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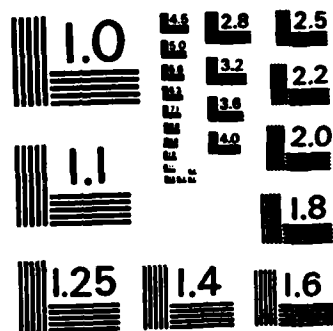
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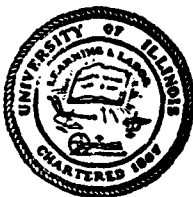
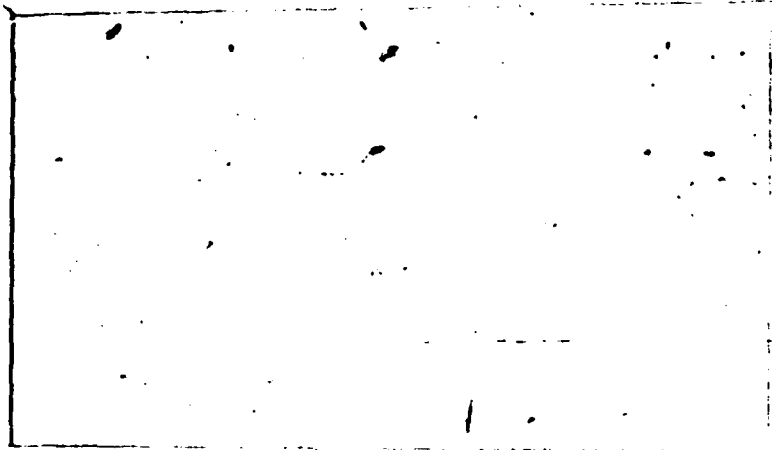
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Technical Report No. 4  
Contract No.: US NAVY-N-00014-78-C-0279

DENSIFICATION OF MONOCLINIC  $ZrO_2$   
WITH VANADATE ADDITIVES

by

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July 1982

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Sintering of monoclinic ZrO <sub>2</sub> ceramic powders was carried out < 1150°C using 1-8 wt% V <sub>2</sub> O <sub>5</sub> (or ZrV <sub>2</sub> O <sub>7</sub> , equivalent) as flux additive. Densities > 92% ThD were achieved using a relatively coarse commercial (PS ~ 1.5 µm) ZrO <sub>2</sub> powder with 1.5-2.0 wt% V <sub>2</sub> O <sub>5</sub> additive by sintering in air at 1100°C for up to 24 h. High pressed densities were found to be correlated to high fired densities, thus ZrO <sub>2</sub> powders with average particle size < 1 µm gave lower densities. |                                     |                                                                                            |

Microstructural and chemical analysis of the sintered samples were carried out to determine the composition and relative distribution of the  $\text{ZrO}_2$  and intergranular phases. Methods used included: SEM, TEM, X-ray microanalysis (EDAX), EPR, DTA, TGA, and arc emission spectroscopy techniques. Results showed the solubility of vanadium in the  $\text{ZrO}_2$  phase to be low ( $\sim 0.2$  at.-%-indicated to be  $\text{V}^{4+}$  ions). The bulk of the added vanadium was found in the grain boundary region which together with Ca, Si, and Mg impurities formed the amorphous bonding phase. This indicates densification by reactive liquid phase sintering aided perhaps by defect migration. The optimum combination of density, strength, electrical conductivity, and expansion coefficient was found for a  $\text{V}_2\text{O}_5$  content of 1.5 wt%.

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# DENSIFICATION OF MONOCLINIC $\text{ZrO}_2$ WITH VANADATE ADDITIVES

by

R. C. Buchanan and H. D. DeFord

## Abstract

→ Sintering of monoclinic  $\text{ZrO}_2$  ceramic powders was carried out  $< 1150^\circ\text{C}$  using 1-8 wt%  $\text{V}_2\text{O}_5$  (or  $\text{ZrV}_2\text{O}_7$  equivalent) as flux additive. Densities APPROX. 1.5 wt  $> 92\%$  ThD were achieved using a relatively coarse commercial (PS  $\sim 1.5 \mu\text{m}$ )  $\text{ZrO}_2$  powder with 1.5-2.0 wt%  $\text{V}_2\text{O}_5$  additive by sintering in air at  $1100^\circ\text{C}$  for up to 24 hr. High pressed densities were found to be correlated to high micro meta fired densities, thus  $\text{ZrO}_2$  powders with average particle size  $< 1 \mu\text{m}$  gave lower densities.

