

Selective Carbonization and Nitridation of Titanium in (ZrTi)O₂ Powders Synthesized by Coprecipitation Method

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Abstract Solid solutions of (Zr/Ti)O₂ were prepared in powder form by the coprecipitation technique. After mixing with carbon or exposing to nitrogen gas at elevated temperature, titanium cations selectively diffused out from the oxide compound to form titanium carbide (TiC) or titanium nitride (TiN), respectively. TiN formed strong interfacial contacts between the oxide grains. In contrast, TiC formed as small crystallites on oxide grains but did not bind the matrix grains together. TiN therefore played a role in strengthening the interparticle bonding, but TiC weakened the bonding between grains. Partial diffusion of titanium cations also led to nanolayered structure being formed between the oxide grains, which provided weak interfacial layers that fractured in a step-wise fashion.

Key words nanocomposites, ZrO₂, TiC, TiN, selective reaction.

1. Introduction

Deformation of ceramics takes place mainly via grain boundary sliding, in contrast to the dislocation slips in metallic materials at ambient temperature. Increasing the number of weak intergranular interfaces in ceramics is expected to improve their toughness and strength. To active the weak interface, two strategies have been used by the introduction of nanocomposites and formation of a laminar structure, such as in multilayered structural ceramics. The nanocomposite approach is known as to greatly improve the strength of ceramic materials. Niihara et al. reported that the addition of 5 vol% SiC nano particles. The fracture strength of alumina was increased from 350 to 1500 MPa with addition of 5 vol%.¹⁾ These nanocomposites also exhibited excellent deformation behavior that can be used to sinter-forged complicated mechanical parts from zirconia.²⁾ Multilayered structural ceramics fracture primarily along the weak interlayer and exhibit reasonable increases in apparent toughness.^{3,4)} Indeed, nacre shell occurring as natural materials shows a elegant examples of how nanophase particles can be combined with layered structure to form strong and tough bodies.

Some of the methods proposed for combining nanophases with layered structure in ceramic materials are eutectic crystallization, spinodal decomposition and

annealing dissolution of supersaturated solid solution compounds.⁵⁾ The differences in reaction behavior (for example, diffusion rates, reduction/oxidation and high temperature stability) between the material's components can also be used to form a controlled and fine microstructure.

Zirconia (ZrO₂) is known as a tough ceramic, sometimes referred to as "ceramic steel". Such a high toughness is due to the approximately 5 vol% expansion that accompanies the transformation from tetragonal to monoclinic phases. The transformation produces a compressive force that prevents crack tips opening. The high-temperature tetragonal phase must be partially stabilized to ambient temperature by addition of Mg, Y and/or Ce. Titanium oxide (TiO₂) also has a stabilizing effect on tetragonal (t)-ZrO₂ by forming solid solutions.⁶⁾ The maximum solubility of TiO₂ in ZrO₂ is approximately 18 mol%.^{6, 7)} Excessive TiO₂ results in the formation of Ti/Zr compounds, or TiO₂ solid solutions at high TiO₂ contents. The co-precipitation method, however, can produce (Zr/Ti)O₂ solid solution with high content of TiO₂.^{6,7)}

In order to prepare ZrO₂ based nanocomposites for wear applications, we attempted to synthesize nanosize of in-site TiC/TiN particle using in the Zr-Ti complex oxides.⁸⁾ In this paper, the carbonization and nitridation of co-precipitated (Zr/Ti)O₂ powders and their resulting compositions and morphology have been investigated.

