



WEAR BEHAVIOUR OF SOME MULLITE BASED CERAMIC COUPLES

S.M.Naga *)

S.A.R.Naga **)

ABSTRACT

In the last few decades, ceramics have found their way in many engineering and aeronautical applications. The types, origin and methods of ceramic preparation have shown to largely affect the chemical, physical, mechanical and tribological behaviour of used ceramic.

This work aims to prepare dense mullite-based ceramic bodies from the available raw materials. The effect of batch composition and firing temperature on the densification and phase composition of the prepared bodies is herein discussed. Results have confirmed that dense mullite-based ceramics can be produced by firing clay-alumina-talc-albite upto 1500°C without any additional mineralizers.

The present work gives also a particular consideration to the relative wear between attained ceramic bodies under pure sliding conditions to assess the contribution of mullite formation on the ceramic wear mechanism. Low firing temperature results softer ceramic bodies with higher wear rates.

INTRODUCTION

Hard ceramics with distinguished mechanical, thermal and chemical properties, e.g. composites based on corundum (Al_2O_3), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), silicon carbide and nitride ($\text{SiC} \cdot \text{Si}_3\text{N}_4$) have wide possible future application as engineering materials. They would be extensively applied as parts of machines and devices subject to wear and friction. The application of such materials replacing the conventional engineering materials -e.g. metals and alloys- leads to a cost-effective response to many wear situations [1-4].

Generally, the tribological behaviour of ceramics is of a complicated nature. It has been claimed that adhesion theory can explain

*) Associate Professor, Ceramic Department, National Research Center, Cairo- Egypt

**) Associate Professor, Mech. Design Department, Faculty of Engineering and Technology (Mataria), Helwan University, Cairo- Egypt

the friction mechanism of ceramics as a brittle material. However, there are some recent work to identify a tribochemical mechanism responsible for ceramics frictional and wear behaviour [5,6]. In this context, experimental findings have shown that microstructure of ceramic bodies and their reaction with lubricant and environmental conditions play a substantial role in dictating the final frictional behaviour [6,7]

Mullite ($3\text{Al}_2\text{O}_3, 2\text{SiO}_2$) is the only binary crystalline phase formed at high temperatures (1200°C) within the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system [8]. It is a stable refractory phase up to 1900°C and has excellent mechanical properties and chemical stability as well as low thermal expansion and conductivity. Therefore, dense mullite-based materials are recommended as wear resisting engineering composite under different frictional, thermal and chemical conditions [9-12]

Mullite has to be synthesized commercially because no adequate mineral deposits are available. Two main processes are used, namely: electric arc fusion and high temperature sintering to give fused and sintered mullite-bearing bodies, respectively. The microstructure and properties of the mullite-based ceramics are greatly affected by batch composition and kinetics of production process. Many investigators have studied the effect of mineralizers, e.g. MgO , TiO_2 , ZnO and talc on increasing the yield of mullite in the fired bodies. In addition, these mineralizers were found to enhance the densification of the fired bodies by solid-state sintering and/or by liquid phase [9,13-15].

The aim of the present work is, therefore, to prepare dense mullite-based ceramic bodies from the available raw materials taking into account the effect of batch composition and firing temperature on the densification and phase composition of the prepared bodies. The wear behaviour of the attained ceramic bodies has been investigated experimentally in an endeavor to correlate the wear behaviour to the mullite formation.

EXPERIMENTAL PROCEDURE

Pure Al_2O_3 and some local clay materials; namely: Kalabsha clay (Aswan), Bentonite clay (Fayoum) are the main raw materials used in preparing the required mullite-based ceramics. In addition to these materials, some talc (Eastern Desert) and Soda Feldspar (Sinai) were added in limited amounts. Also, minor amounts of pure TiO_2 , ZnO and MgO were separately added on weight to some batches as mineralizers. The chemical composition of the used raw materials is given in Table (1).