Microstructural and chemical analysis of the sintered samples were carried out to determine the composition and relative distribution of the  $\text{ZrO}_2$  and intergranular phases. Methods used included: SEM, TEM, X-ray microanalysis (EDAX), EPR, DTA, TGA, and arc emission spectroscopy techniques. Results showed the solubility of vanadium in the  $\text{ZrO}_2$  phase to be low ( $\sim 0.2$  at.%--indicated to be  $\text{V}^{4+}$  ions). The bulk of the added vanadium was found in the grain boundary region which together with Ca, Si, and Mg impurities formed the amorphous bonding phase. This indicates densification by reactive liquid phase sintering aided perhaps by defect migration. The optimum combination of density, strength, electrical conductivity, and expansion coefficient was found for a  $\text{V}_2\text{O}_5$  content of 1.5 wt%. ←

## DENSIFICATION OF MONOCLINIC $\text{ZrO}_2$ WITH VANADATE ADDITIVES

### I. Introduction

Widespread use is made of zirconium dioxide as a refractory material for high temperature furnace applications and increasingly for solid electrolyte fuel cell and oxygen sensor applications.  $\text{ZrO}_2$  exhibits three polymorphs, namely, the monoclinic, tetragonal, and cubic phases. The monoclinic phase is stable at room temperature but transforms to the tetragonal phase at  $\sim 1150^\circ\text{C}$  (depending on purity, particle size, and heating rate) with a volume decrease of 4-5%. High densities for  $\text{ZrO}_2$  can be obtained by sintering in air above  $1700^\circ\text{C}$ , but the volume expansion accompanying the transformation to the monoclinic phase on cooling results in microcracking and severe loss of strength. Use of the monoclinic  $\text{ZrO}_2$  phase, therefore, would require that the material be sintered below the transformation range. In practice, the destructive transformation is avoided by use of the cubic stabilized phase, formed by solid solution with up to 15 mol% of such oxides as  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{Y}_2\text{O}_3$ .<sup>1,2</sup> Presence of the  $\text{CaO}$  and  $\text{Y}_2\text{O}_3$  additives increases the oxygen ion mobility and ionic conductivity of the  $\text{ZrO}_2$ , but precise control of the microstructure is difficult to achieve at these high temperatures. A significant reduction in the sintering temperatures would, therefore, allow for greater control of microstructure and second phases.

This research was initiated to develop a procedure for lowering the sintering temperature of unstabilized  $\text{ZrO}_2$  (USZ) to below the monoclinic-tetragonal transformation temperature. This would allow the production of a dense, low expansion ( $\sim 7 \times 10^{-6}/^\circ\text{C}$  for USZ) ceramic body

which could be used at temperatures below 1100°C for substrate and similar type applications.

Three methods have been commonly used to improve the sintering behavior of refractory oxides: 1) the use of fine, reactive powders ( $< 0.5 \mu\text{m}$ ), 2) the use of low melting additives, and 3) hot-pressing. All three methods were evaluated; however, a high degree of densification below the transformation temperature was obtained only by liquid phase sintering.

The addition of a low melting second phase, in which the refractory phase is soluble, can result in a high degree of densification from particle rearrangement and solution-precipitation processes. Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) was found to be a suitable additive for low temperature sintering.  $\text{V}_2\text{O}_5$  forms a very fluid melt ( $< 5 \text{ P}$  just above its melting point-690°C),<sup>3</sup> forms a eutectic with USZ at  $\sim 670^\circ\text{C}$ ,<sup>4</sup> takes USZ into solution,<sup>5</sup> and has been shown to enhance densification in other oxide systems by formation of a reactive liquid phase and the creation of lattice defects.<sup>6-11</sup>