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2. Experimental Procedure

2.1 Synthesis of coprecipitated (Zr/Ti)O₂ powders

Chemicals of ZrOCl₂·8H₂O (Aldrich Chemicals, 99.0%) and Ti(SO₄)₂ (Aldrich Chemicals, 99.9%) were mixed in deionized water to give a ratio of TiO₂/ZrO₂=28 wt%. Then, NH₄OH (Junsei Chemical Co. Ltd.) was added dropwise into the solution to initiate the co-precipitation reaction at pH=9.3. Y₂O₃ (Yakuri Pure Chemicals Co., Ltd.) was added to the solution in the form of Y(NO₃)₂ (Yakuri Pure Chemicals Co., Ltd.) to stabilize the t-ZrO₂ (Yakuri Pure Chemicals Co., Ltd.). While the process proceeded, the suspension produced by the co-precipitation process was maintained at pH=9 to make the co-precipitation occur homogeneously. The precipitates were filtered and washed with deionized water five times to remove any anions adsorbed onto precipitates from the starting materials. And then, the precipitates were washed with ethanol twice to remove water. Finally, after drying at 353 K and calcining at 1073 K in air for 1 hr, the precipitates were identified as containing a single phase of t-(Zr/Ti)O₂ solid solution by X-ray diffraction.

2.2 Carbonization and nitridation of the oxide

Sucrose was mixed into the resultant powders as a source of carbon to give a TiC content of 15 vol% of the final powder. The mixture was pressed into pellets and then placed into a graphite-chamber and heated at temperatures of 1673, 1723, 1823, and 1923 K, for 2hrs. The reaction atmosphere was either flowing argon gas or nitrogen gas. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) were used to observe the morphology and analyze the chemical composition of the resultant powder.

3. Results and Discussion

3.1 Carbonization of (Zr/Ti)O₂

Fig. 1 shows (Zr/Ti)O₂ powder after calcination. The particles show round shape with approximately 3 μm in diameter. Mixtures of the complex oxide with carbon (sucrose) were heated at 1623, 1723, 1823, and 1923 K in Ar gas for 2 hrs. X-ray diffractometry (XRD) analysis after heating shows that the content of TiC in the powder carbonized at 1623 K is very low, which indicates that the carbonizing temperature is not high enough or the carbonizing time is not long enough for TiO₂ to react completely

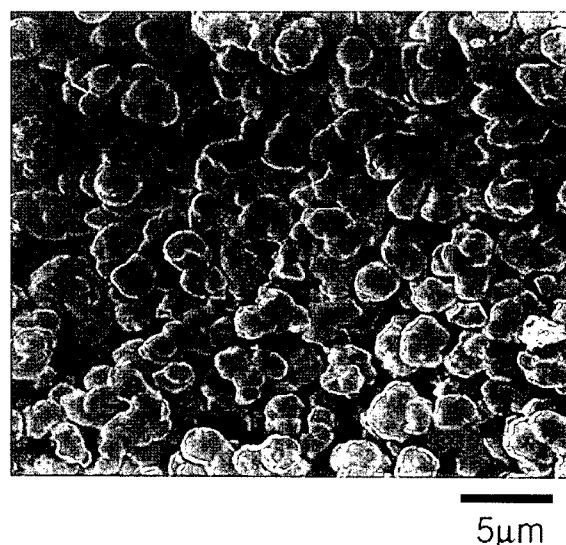


Fig. 1. SEM micrograph of (Zr/Ti)O₂ solid solution particles.

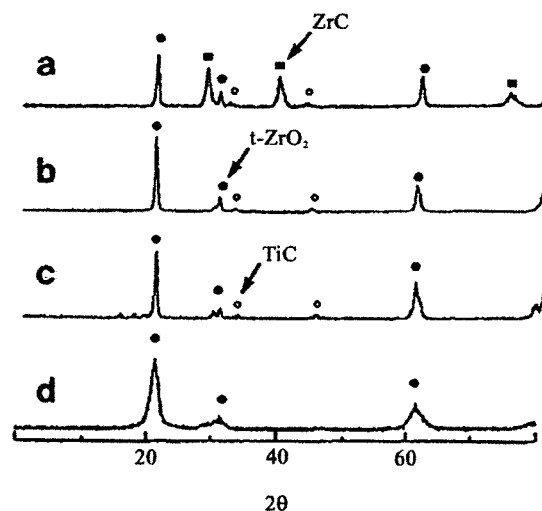


Fig. 2. X-ray patterns of the powders annealed at a) 1923 K, b) 1823 K, c) 1723 K, and d) 1623 K.

