % of SiO_2 and the balance; the alumina and titania powder mixture (1:1 mole). After sintering these batches at 1600 °C for about 12 h, their mechanical properties (the compression and hardness testings) and phase ratios (the XRD analysis) were analyzed and compared with the control group containing the laboratory scale (analytical purity) alumina instead of the Seydişehir alumina. Following the characterization (the SEM and the EDS analysis) of the substrate material, the comparison of two different kinds of materials was carried out. Following the production of the alumina-titania biocomposite, the thermal spray coating using the flame spray process by bovine hydroxyapatite was applied and the characterization of the coating layers (the SEM & EDS analysis and the microhardness measurements) was performed.

SYMBOLS

E : Elastic Modulus

Å : Armstrong

°C: Celcius

α : Linear dilatation coefficient

Al₂O₃ : Aluminum Oxide-Alumina

SiO₂ : Silicium Oxide-Silica

Fe₂O₃ : Iron Oxide

Na₂O : Sodium Oxide

Al(OH)₃ : Aluminum hydroxide

CaO : Calcium oxide-Calcia

MgO : Magnesium oxide-Magnesia

TiO₂ : Titanium oxide-Titania

Al₂TiO₅ : Aluminum titanate

La₂O₃ : Lantalum oxide

SnO₂ : Tin oxide

C : Carbon

S : Silicium

ABBREVIATIONS

HA : Hydroxyapatite

EU : European Union

USA : United States of America

Ti-OH : Titanium hydroxide

Bov. HA : Bovine Hydroxyapatite

β-TCP : β-tricalcium phosphate

TTCP : Tetracalcium phosphate

ACP : Amorphous calcium phosphate

AT : Aluminum titanate

CaP : Calcium phosphate

SEM : Scanning Electron Microscopy

EDS : Energy Dispersive Spectrometry

XRF : X-Ray Fluorescence Spectrometry

XRD : X-Ray Diffraction

LIST of FIGURES

Page

Figure 2.1. Example of the acetabular cup (The Exceed ABT Acetabular system for hip prosthesis co-designed by Mr Smith ¹ in conjunction with Biomet [®] Inc.).....	3
Figure 2.2. Thermal transformation sequence of the aluminum hydroxides.....	4
Figure 2.3. The crystal structure of alpha alumina.....	4
Figure 2.4. Flow chart for the Bayer Process.....	6
Figure 2.5. The atomic configuration of rutile.....	7
Figure 2.6. Conventional crystal structure of Al_2TiO_5 showing both the (a) distorted, edge-shared oxygen octahedra about each metal site and (b) the oxygen-metal bonds (green: Al, purple: Ti, red: O). The square structure on each image is the outline of a single unit-cell.....	14
Figure 2.7. The binary phase diagram of Al_2O_3 - TiO_2	14
Figure 2.8. The ternary phase diagram of Al_2O_3 - TiO_2 - MgO	15
Figure 2.9. Formation solid solution substituting some Al^{3+} ions by Mg^{2+} into tialite crystal. (Red:O, Green:Al, Blue: Mg, V: Void).....	16
Figure 2.10. The crystal structure of Al_2TiO_5 showing the oxygen-metal bonds after the addition of MgO (Mg^{2+} ions) as sintering aid and substituting some Al^{3+} ions (green: Al, purple: Ti, red:O, blue: Mg).....	16
Figure 2.11. The cortical or compact bone, the trabecular or spongy bone and the arrangement of carbonate hydroxyapatite and collagen in the formation of hard tissues.....	17
Figure 2.12. Crystal structure of carbonate hydroxyapatite and the powder X-ray diffraction patterns and infrared spectra of enamel, dentine and bone.....	18
Figure 2.13. Hydroxyapatite structure projected down the c-axis onto the basal plane.....	20
Figure 2.14. X-ray diffraction pattern of the Bov.HA powder (●, HA; ▲, FA; ■, HA (OH, Cl, F rich); β, whitlockite) (Before thermal spray coating process, bottom).	

X-ray diffraction pattern of the Bov.HA after plasma spray { ▲, FA; ●, HA; ■, HA (OH, Cl, F rich); ○, CaO} (After thermal spray coating process, above).....	21
Figure 2.15. Powder flame spray system.....	23
Figure 3.1. Experiment set up of our procedure.....	27
Figure 3.2. Procedure of beneficiation of Seydişehir alumina; a) alumina powder as taken (at left), b) leaching procedure b) on heating magnetic stirrer, c) After boiling with distilled d) water and decantation of the excess water.....	28
Figure 3.3. Powders of alumina after beneficiation when drying at the drying oven (at left) and when sintering in the furnace (at right).....	28
Figure 3.4. The standard calibration samples.....	30
Figure 3.5. The calibration lines of standard samples.....	30
Figure 3.6. The basic ball milling process we applied for grinding and also homogenization of the specimens.....	33
Figure 3.7. Pressing procedure; (a) the uniaxial manual pressing, (b) steel mold, (c) powder, (d), filled powder into the mold, (e) piston in the mold, (f) mold in the pressing, (g) pressing, (h) pressure applied onto the press (2000 psi), (i) and j) relieving of pression (0 psi), (k) ejection of the pellet from the mold.....	34
Figure 3.8. Sintered specimens of the first group of –S- type specimens, from left to right, S1 group to S4 group.....	34
Figure 3.9. Crushing and grinding of bioceramic pellets for XRD powder analysis measurements.....	35
Figure 3.10. Our process of HA flame spray coating; a) Cleaned powder filler, b) Combustion Flame Spray System, c) Oxygen tubers, d) Acetylen tube, e) Our specimens put in the order for the process, f) and g) Bond coating application (specific color and shape of the flame; White and irregular), h) and i) Bovine HA coating application (specific color and shape of the flame; Yellowish orange and long curved), j) At the and	