The system  $\text{ZrO}_2\text{-V}_2\text{O}_5$  itself has not been much studied. Peyronel<sup>12</sup> prepared the compound  $\text{ZrV}_2\text{O}_7$  from an aqueous mixture of ammonium vanadate and zirconyl nitrate solutions and reported the structure to be cubic, melting incongruently at  $\sim 747^\circ\text{C}$  to liquid and  $\text{ZrO}_2$ . More extensive phase studies by Burdese and Bolera<sup>4</sup> developed the phase diagram shown in Fig. 1. As indicated the only compound which exists in the system is  $\text{ZrV}_2\text{O}_7$  and there is apparently little or no mutual solid solubility of either constituent. Work by King and Suber<sup>13</sup> and Cirilli, et al.<sup>14</sup> indicate that solid state formation of the compound from  $\text{ZrO}_2$  and  $\text{V}_2\text{O}_5$  takes place only slowly and with some difficulty between 600-800°C. Craig and Hummel,<sup>15</sup>

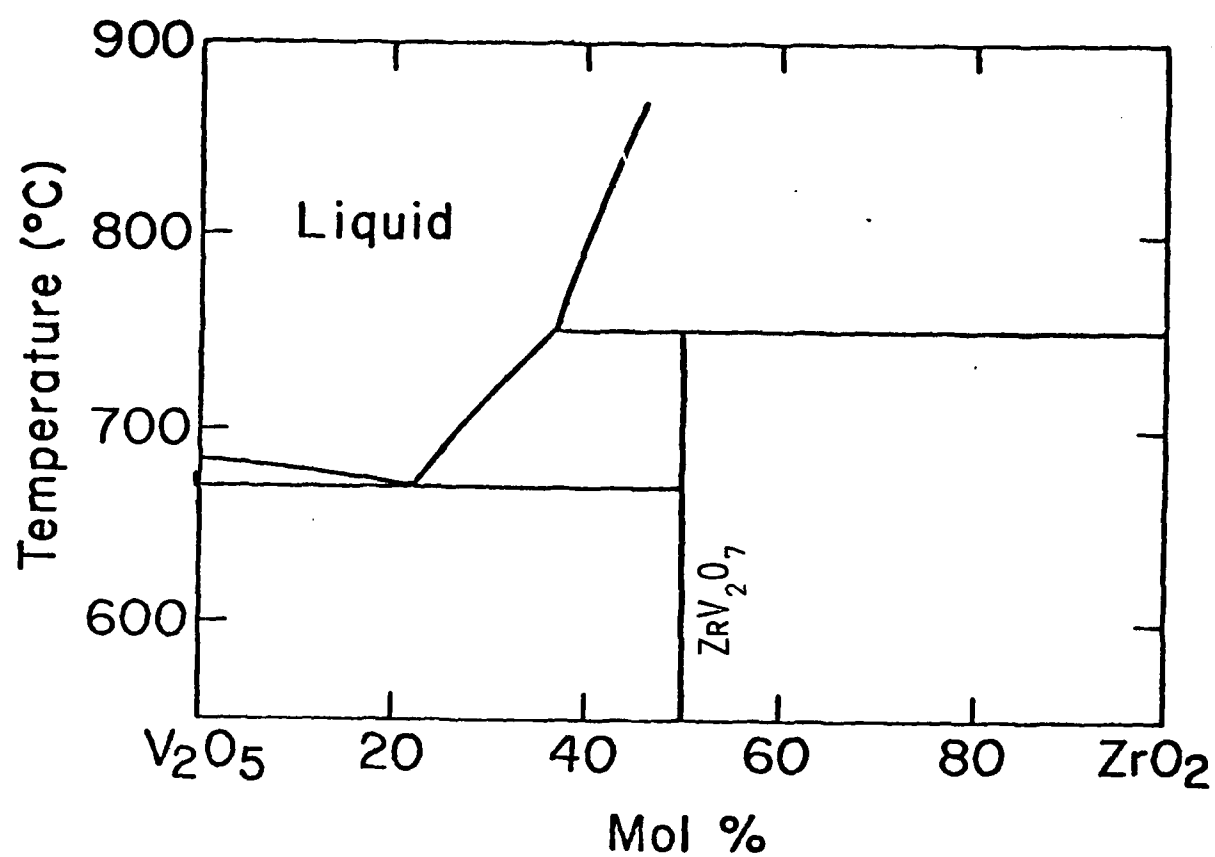


FIGURE 1. Phase diagram for  $\text{ZrO}_2$ - $\text{V}_2\text{O}_5$  system (Burdese and Bolera<sup>4</sup>)

however, prepared the compound by successive heat treatments at 600° and 700°C for 100 h in a sealed platinum tube and confirmed the existence of the cubic structure.