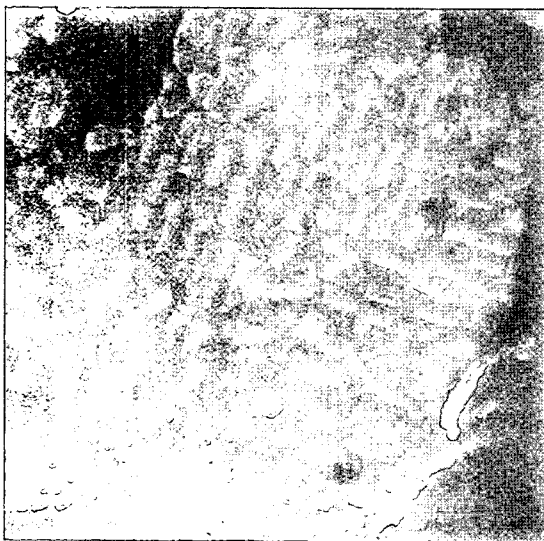
in the coprecipitation power. The powder carbonized at 1723 K is composed of t-ZrO₂ and TiC. Some ZrC is formed in the powder carbonized at 1923 K, which indicates that the temperature of ZrC formation is much lower than the temperature calculated from thermodynamics as shown in the report of Swalin⁸⁾. The reason for the decrease of the carbonizing temperature of ZrO₂ in the current system is not clear. I guess that the TiC formed before the carbonization of ZrO₂ takes place may have a catalyzing function, but this needs to be proved by further experiments. Consequently, temperatures up to 1723 K were not adequate for the selective reduction of Ti, as shown in Fig. 2. Temperatures over 1823 K resulted in

carbonization of ZrO_2 as well as TiO.

Fig. 3 shows the surface of a particle reacted at 1723 K. TiC fine crystallites was protruding from the amorphous carbon surrounding the oxide particles. EDAX data indicates that approximately 3-5 mol% Zr was present in the TiC phase.

3.2 Nitridation of $(Zr/Ti)O_2$

The coprecipitated oxide powder was also heated in flowing N_2 atmosphere without addition of a carbon source. The reaction temperature was 1723 K. After 2 hrs reaction in N_2 gas, TiN was detected by X-ray diffraction, as shown in Fig. 4. SEM micrograph shows the reacted



0.1 μm

Fig. 3. The morphology of TiC crystals formed as protrusive type on oxide grains.

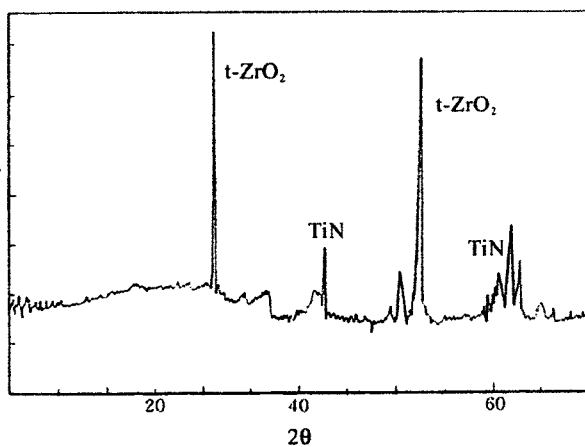
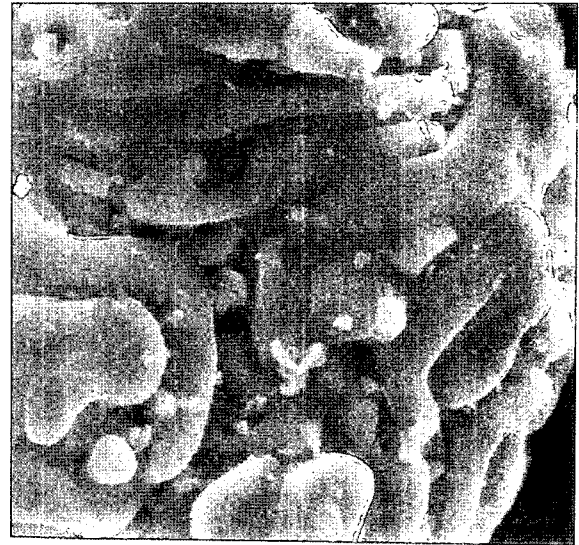


Fig. 4. X-ray diffraction pattern of nitridated $(Zr/Ti)O_2$ powders.

