



Microwave Sintering of Niobium Co-doped Yttria Stabilized Zirconia

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Abstract

Y_2O_3 and Nb_2O_5 doped tetragonal zirconia polycrystals were sintered at $1550^\circ C$ by conventional and microwave sintering. The effect of co-doping yttria stabilized tetragonal zirconia polycrystal with Nb_2O_5 was analyzed. The micro structural changes due to conventional and microwave sintering was studied using SEM and it was found that microwave sintering resulted in uniform microstructure with small grains. The phases were analyzed using X-ray diffraction analysis.

Keywords: Tetragonal zirconia polycrystals, Y_2O_3 and Nb_2O_5 co doped zirconia, Microwave sintering

1. Introduction

Partially stabilized tetragonal and fully stabilized cubic zirconia are important engineering ceramics with numerous applications. When ZrO_2 is utilized for technical applications the high temperature polymorphs cubic and tetragonal phases should be stabilized at room temperature by the formation of solid solutions which prevent deleterious tetragonal to monoclinic transformation (T.K.Gupta et al 1977). The alloying oxides which lead to the stabilization are alkaline earth, rare earth and actinide oxides.

Tetragonal zirconia polycrystals has been known as a structural ceramic due to its high strength and fracture toughness. Tetragonal zirconia polycrystals stabilized by doping with oxides such as Y_2O_3 and CeO_2 show a rising crack growth resistance with crack extension due to the formation of the transformation zone behind the crack tip as a result of the stress induced phase transformation (Ping Li et al 1994, 1993). Although yttria stabilized tetragonal zirconia polycrystals possess high strength and toughness at room temperature, they suffer low temperature strength degradation because of the spontaneous tetragonal (t) to monoclinic (m) phase transformation when annealed at temperatures from 100 to $500^\circ C$ in air.

The addition of Ta_2O_5 , Nb_2O_5 and HfO_2 to bulk Y_2O_3 stabilized ZrO_2 increases the transformability (t to m transformation temperature) of the resulting zirconia ceramics. The enhanced transformability is related to the alloying effect on the tetragonality (c/a – cell parameters ratio) of stabilized tetragonal ZrO_2 , so the addition of these oxides increases the tetragonal distortion of the cubic lattice. The increase in the tetragonality due to alloying is consistent with the increase in the fracture toughness and the increase in the t to m transformation temperature. Evidently from t- ZrO_2 become unstable as their tetragonality increases towards 1.020, which corresponds to the c/b ratio of m- ZrO_2 at room temperature. On the other hand, they become stable as the tetragonality decreases towards unity, which corresponds to c- ZrO_2 . This relationship allows the classification of oxides into either a stabilizer (decreasing tetragonality) or destabilizer (increasing tetragonality) for the t- ZrO_2 phase (Ping Li et al 1994, Bartalome et al 2007).

Numerous investigations, so far, have explored the effectiveness of microwave sintering on the evolution of densification in ceramic systems. Rapid developments in the microstructure of basic ceramics have introduced many materials for many applications. The properties of these materials are determined by their microstructures; therefore, to control their micro structural development and to achieve fine microstructures, the sintering parameters must be optimized (Xin Guo et al 1998, Sharon A Nightingale et al 1997, Mehdi Mazaheri et al 2008).

Employing microwave radiation for sintering of ceramic components has recently appeared as a newly focused scientific approach. Microwave sintering has numerical advantages such as rapid end volumetric heating, improved production rate, enhancement in densification and grain growth prohibition of ceramics. Heating under microwave is a

result of an interaction between electromagnetic waves and the molecules of the material. The intrinsic characteristics of the material are, therefore influence on the responds of the so – called element against the sintering heat.

The present work is aimed at exploring the general effect of microwave heating on the sintering procedure of tetragonal zirconia polycrystals co doped with yttria and niobium oxide and on revealing the major contribution of high heating rates on the micro structural improvement of microwave sintered samples.