One system of interest in which  $V_2O_5$  exhibits catalytic behavior is the  $ZrO-SiO_2-V_2O_5$  system. Additions of 2-30 wt% of  $V_2O_5$  to equimolar mixtures of  $ZrO_2$  and  $SiO_2$  reduced the formation temperature for zircon ( $ZrSiO_4$ ) from ~ 1350°C to as low as ~ 800°C. This is illustrated in Fig. 2 from the work of Bystrikov and Cherepanov.<sup>16</sup> Work by Demiray, et al.<sup>17</sup> and Matkovitch and Corbett,<sup>18</sup> indicate that ~ 2-4 wt% of the  $V_2O_5$  went into solid solution in the structure during the formation of the zircon. The vanadium diffused into the lattice as  $V^{4+}$  ions, and according to Bystrikov,<sup>19</sup> this was possible only during the formation of zircon. Prolonged heating at temperatures in excess of 1000°C resulted in exsolution of  $V^{4+}$  from the zircon lattice, which could then be reoxidized to  $VO_2$  or  $V_2O_5$ .

Dmitriev Semin, et al.<sup>20</sup> have suggested another mechanism for the observed accelerated effect of small amounts of  $V_2O_5$  (~ 2 wt%) on phenacite ( $Be_2SiO_4$ ) formation and on sintering in the system  $BeO-SiO_2-V_2O_5$ . Partial surface reduction of  $V_2O_5$  to  $VO_2$  and subsequent diffusion of  $V^{4+}$  into the host lattice was also noted for this system. A crucial condition for the solid state reactions to occur appeared to be the formation, with  $V_2O_5$ , of a low melting microeutectic surface phase around the particles to be sintered. This had the effect of reducing the activation energy for the reaction, and providing for faster diffusion of the reacting species. Melting of the eutectic phase was also found to accelerate the formation of phenacite.

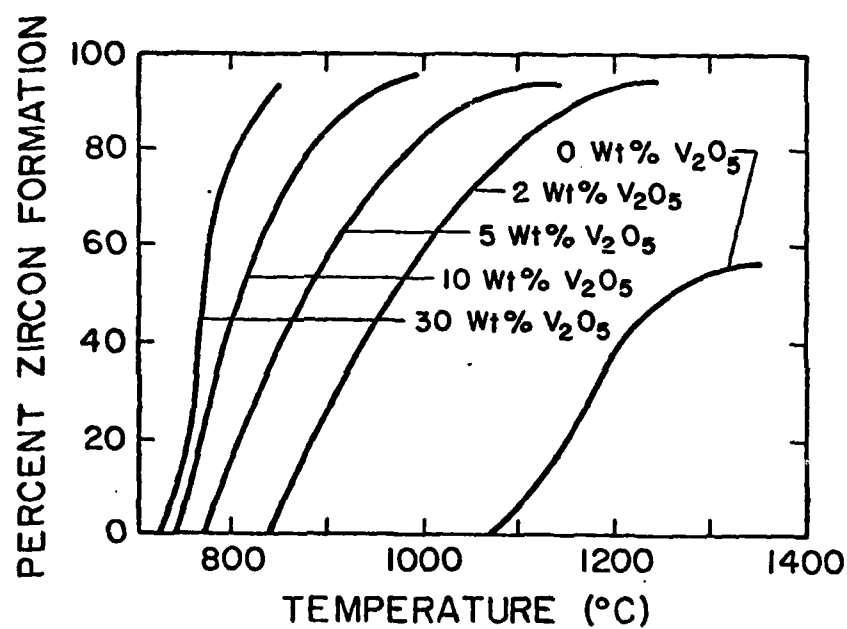


FIGURE 2. Accelerated formation of Zircon with  $V_2O_5$  (after Bystrikov and Cherepanov<sup>16</sup>)