of the application, our specimens, k) Our specimens when cooled down to the room temperature.....	37
Figure 4.1. The DTA thermogram of Seydisehir alumina before beneficiation and calcination.....	38
Figure 4.2. The calibration lines of Seydisehir alumina samples.....	39
Figure 4.3. The XRD patterns of raw Seydisehir alumina and Seydisehir alumina powders after beneficiation and calcination at 1200 °C.....	40
Figure 4.4. SEM micrographs of Seydisehir alumina powders (x90 magnification); Seydisehir raw alumina powder (upleft), after 3 hours of beneficiation and after calcination at 1200 °C (downleft), after 5 hours of beneficiation and after calcination at 1200 °C for 2 hours (downright).....	41
Figure 4.5. The average particle size distribution of Seydisehir alumina powders after beneficiation and calcination before ball milling.....	42
Figure 4.6. Graphical comparison of the specimens' density (1-4; S1-4 and 5-8; L1-4).....	43
Figure 4.7. The XRD peaks of –S- type specimens.....	44
Figure 4.8. The XRD peaks of –L- type specimens.....	44
Figure 4.9. The comparison of XRD peaks of our specimens.....	45
Figure 4.10. Comparison of all the batches sintered at the same temperature (1600 °C) with the same magnification (x500, back scattering mode).....	47
Figure 4.11. Comparison of all the batches sintered at the same temperature (1600 °C) with the same magnification (x2000, back scattering mode).....	48
Figure 4.12. SEM microstructure (x5000, back scattering mode) and the related EDS analysis of L1 type specimen.....	50
Figure 4.13. SEM microstructure (x5000, back scattering mode) and the related EDS analysis of S1 specimen.....	51
Figure 4.14. SEM microstructure (x2000, back scattering mode) and the related EDS analysis of L4 specimen indicating different composition at the different places of the structure “n1” and “n2”.....	53
Figure 4.15. SEM microstructure (x2000, back scattering mode) and the related EDS analysis of S4 specimen indicating	

different composition at the different places of the structure “1” and “2”.....	55
Figure 4.16. Comparison of the specimens’ hardnesses (1: S1, 2: S2, 3: S3, 4: S4, 5: L1, 6: L2, 7: L3, 8: L4).....	56
Figure 4.17. Comparison of the specimens’ compressive strength. (1: S1, 2: S2, 3: S3, 4: S4, 5: L1, 6: L2, 7: L3, 8: L4).....	57
Figure 4.18. Comparison of the specimens’ hardnesses after coating (1: S1, 2: S2, 3: S3, 4: S4, 5: L1, 6: L2, 7: L3, 8: L4).....	59
Figure 4.19. Trace of diamond probe of Vickers microhardness measurement device taken on the coating’s cross-section.....	59
Figure 4.20. Stereomicroscopy (x50 at upper left and x 100 at upper right middle respectively) and SEM images (x250, back scattering mode, down) of the L1 type specimen.....	61
Figure 4.21. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back scattering mode, at right) of the L2 type specimen.....	61
Figure 4.22. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back scattering mode, at right) of the L3 type specimen.....	62
Figure 4.23. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back scattering mode, at right) of the L4 type specimen.....	62
Figure 4.24. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back scattering mode, at right) of the S1 type specimen.....	62
Figure 4.25. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back scattering mode) of the S2 type specimen.....	63
Figure 4.26. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back scattering mode) of the S3 type specimen.....	63
Figure 4.27. Stereomicroscopy (x50 at left and x 100 in the middle respectively) and SEM images (x250, back	

scattering mode) of the S4 type specimen.....63

Figure 4.28. SEM microstructure (x2000, back scattering mode) and the related EDS analysis of L2 specimen indicating different composition at the different places of the structure “1” ,“2” and “3”67

Figure 4.29. SEM microstructure (x2000, back scattering mode) and the related EDS analysis of S2 specimen indicating different composition at the different places of the structure “1” ,“2” and “3”71

LIST of TABLES

Page

Table 2.1. Chemical composition and physical property requirements of Alumina.....	3
Table 2.2. The impurity content of Seydişehir alumina powders.....	5
Table 2.3. Physical properties of titanium oxide (Rutile phase).....	7
Table 2.4. The typical physical properties of aluminum titanate.....	10
Table 3.1. The standard samples' composition (weight %).....	29
Table 3.2. The standard samples' composition (mass %).....	30
Table 3.3. The powder composition of each batch in the slurry.....	32
Table 4.1. Seydisehir alumina (raw and with different leaching times) samples' composition (mass %) [51].....	39
Table 4.2. Results of Archimèdes density measurements.....	42
Table 4.3. Results of microhardness testing of the alumina-titania biocomposite.....	55
Table 4.4. Results of compressive strength testing results.....	57
Table 4.5. Results of microhardness testing of the alumina-titania biocomposite coated with HA using the combustion flam spray method.....	58