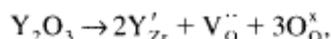
2. Experimental Procedure

The starting powders were prepared by mixing ZrO_2 [obtained by sol – gel synthesis using zirconium oxy-chloride and oxalic acid as starting materials], Y_2O_3 [99.5% purity] and Nb_2O_5 [99.5% purity] using ball mill for 24 hours in an ethanol medium. Zirconia balls were used for the milling process. After milling the powders were dried at 110 °C. The dried powders were pressed into pellets and then sintered by conventional sintering and microwave sintering. Conventional sintering was carried out at 1550 °C using the heating rate of 5°C/min without any holding time at the maximum temperature. Microwave sintering was conducted in a 1.1kW, 2.45 – GHz multimode microwave cavity using susceptor materials as auxiliary heating elements. The final densities of the compacts were measured by the Archimedes method and 99% theoretical density was achieved. The microstructures of the conventional sintered and microwave sintered samples were analyzed using the scanning electron microscope. X-ray diffraction studies was done on the sintered specimens to identify the phases present.

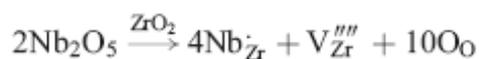
3. Results and Discussion

3.1 Effect of co-doping with Nb_2O_5

When a trivalent oxide e.g Y_2O_3 is added to ZrO_2 as a stabilizer, a certain amount of lattice defects e.g oxygen vacancies and negatively charged solutes are produced in the ZrO_2 lattice. Pentavalent oxides are positively charged, opposite to the stabilizer, when dissolved in the ZrO_2 lattice, the addition of these oxides in the partially stabilized zirconia will definitely affect the original defect structure, thus also its properties. The effect of doping with pentavalent oxides such as niobia indicate that the ions reside as substitutional defects in the zirconium lattice annihilating oxygen vacancies generated by yttria doping (T.Ebadzadeh et al 2008) . The addition of pentavalent oxides such as Nb_2O_5 enhances the transformability and thus the instability of tetragonal zirconia as evidenced by the increase in the t to m and m to t phase transformation temperature. The instability probably originated from an increased internal strain in the tetragonal lattice that was caused by the annihilation of oxygen vacancies in the tetragonal zirconia which results in a strained cation network and oxygen overcrowding in t- ZrO_2 . The oxygen vacancies in tetragonal zirconia are formed to maintain electrical neutrality ; Y^{3+} ions substitute for Zr^{4+} ions following the reaction



Where Y'_{Zr} represents the negatively charged yttrium ion that substitutes for the zirconium ion and V_o represents the positively charged oxygen vacancy. Doping of Nb_2O_5 into yttria stabilized zirconia is likely to diminish the number of oxygen vacancies in the above reaction because of the substitution of Nb^{5+} ions for Zr^{4+} ions according to the reaction



The probable reduction in the vacancy concentration can be revealed in the change in the properties of niobium codoped yttria stabilized zirconia (Deuk Yong Lee et al 2002, 1998, Dae- Joon Kim et al 1990, 1998, Xin Guo et al 1997, Sharon A Nightingale et al 1997)

3.2 Microstructural Studies

“Figure 1a & b” shows the SEM micrographs of the specimens sintered under conventional sintering and microwave sintering. From the figure, one can observe a uniform microstructure with small grains it was also observed that in microwave sintering the grains were spherical and uniform in shape when compared with conventional sintering where the grains were large and irregular in shape. It was also confirmed that in microwave sintering better densification and microstructure can be achieved in comparison with conventional sintering.

3.3 X-ray Diffraction Studies

The powders was subjected to X-ray diffraction analysis using a Reich – Seifert Diffractometer with $Cu K\alpha$ ($\lambda = 1.5418\text{\AA}$) radiation as shown in the “Figure 2 a & b” The sample was scanned over the range 10 to 60 degree at a scan rate of 2 degree/minute. The experimental values were found to agree well with the calculated ‘d’ values. It