This mechanism is similar to that postulated by Tacvorian<sup>21</sup> for the sintering of  $\text{ThO}_2$  and similar refractory oxides at temperatures substantially below their melting points. The microeutectic phase may be produced during the sintering reaction or alternately be thoroughly dispersed on the particles prior to sintering. Thus for the  $\text{ZrO}-\text{V}_2\text{O}_5$  system, the  $\text{V}_2\text{O}_5$  could be added directly to the  $\text{ZrO}_2$  powder, or a prereacted  $\text{ZrV}_2\text{O}_7$  phase could be added as the sintering aid. Thus, the observed effectiveness of vanadate additives as a sintering aid appear from the discussion to be a complex reaction sequence requiring some or all of the following steps:

- a. Complete coating of the particles to be sintered by the dispersed vanadate phase.
- b. Formation on heating, of a low melting surface eutectic compound. This lowers the sintering activation energy.
- c. Coalescence of the eutectic phase on further heating through solid state and surface migration of generated vacancies and diffusion of  $\text{V}^{4+}$  ions into the host lattice.
- d. Liquid phase sintering by rearrangement and solution precipitation on melting of the eutectic phase.

The latter mechanism would be expected to be dominant. In addition to the aforementioned objectives, therefore, this study was aimed at developing and understanding the sintering mechanisms, process parameters and optimum composition to achieve dense fired monoclinic  $\text{ZrO}_2$  bodies at temperatures below  $\sim 1150^\circ\text{C}$ . Optimization of the mechanical, electrical and thermal stability characteristics of the sintered  $\text{ZrO}_2$  bodies, analysis of the

microstructures and correlation of these to the densification mechanism(s) and properties, were also prime considerations.

Results given are for samples fired at 1100°C for 24 h, unless otherwise specified.

## II. Experimental Procedure

Several unstabilized  $\text{ZrO}_2$  (USZ) powders were used in this investigation; USZ-1<sup>a</sup> (avg particle size 1.5  $\mu\text{m}$ ) was the most responsive of these powders, and is primarily reported on in this study.

Vanadium was added in the form of either the pentavalent oxide,  $\text{V}_2\text{O}_5$ <sup>b</sup> (avg ps < 0.5  $\mu\text{m}$ ), or as zirconium pyrovanadate,  $\text{ZrV}_2\text{O}_7$  (avg ps < 0.5  $\mu\text{m}$ ), which was prepared by a precipitation procedure.<sup>12</sup> Both additives were essentially equivalent as sintering aids, but  $\text{V}_2\text{O}_5$  was primarily used because of availability. Batches of  $\text{ZrO}_2$  containing additions of 0-8 wt%  $\text{V}_2\text{O}_5$  were weighed, wet-milled for 5 h in polypropylene jars containing dense  $\text{ZrO}_2$  pellets in isopropanol, and were then air-dried followed by dry milling for 5 h.

Approximately 2 wt% binder<sup>c</sup> was added. The powders were then dried to ~ 3 wt%  $\text{H}_2\text{O}$  content, followed by granulation through a 35-mesh sieve. Sample discs ~ 1.6 cm in diameter and ~ 0.3 cm thick were formed at uniaxial pressures ranging from 34.5-345.0 MPa. Bulk green densities were determined from the calcined weights and measured dimensions of the pressed samples.

Some samples containing 2 wt%  $\text{V}_2\text{O}_5$  were hot-pressed at 1025°C for 1.5 h

a) Zircoa A; Zirconia Corp. of America.

b) Fisher Certified; Fisher Scientific Co.

c) Carbowax 4000; Union Carbide Corp.

at 48 MPa. All other samples were sintered in a muffle furnace using SiC heating elements at 1100°C for up to 24 h on platinum sheets supported by ZrO<sub>2</sub> setter plates. Some exudation of the liquid phase, especially noticeable for V<sub>2</sub>O<sub>5</sub> contents > 2.0 wt%, was observed for samples which were furnace cooled. Air-quenching of the samples eliminated the exudation, resulting in a homogeneous fired ceramic.