Five batches were designed to give after mixing the proper ratios of the raw materials as well as additives and firing up to 1500°C , dense ceramic bodies composing mainly of mullite. The five ceramic batches were prepared by intimate wet mixing of the finely ground starting materials ($\approx 76\mu\text{m}$) in a porcelain ball mill. The dried batches were semi-dry pressed into discs of 2 and 5 cm diameter and about 0.3 cm thickness under a pressure of 20 bar (2 MPa). The formed discs were then dried overnight at 110°C , subsequently, fired

in an electrical furnace up to temperatures ranging between 1200°C and 1500°C. The samples were soaked at the fired maximum temperature for one hour. The densification of the fired samples was followed by determining their bulk density and apparent porosity as a function of firing temperature according to the ASTM C20-1974 test. On the other hand, the main crystalline phases as well as glassy phase existing in the fired bodies were semi quantitatively determined by X-Ray diffraction technique using CaF₂ as an international standard. The following diffraction lines were considered: 5.39 Å for mullite, 4.26 Å for quartz, 4.05 Å for cristaballite and 1.93 Å for CaF₂. The microstructure of the dense ceramic bodies was studied by examining its polished surface after etching, by a Scanning electron microscope type Jeol-U3, which was attached with an energy dispersive X-Ray analysing system.

The wear of mullite bodies was studied using a modified pin on disc machine as shown in figure (1). The pin (in the form of a radially fixed ceramic specimens 20 mm diameter, 3 mm thickness) rubs against a rotating ceramic disc of a mullite ceramic body fired at 1450°C with 50 mm diameter. Normal loads up to 15 N were applied directly on the specimen, as shown in figure (1), in a radial direction by means of a dead weight. The wear tests were carried out at an average speed of 1.6 m/s for a duration of 15 seconds.

In the wear tests, the disc material was kept the same (ceramic body fired at 1450°C) as being the hard matrix attained, whereas, the mating ceramic bodies were specimens fired at 1200°C, 1250°C, 1300°C, 1400°C, 1450°C and 1500°C.

By measuring the extent of formed scratch (L) on the specimen, the wear volume (V) could be, as shown in Figure (1), calculated by the following relation:

$$V = 3 \left\{ \sin^{-1} \left(\frac{L}{2R} \right) R^2 - \frac{L}{2} \sqrt{R^2 - \left(\frac{L}{2} \right)^2} \right\}$$

RESULTS AND DISCUSSION

Table (2) summarized the batch composition in weight ratios as well as the calculated chemical composition in weight percentages of the investigated five batches. These were designed to give, after firing, dense bodies composed mainly of mullite. Pure Al₂O₃ was added in amounts ranging between 30% and 35% to china clay in batches M1, M2 and M3 and to Kalabsha clay in batches M4 and M5. In the latter batch (M5) about 15% of bentonitic clay was added at the expense of Kalabsha clay to improve its plasticity and to raise its content of fluxing oxides. Also, 5% talc and 4% soda feldspar (albite) were added in all batches to act as mineralizing and/or fluxing agents. In batches M1, M2 and M3 1.5% of TiO₂ or ZnO or MgO was added on weight, respectively to study its effect on increasing mullite content. M4 contains 0.5% TiO₂ owing to the high TiO₂ content of Kalabsha clay as given in table (1). In M5 no pure oxides were added due to the presence of 5% TiO₂, MgO and Fe₂O₃ oxides obtained from Kalabsha and bentonitic clays.

4 - 6 May 1993, CAIRO

The verification parameters of the ceramic bodies are given in table (3). It is worthy to note here that samples fired at 1200°C and up to 1350°C were soft and their verification parameters could not be consequently measured. From table (3), it is evident that the rate of densification of M5 is appreciably higher than that of the other batches as indicated from the higher bulk density values and the lower apparent porosity percentage of M5. This could be attributed to the relatively higher fluxing oxides content of M5 (about 7%) as compared with the other bodies (around 5%). The increase of the content of these oxides, especially CaO and alkali oxides leads to raise the amount of liquid phase formed on firing up to 1500°C with lowering its viscosity. So, the rate of diffusion of liquid phase to close up the open pores is increased and more dense bodies of M5 are produced. The obtained results indicate also the effect of rising the firing temperature on improving the densification of the fired bodies by liquid phase. Denser bodies are, generally, always obtained on firing at 1500°C in comparison with those fired at lower temperatures.

The results of phase composition of the fired samples as determined semi-quantitatively are plotted in figures (2) and (3). Figure (2) shows that the mullite content of the bodies fired at 1500°C gradually increases from 38% to 48% in bodies M1 to M4 respectively, whereas, the higher mullite content is encountered in M5 (65%). These results reveal that the role of the added pure oxides in mullitization of the studied ceramic bodies increases in the order TiO₂, ZnO, MgO. On the other hand, the combination of TiO₂, Fe₂O₃ and MgO in the presence of relatively higher Al₂O₃ content in M5 appreciably accelerates its mullitization at 1500°C.