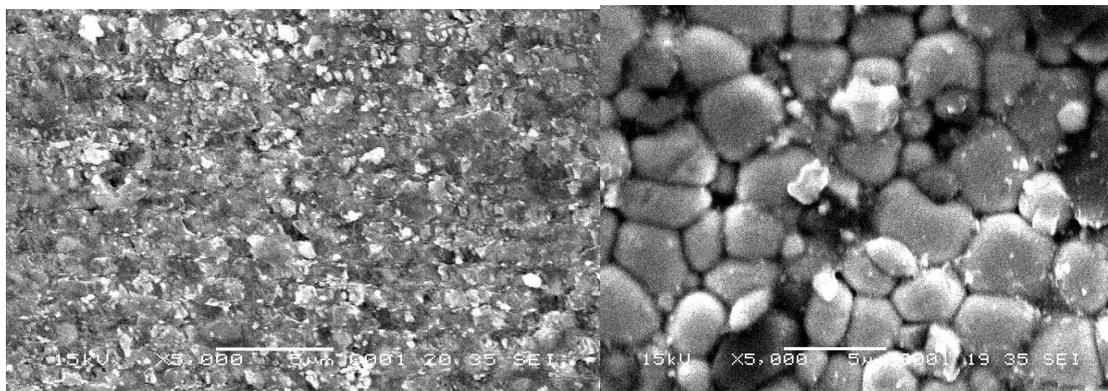
was found that monoclinic phase was formed and it was found that the crystalline quality of yttria, niobium stabilized zirconia by microwave sintering is good when compared to conventional sintering shown in “Figure 2a & b”.

4. Conclusion

The combination of transformation toughening and ductile particle reinforcements improves substantially the crack growth resistance and flaw tolerance. The presence of Nb₂O₅ is beneficial to tetragonal to monoclinic transformation. Dense, uniform and fine microstructure was obtained using microwave sintering. Decrease in grain size is attributed to fast heating and cooling rate in the case of microwave sintering.

References

- Bartolome J.H, Gutierrez-Gonzalez.C.F, Pecharroman.C, & Moya,J,S (2007). Synergetic Toughening Mechanism in 3Y-TZP/Nb Composites. *Acta Materialia*, 55, 5924 – 5933.
- Dae – Joon Kim. (1990). Effect of Ta₂O₅, Nb₂O₅ and HfO₂ alloying on the transformability of Y₂O₃ stabilized Tetragonal ZrO₂, *Journal of American Ceramic Society*, 73[1], 115-120.
- Dae-Joon Kim, Hyung – Jin Jung, Joo-Wung Jang, Hong – Lim Lee (1998). Fracture Toughness, Ionic Conductivity, and Low Temperature Phase Stability of tetragonal Zirconia codoped with Yttria and Niobium Oxide, *Journal of American Ceramic Society*, 81[9]2309 – 2314
- Deuk Yong lee, Dae-Joon Kim, Bae – Yeon Kim. (2002). Influence of alumina particle size on fracture toughness of (Y,Nb) – TZP/Al₂O₃ composites, *Journal of European Ceramic Society*, 2173 – 2179.
- Deuk Yong Lee, Dae –Joon Kim, Duk-Ho Cho, (1998). Low Temperature Phase Stability and Mechanical Properties of Y₂O₃ and Nb₂O₅ co-doped Tetragonal Zirconia Polycrystal Ceramics. *Journal of Material Science Letters* 17, 185-187
- Ebadzadeh.T & Valefi.M(2008). Microwave Assisted Sintering of Zircon, *Journal of Alloys & Compounds*, 448, 246 – 249.
- Gupta T.K, .Bechtold.J.H, Kuznicki.R.C, Cadoff .L.H & Rossing. R.D (1977). Stabilization of Tetragonal Phase in Polycrystalline Zirconia. *Journal of Material Science*, 12, 2421 – 2426.
- Mehdi Mazaheri, Zahedi.A.M, & Hejazi.M.M. (2008). Processing of Nanocrystalline 8mol% YSZ by Conventional, Microwave Assisted and Two Step Sintering. *Material Science & Engineering A*, 261 – 267.
- Ping Li & Wei Chen. (1994). Effect of Dopants on Zirconia Stabilization – An X-ray Absorption Study : I Trivalent Dopants. *Journal of American Ceramic Society*, 77[1], 118 – 128.
- Ping Li, I-Wei Chen & James E Penner Hahn. (1993). X-ray absorption studies of ZrO₂ polymorphs II Effect of Y₂O₃ dopant on ZrO₂ Microstructure, *Physical Review B*, 48[14], 10074 – 10081.
- Ping Li, I-Wei Chen, James E Penner Hahn. (1994). Effect of Dopants on Zirconia Stabilization – An X-ray Absorption Study : III Charge Compensating Dopants. *Journal of American Ceramic Society*, 77[5], 1289 – 1295.
- Sharon A Nightingale, Worner H.K, Dunne .D.P (1997). Microstructural Development during the Microwave Sintering of Yttria – Zirconia Ceramics, *Journal of American Ceramic Society*, 80[2], 394 – 400.
- Sharon A Nightingale, Worner.H.K & Dunne.D.P. (1997). Microstructural Development during the Microwave Sintering of Yttria – Zirconia Ceramics, *Journal of American Ceramic Society*, 394 – 400.
- Xin Guo. (1997). Effect of Nb₂O₅ on the space charge conduction of Y₂O₃ stabilized ZrO₂, *Solid State Ionics*, 99, 137 – 142.
- Xin Guo, & Zhu Wang. (1998). Effect of Niobia on the Defect Structure of Yttria Stabilized Zirconia, *Journal of European Ceramic Society*, 18, 237 – 240.