DTA, TGA, X-ray diffraction (XRD), and Hot-Stage XRD techniques were used to analyze the reactions and phase changes which occurred during the sintering cycle. Electron paramagnetic resonance (EPR) was used to determine the presence of V<sup>4+</sup> ions in the fired samples. Arc emission spectroscopy was used to determine the approximate amount of vanadium which diffused into the ZrO<sub>2</sub> grains during sintering. The samples were repeatedly wet-milled and washed to remove the intergranular phase prior to analysis. Weight loss data was obtained from calcined samples which were weighed, fired at 1100°C for 24 h, and then reweighed. Fired densities were determined from the weights and geometric dimensions or by liquid displacement techniques.

A scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer was used for microstructural analysis of polished and fractured sections of the fired samples. A transmission electron microscope (TEM) equipped with an energy dispersive X-ray analyzer was used for analysis of ion-milled samples.

DC electrical resistivity measurements were made up to 800°C using a shielded furnace and electrometer. Thermal expansion measurements up to 950°C were made with a quartz dilatometer. Tensile strengths of the fired samples were calculated from dimensions and failure loads of sample discs which were loaded diametrically (in compression) to failure. Sample discs

of high density  $\text{Al}_2\text{O}_3$ , for which the tensile and flexure strengths were known, were used to calibrate the system and obtain estimates of the flexural strengths of the fired  $\text{ZrO}_2$  samples by comparison.

### III. Results and Discussion

#### A. Processing and Characterization

Hot-stage X-ray diffraction (XRD) data collected at 1100° and 1150°C are shown in Fig. 3 for previously unfired  $\text{ZrO}_2$  samples containing 0.0, 1.5, 2.0, and 8.0 wt%  $\text{V}_2\text{O}_5$ . In the region of 18° to 32°  $2\theta$ . The monoclinic phase was indicated by the presence of the monoclinic (1 $\bar{1}$ 1) and (111) XRD peaks, and the tetragonal phase by the tetragonal (111) XRD peak. At 1100°C, only the  $\text{ZrO}_2$  sample with no  $\text{V}_2\text{O}_5$  contained the tetragonal phase. At 1150°C, all the samples contained some tetragonal phase, indicating that the optimum sintering temperature for samples containing  $\text{V}_2\text{O}_5$  would be between 1100° and 1150°C. The  $\text{ZrO}_2$  powder containing no  $\text{V}_2\text{O}_5$  was completely transformed to the tetragonal phase at 1150°C, and the amount of tetragonal phase in the other samples steadily decreased as the  $\text{V}_2\text{O}_5$  content was increased to 2 wt%. For additions > 2 wt%, the amount of tetragonal phase present at 1150°C was constant, indicating that the solid solubility limit of vanadium ions in the  $\text{ZrO}_2$  lattice had been reached. This data essentially dictated the choice of 1100°C as the sintering temperature for the  $\text{ZrO}_2$ - $\text{V}_2\text{O}_5$  samples.

DTA heating (to 1100°C) and cooling curves of unfired  $\text{ZrO}_2$  samples containing 0.0, 1.0, 1.5, and 2.0 wt%  $\text{V}_2\text{O}_5$  are shown in Fig. 4. As indicated also by the hot-stage XRD data, heating of the  $\text{ZrO}_2$  sample containing no  $\text{V}_2\text{O}_5$  to 1100°C, resulted in partial transformation to the tetragonal phase, shown in Fig. 4 by the endotherm beginning at ~ 1040°C.