The effect of firing temperature on the phase composition of M5 is shown in figure (3). It is evident that on raising firing temperature from 1200°C to 1300°C the mullite content is highly increased with simultaneous dissolution of cristoballite and residual quartz. This results in the development of liquid phase (glassy phase) up to about 65% at 1300°C. On raising firing temperature up to 1400°C sharp increase in mullite content at the expense of glassy phase is observed. This is mainly attributed to the enhancement of secondary mullite formation, which could be recrystallized from the liquid phase on cooling. The enrichment of the liquid phase with Al₂O₃ and SiO₂ and the lowering of its viscosity due to the presence of lime and alkali oxides may explain these results !16-18!. At higher temperatures between 1400°C and 1500°C, secondary mullite is slightly increased. This indicates that no further primary mullite is dissolved in the liquid phase due to its saturation with Al₂O₃ and SiO₂ !17!.

The microstructure of the ceramic body M5 is revealed by examining its etched surface with SEM as shown in figure (4). It exhibits two images at two magnifications. The first, figure (4a) shows the mullite aggregates (dark gray) and some secondary mullite crystals (bright). These crystals are magnified in figure (4b) to exhibit the needle and prismatic form of the secondary mullite which is recrystallized in the interstitial spaces of the fired samples during its cooling from 1500°C to room temperature.

The effect of firing temperature of ceramic bodies on the wear behaviour when rubbing against dense ceramic body fired at 1450°C is displayed in figure (5). The results illustrate that the wear volume follows in its increase a trend of behaviour analogous to that proposed earlier by Archard [5,19-21] where the wear increases with the applied load and inversely with hardness. As indicated in figure (5), softer ceramic bodies with relatively low mullite percentages exhibit higher wear rates which increase largely with the increase in the applied loads. By way of example, a ceramic body fired at 1200°C may display wear volume as much as ten times that of ceramic body fired at 1300°C , 1350°C and 1400°C . Moreover, for ceramic bodies fired at 1450°C and 1500°C no noticeable wear could be recorded within the test range.

In accordance with known mechanisms of mechanical wear, namely: adhesion, abrasion and fatigue [20], it is clear that both adhesion and abrasion are prevailing and mainly responsible for wear behaviour as well as frictional behaviour [7,20-22]. Under applied loads the intimate contact of ceramic bodies at the top of the asperities leads to adhesion with subsequential wear. However, the wear fragments and asperities of the hard mating ceramic body fired at 1450°C would also play a role as contributors to abrasion mechanism to enhance abrasion wear mechanism component. The abrasion wear would be much appreciated when using soft ceramic bodies fired at 1200°C rubbing against the hard mating disc fired at 1450°C . Whenever there is no or slight hardness difference between rubbing surfaces, adhesion wear should be predominant with negligible effect of abrasion.

CONCLUSIONS

1. Dense mullite-based ceramics can be produced by firing clay-alumina-talc-albite available locally up to 1500°C without any addition of mineralizers
2. The increase of densification and mullite content of ceramic bodies by raising firing temperature up to 1500°C decreases the wear of ceramic couples.
3. Wear behaviour of ceramic couples is typically due to both adhesion and abrasion and follows a trend of increase in a some direct proportion to the applied loads.