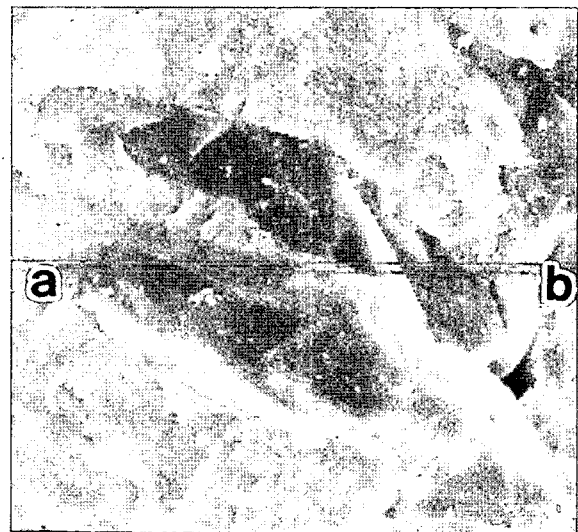
surfaces of the particles (Fig. 5). The particle morphology is quite different from that of the TiC particles shown in Fig. 3.

It was showed from SEM observation that the TiN phase in dense materials formed plate-like crystallites and were arranged in a modulated structure within the ZrO_2 grains. Fig. 6 shows the crystallites of TiN in the ZrO_2 matrix. The width of the TiN plates is 0.1-0.3 μm . Fig. 7 shows line analysis profiles of the four elements along the line ab in



0.2 μm

Fig. 5. TiN crystallites grown on the surface of oxide matrix grains.



0.2 μm

Fig. 6. TiN crystallites formed within the ZrO_2 grains.

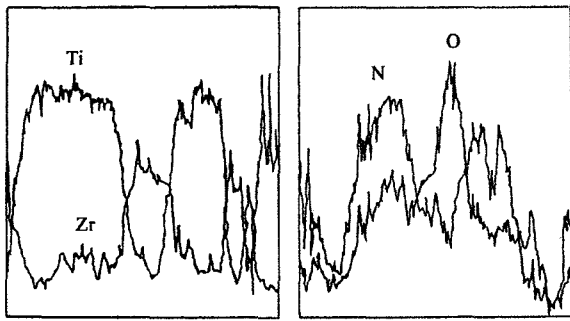


Fig. 7. Line analysis of elements Ti, Zr, N and O.

Fig. 6. The concentration of Ti increased when the Zr concentration decreased, and vice versa. The concentration of N followed the same pattern as Ti and the O concentration the same as Zr. These results indicate that Ti has been selectively nitrided and separated from the (Zr/Ti)O₂ solid solution. Composition analysis by EDAX revealed that the TiN phase contained 3-18 at% Zr. Ti was also detected in the ZrO₂ grains. The separation, therefore, was not complete, probably due to the short reaction time.

3.3 Structure of the reaction boundaries

Fig. 8 shows SEM micrographs of interfaces between bonded particles. The grain boundaries between (Zr/Ti)O₂ oxide grains were well-defined (Fig. 8(a)). The boundary in Fig. 8(a) contained TiN that formed along the surfaces of the oxide. The TiN boundary phase surrounded almost all the oxide grains. EDAX analysis showed the boundary phase to be a Ti/Zr/O/N solid solution. This layer phase was in close contact with the matrix grains on both sides

and is expected to strengthen the boundary both chemically and mechanically. This strengthening effect is in contrast to the weakening effect of the TiC boundary phase, shown in Fig. 8(b).