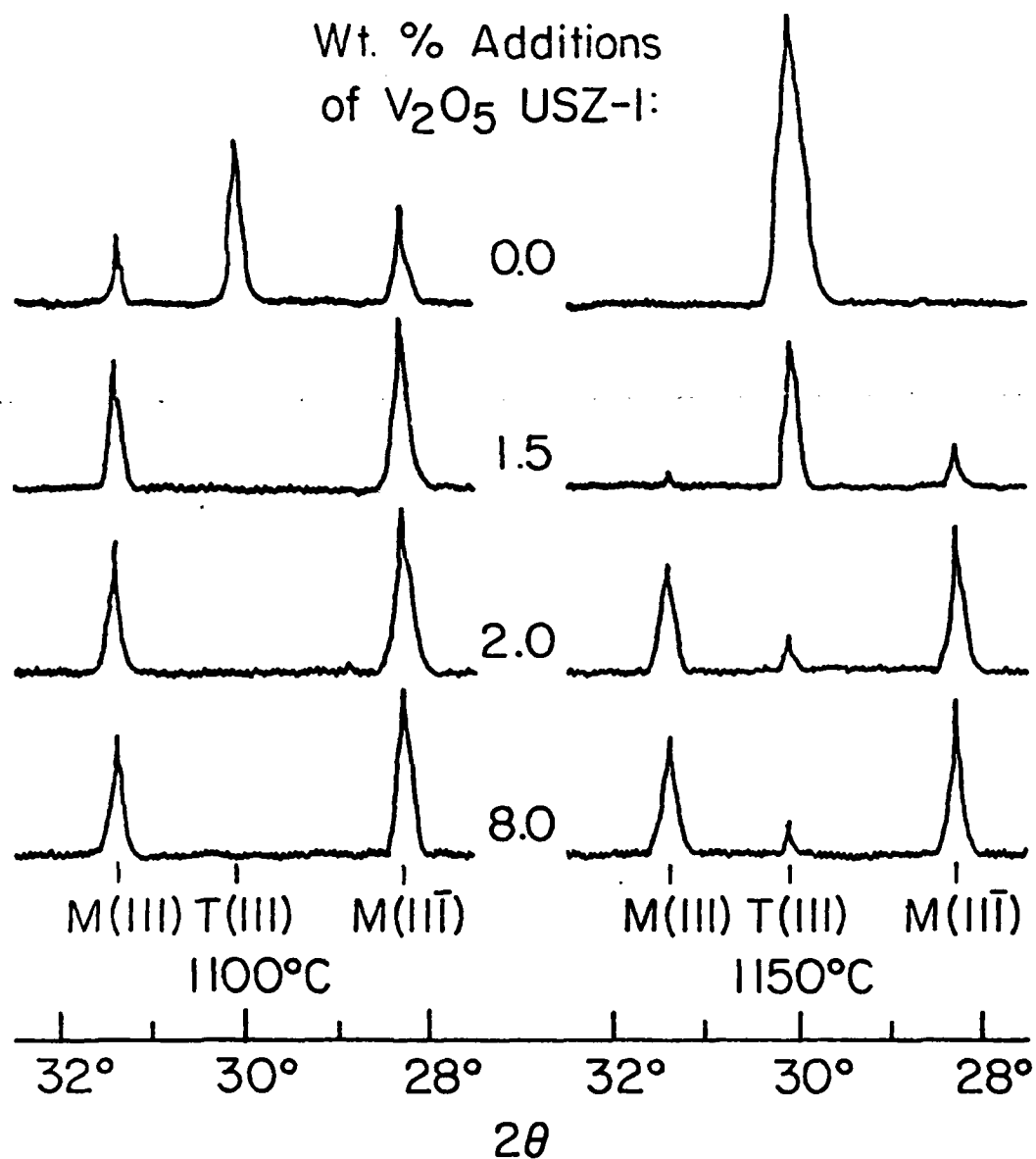


FIGURE 3. Hot stage X-ray diffraction data for  $ZrO_2$  as a function of  $V_2O_5$  content at 1100° and 1150°C.