REFERENCES

- 1- M.L.Booth, "Engineering Ceramics-Materials for a multitude of Applications", CME, Vol.24, No.5, pp.66-69,(1977).
- 2- D.W.Richardson, "Modern Ceramic Engineering" Marcel Dekker Inc., New York (1982).
- 3- R.Morrell, "Handbook of Properties of Technical and Engineering Ceramics, Part 1" pp.136-40, H.M.S.O., London,(1985).
- 4- C.R.Diamond, "Oxide Ceramics-erosion resistant material", 3rd European Symposium on Engineering Ceramics, Ed. F.L.Riley, Elsevier Applied Science, pp.69-82, London, (1991).
- 5- F.P.Bowden and D.Tabor, "Friction and Lubrication of Solids", Claredon Press, Oxford (GB)(1964).
- 6- T.E.Fischer and W.M.Mullins, "Relation between Surface Chemistry of Ceramics and their Tribological Behaviour", paper presented at the 7th International Colloquium on Automotive Lubrication, Technische Akademie Esslingen, FRG, January 16-18,(1990).
- 7- S.A.R.Naga; S.M.H.Naga; M.O.A.Mokhtar, "A Study of Frictional Behaviour of $3Al_2O_3 \cdot 2SiO_2$ Ceramics", 17th Leeds/Lyon Symposium, Sept. 4-7,(1990).
- 8- S.Aramaki and R.Ray, "Revised Equilibrium Diagram for the System $Al_2O_3-SiO_2$ ", J.Amer.Ceram.Soc.Vol.45, pp.229-242 (1962).
- 9-T.J.Davies, H.G.Emblem, K.Jones, M.A.Mohd.Abd.Rahman, G.K.Sargeant and R.Wakefield, "Preparation and Properties of Mullite Grain", Br.Ceram.Trans.&J., Vol,89 pp.44-48(1990).
- 10- M.G.M.U.Ismail, Z.Nakai and S.Somya, "Microstructure and Mechanical Properties of Mullite Prepared by the Sol-Gel Method", J.Amer.Ceram.Soc. Vol.70 ppC7-C8(1987).

- 11- P.A.Lessing, R.S.Gordon and K.S.Mazdiyasni, "Creep of Polycrystalline Mullite", J.Amer.Ceram.Soc. Vol.58 (3-4) pp. 149 (1975).
- 12- K.S.Mazdiyasni and L.M.Brown, "Synthesis and Mechanical Properties of Stoichiometric Aluminium Silicate (Mullite)", J.Amer.Ceram.Soc. Vol. 55, pp.548-552(1972).
- 13- E.M.Sallam and W.H.Hennicke, "Effect of Talc Additions on the Crystalline Constituents and Fired Properties of Alumina Porcelains", Trans.J.Br.Ceram.Soc., Vol. 82 pp.102-104 (1983).
- 14- D.McGee Thomas and C.D.Wirkus, "Mullitization of Alumino-Silicate Gels", Ceramic Bulletin, Vol.51, pp.577-581, (1972).
- 15- Das, "Role of Magnesium Compounds on Mullitization of Clay-Alumina Mixtures", Trans. & J.Br.Ceram. Soc., Vol.78, pp78, 113(1979).
- 16-F.H.Norton, "Fine Ceramics: Technology and Applications", McGraw Hill, Inc.Book Company, New York-St.Louis, (1970).
- 17- K.H.Schüller, "Structure Development in Porcelain", Ber.Deut.Ges. Vol.38, pp.150-57(1961).
- 18- K.H.Schüller, "Reactions between Mullite and Glassy Phase in Porcelains", Trans.Br.Ceram.Soc. Vol.63, pp.103-117 (1964).
- 19- K.Koto, "Tribology of Ceramics", Wear, Vol.136, pp.117-134, (1990).
- 20- A.D.Sarkar, "Wear of Metals", Int.Series in Materials Science and Technology, Vol.18, 1st Edition, 1976.
- 21- I.V.Kragelesky, "Friction, wear and lubrication-Tribology Handbook", Mir Pub., Moscow, 1981.

TABLE. 1.: CHEMICAL ANALYSIS OF THE RAW MATERIALS

	China clay	Kalabsha clay	Bentonitic clay	Talc	Albite
SiO ₂	54.78	47.22	54.26	62.00	67.96
Al ₂ O ₃	32.22	36.01	20.81	1.60	18.80
Fe ₂ O ₃	0.45	0.77	5.78	0.40	0.17
TiO ₂	-----	2.21	-----	-----	0.31
CaO	0.15	0.77	5.85	0.49	0.69
MgO	0.28	0.10	2.02	30.30	-----
Na ₂ O	0.09	0.11	1.12	0.32	11.54
K ₂ L	0.29	0.14	1.37	0.11	0.05
Ig. loss	11.73	12.39	7.84	4.70	0.63