The selective reduction of complex oxides has the following advantages: growth of nano-crystallites on the matrix grains, epitaxial growth of the crystallites with desirable shape and orientation, preparation of hollow nanoparticles, introduction of nanometer-scale structures inside micrometer grain materials, and improvement in the bonding between boundaries. Fig. 9 shows the fracture

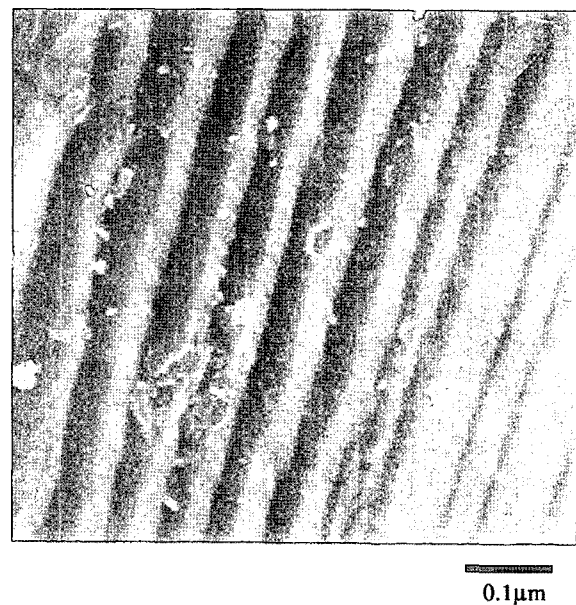


Fig. 9. Step fracture observed in oxide matrix grains.

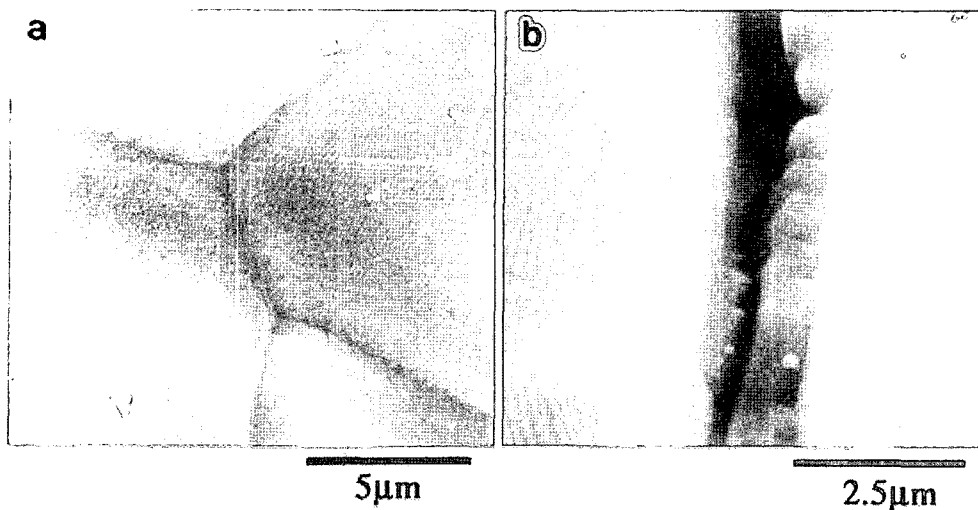


Fig. 8. SEM micrographs showing (a) TiN boundary phase formed around the matrix grain and, (b) TiC formed around the matrix grains with an interface defect.

behavior of the fine structure of nanometer thick layers formed in (Zr/Ti)O₂ grains. The grain in Fig. 9 fractured in a stepwise fashion, as shown by the ridges. The fracture steps were approximately 30-300 nm in height. This stepped fracture occurred as a result of the presence of nanometer TiN layers in the grain. The layers formed as a result of migration and dissolution of Ti ions in the oxide grain at elevated temperature. The weak interfaces between micrometer-sized subgrains and the TiN nanolayers separated easily.

4. Conclusions

Ti selectively migrated out from co-precipitated (Zr/Ti)O₂ grains to form carbide and/or nitride phases (TiC and TiN). Nitridation occurred in preference to carbonization if a nitrogen source was available. TiC and TiN phases actually contained a small amount of Zr. TiN and/or TiC phases formed around the matrix oxide grains. TiN formed strong bonds between the matrix oxide grains and

strengthened the interfaces, while the TiC boundary phase weakened the interfacial bonding of the matrix grains. The partial nitridation and selective reaction of Ti with N₂ also formed a nanolayered structure within the matrix grains. These TiN-ZrO₂ composites showed a step-like fracture with step heights of 30-300 nm.

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