(a)

(b)

Figure 1. SEM Micrographs of samples sintered by (a) Microwave Sintering (b) Conventional Sintering

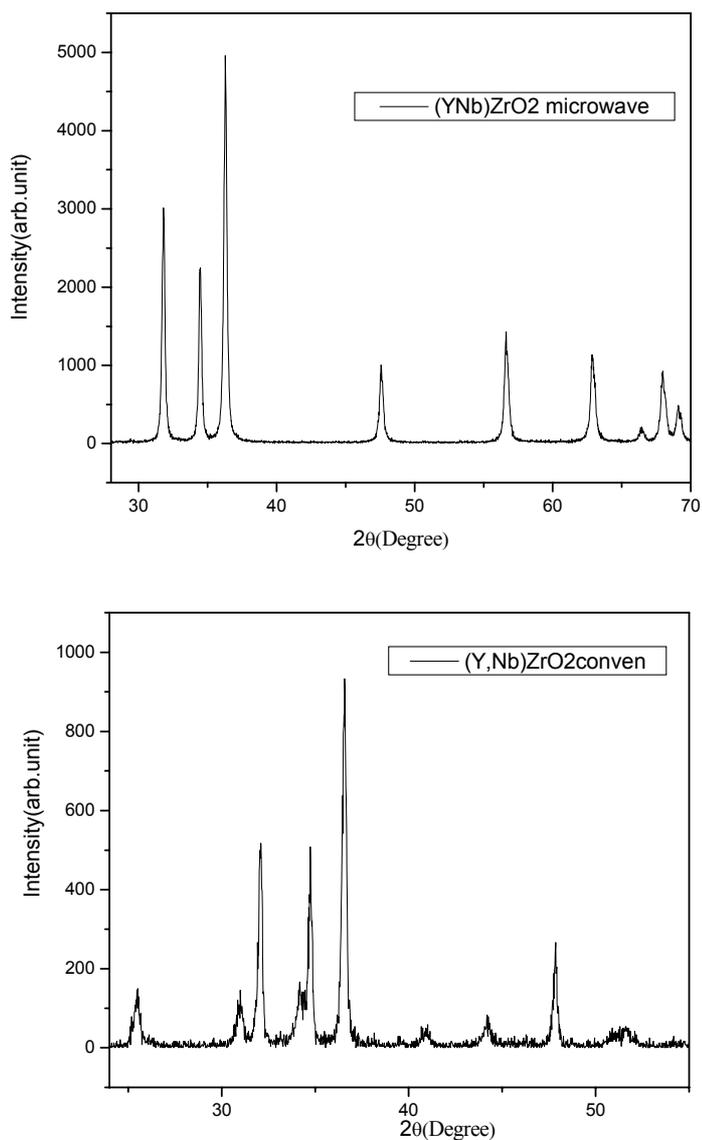


Figure 2. X-ray Diffraction of Samples Sintered at 1550°C (a) Microwave (b) Conventional