TABLE 2: BATCH AND CHEMICAL COMPOSITION OF THE MULLITE-BASED CERAMIC BODIES

Batch No.	Batch Composition								Chemical Composition (%)									
	China Clay	Kalab. Kaolin	Bent. Clay	Alumina	Talc	Albite	TiO ₂	ZnO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	ZnO	CaO	MgO	Na ₂ O	K ₂ O
M1	58	--	--	33	5	4	--	--	1.5	41.39	54.08	0.32	0.12	--	0.15	3.24	0.53	0.19
M2	58	--	--	33	5	4	--	1.5	--	41.39	54.08	0.32	0.12	1.48	0.15	1.75	0.53	0.19
M3	58	--	--	33	5	4	1.5	--	--	41.39	54.08	0.32	1.60	--	0.15	1.75	0.53	0.19
M4	--	60	--	31	5	4	0.5	--	--	36.44	53.82	0.53	1.94	--	0.55	1.58	0.53	0.10
M5	--	45	15	31	5	4	--	--	--	39.26	53.79	1.37	1.15	--	1.41	1.98	0.72	0.31

Table 3.: Vitrification parametres of mullite-based ceramic
bodies fired between 1300°C and 1500°C.

Body	1375°C		1400°C		1450°C		1500°C	
	B.D.	A.P.	B.D.	A.P.	B.D.	A.P.	B.D.	A.P.
	gm/cm ³	%						
M ₁	1.97	31.23	2.10	25.80	2.10	25.59	2.19	21.34
M ₂	1.97	31.83	2.10	25.33	2.11	24.48	2.19	22.03
M ₃	2.05	28.51	2.09	25.26	2.13	23.39	2.18	21.51
M ₄	1.97	33.23	1.97	32.67	2.02	30.55	2.12	27.01
M ₅	2.15	25.16	2.17	23.89	2.17	23.65	2.31	17.21

B.D. : Bulk Density

A.P. : Apparent Porosity

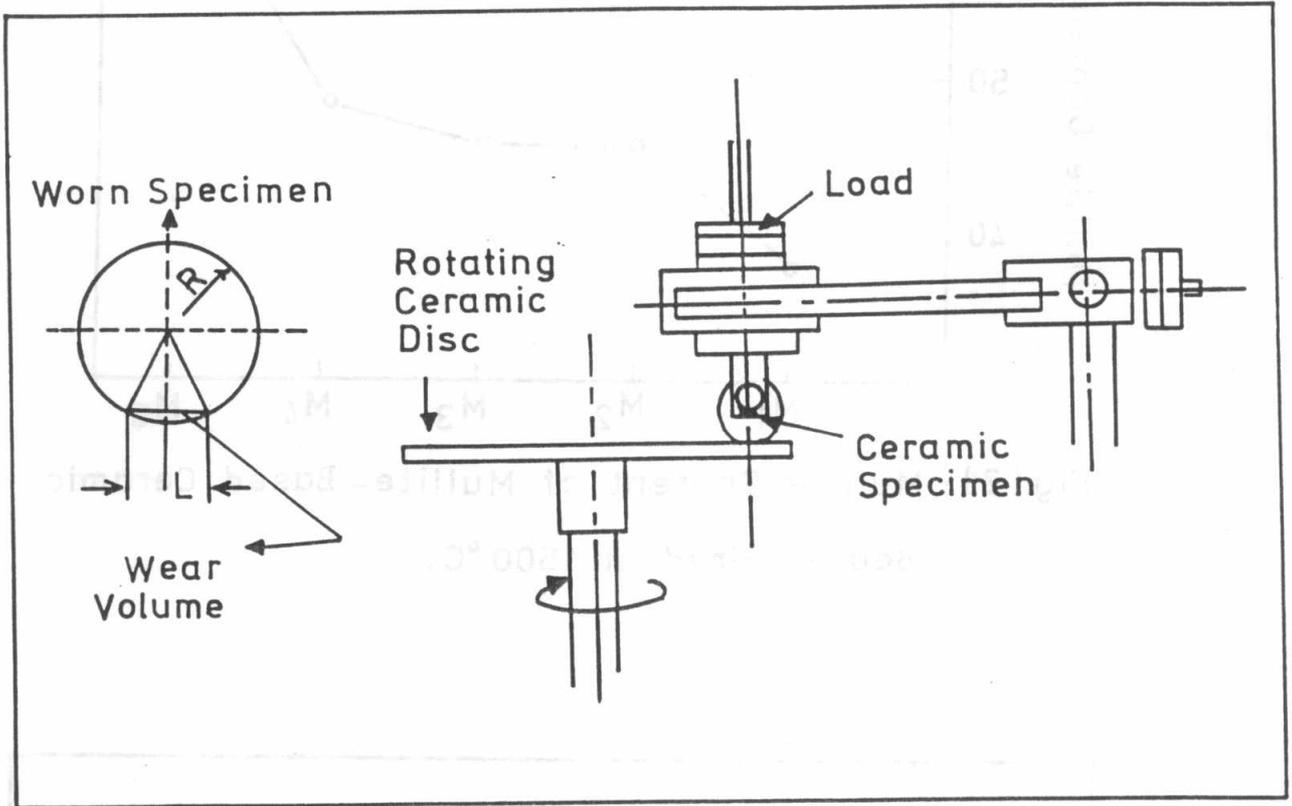


Fig.(1): Schematic Layout of Test Rig and Worn Specimen Configurations.

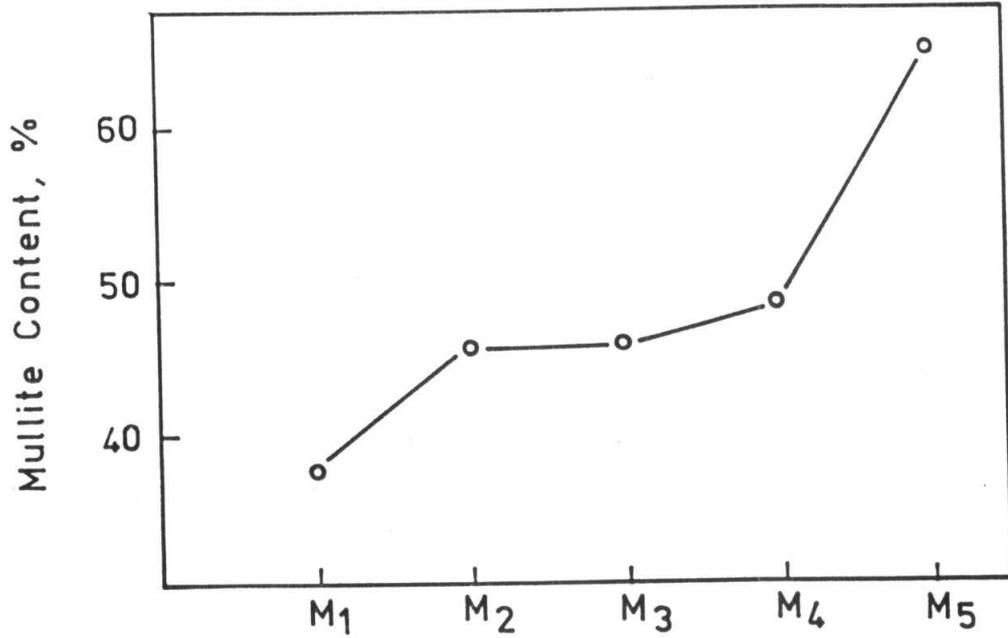


Fig.(2): Mullite Content of Mullite-Based Ceramic Bodies Fired at 1500 °C.

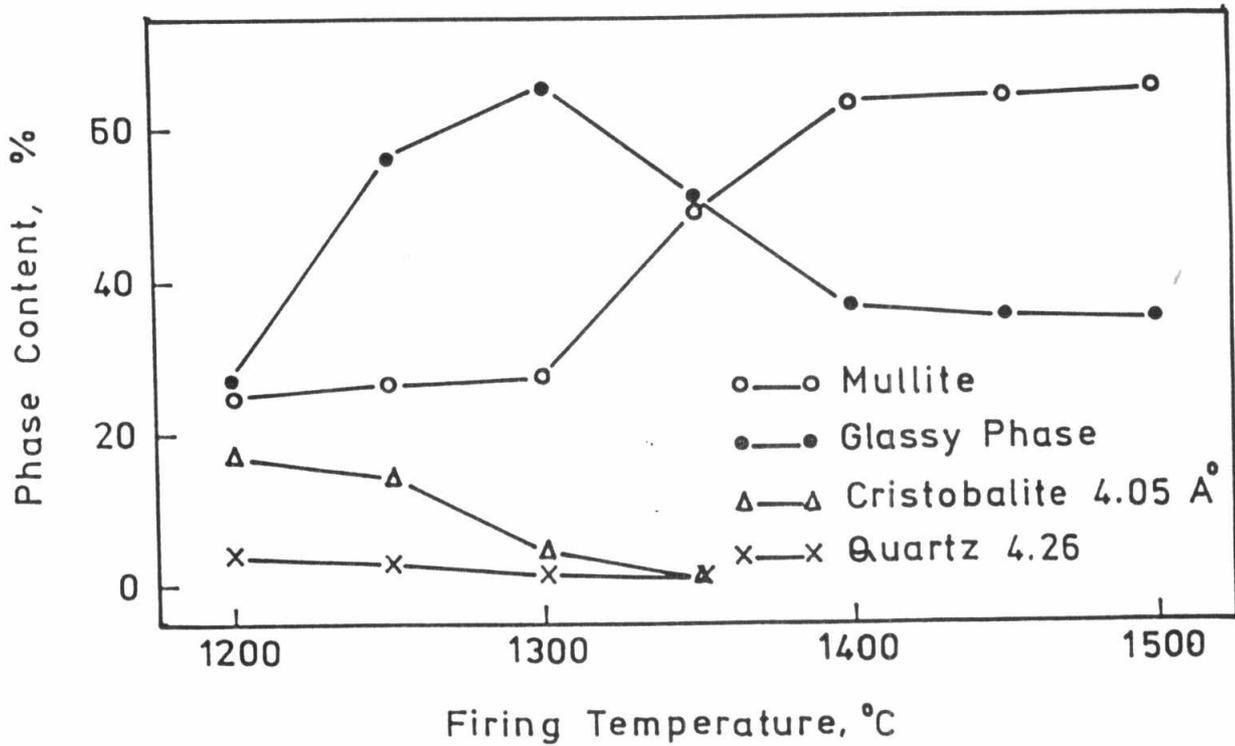


Fig.(3): Effect of Firing Temperature on the Phase Composition of Mullite-Based Ceramic Body M₅.

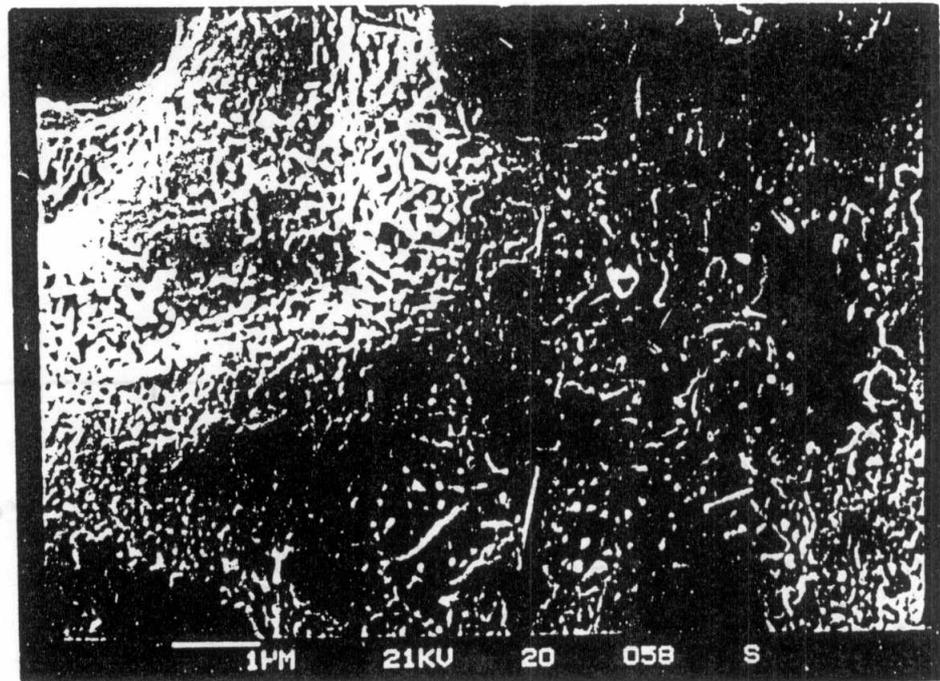


Fig.(4a): The Mullite Aggrigates (Dark Gray) and Some Secondary Mullite Crystals.

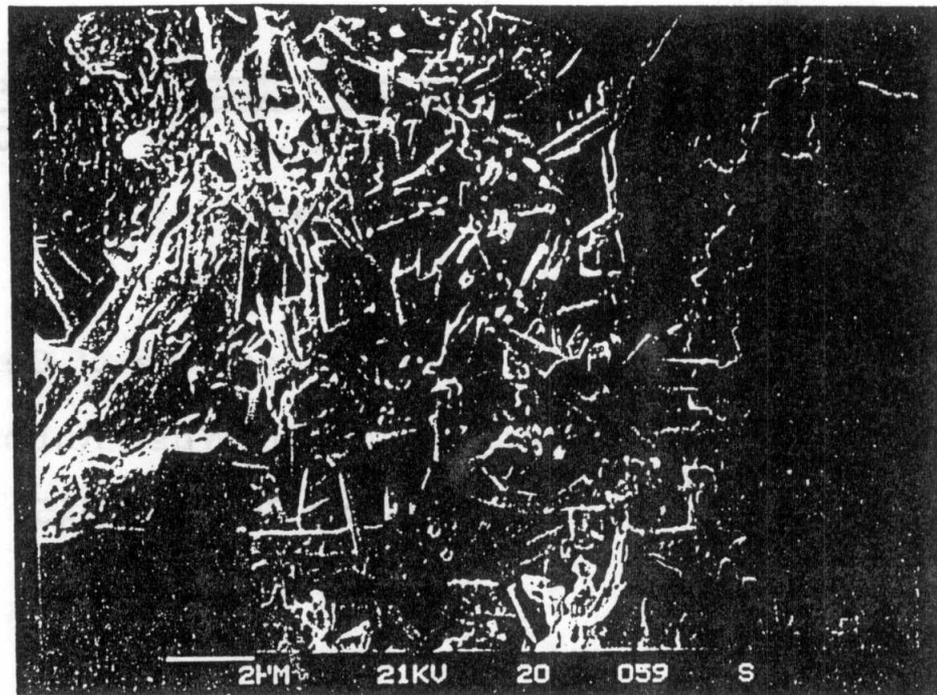


Fig.(4b): The Needle and Prismatic Form of the Secondary Mullite.

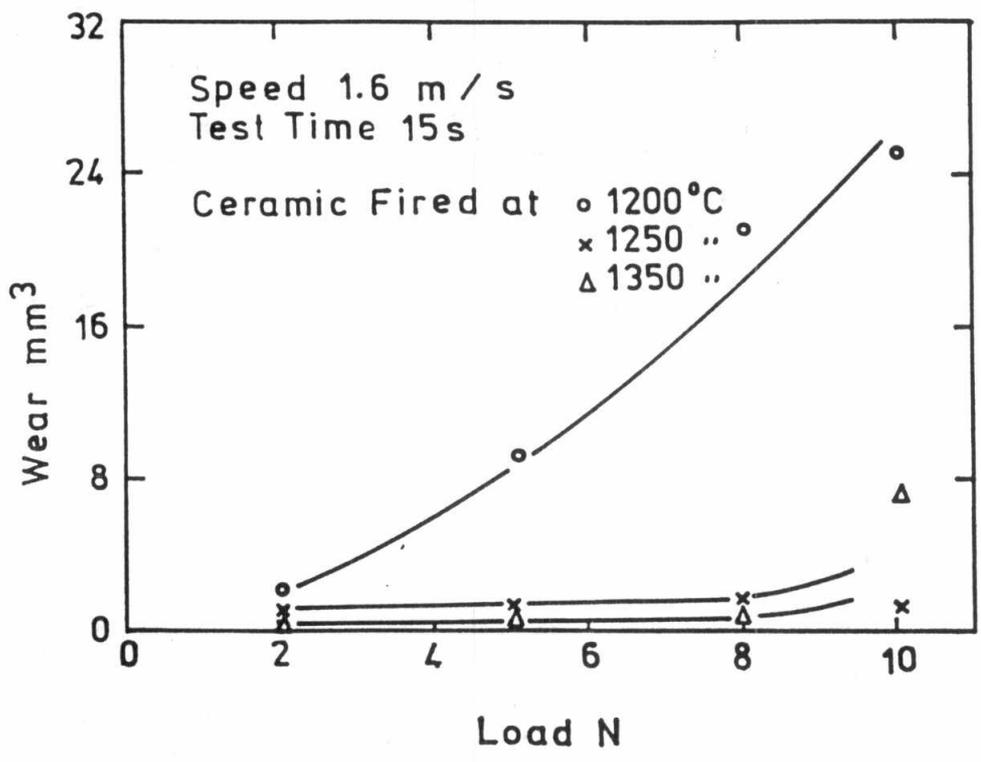


Fig.(5): Effect of Firing Temperature of Ceramic Bodies on the Wear Behaviour When Rubbing Against Dense Ceramic Body Fired at 1450 °C .