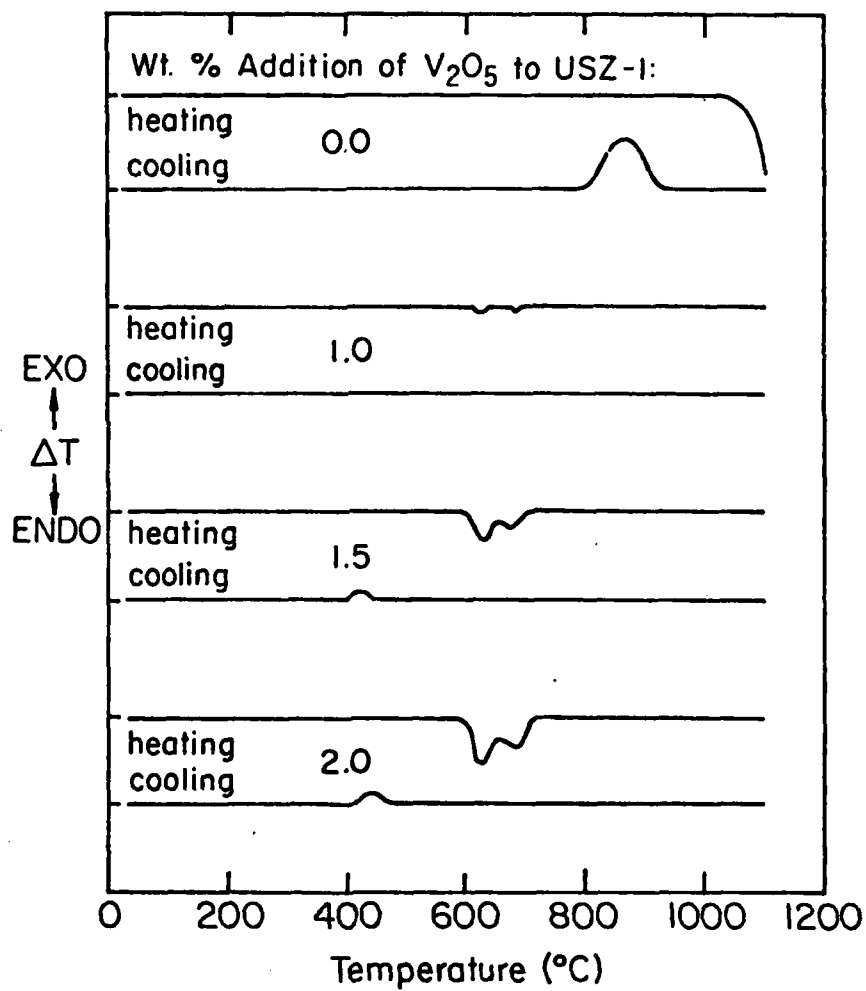


FIGURE 4. DTA heating and cooling curves for  $ZrO_2-V_2O_5$  samples containing 0-2.0 wt%  $V_2O_5$ .

For samples containing  $\geq 1$  wt%  $V_2O_5$ , the transformation had not started by 1100°C. During heating of samples containing  $\geq 1$  wt%  $V_2O_5$ , two endotherms were observed between 600° and 700°C. These increased in size with  $V_2O_5$  content. The second (smaller) endothermic peak occurred at  $\sim 685^\circ\text{C}$ , corresponding closely to the melting point of  $V_2O_5$  ( $\sim 690^\circ\text{C}$ ). The first (larger) endothermic peak occurred at  $\sim 630^\circ$  and apparently corresponded to the melting of a eutectic phase, although the binary eutectic for the  $ZrO_2$ - $V_2O_5$  system has been reported to be  $\sim 670^\circ\text{C}$ .<sup>15</sup> Impurities in the starting powders could possibly have lowered the eutectic melting point. A single exotherm occurred at  $\sim 450^\circ\text{C}$  during cooling of samples containing  $\geq 1.5$  wt%  $V_2O_5$ , and was attributed to crystallization of  $V_2O_5$ .

DTA heating curves of sintered  $ZrO_2$  samples containing 0.0, 1.0, 1.5, and 2.0 wt%  $V_2O_5$  are shown in Fig. 5 for the temperature range of 1000° to 1300°C. The data show an upward shift of the starting temperature for the monoclinic-tetragonal phase transformation, as the  $V_2O_5$  content was increased. A reduction in the width of the transformation peak from  $\sim 160^\circ$  for samples containing no  $V_2O_5$  to  $\sim 35^\circ$  for samples containing  $\geq 2$  wt%  $V_2O_5$  was also observed. Besides the significant decrease in width, the transformation peak also became much larger in amplitude. However, the shape and position of the peak did not change for additions  $> 2$  wt%  $V_2O_5$ .

Densification data for  $ZrO_2$ - $V_2O_5$  samples sintered at 1100°C for 24 h in air, are presented in Table 1. The data is given in terms of  $V_2O_5$  content (1.5-15.0 wt%), percent theoretical density, forming pressure, green density and fired density. In general the fired densities for a given composition were observed to increase almost linearly with green density. This was true

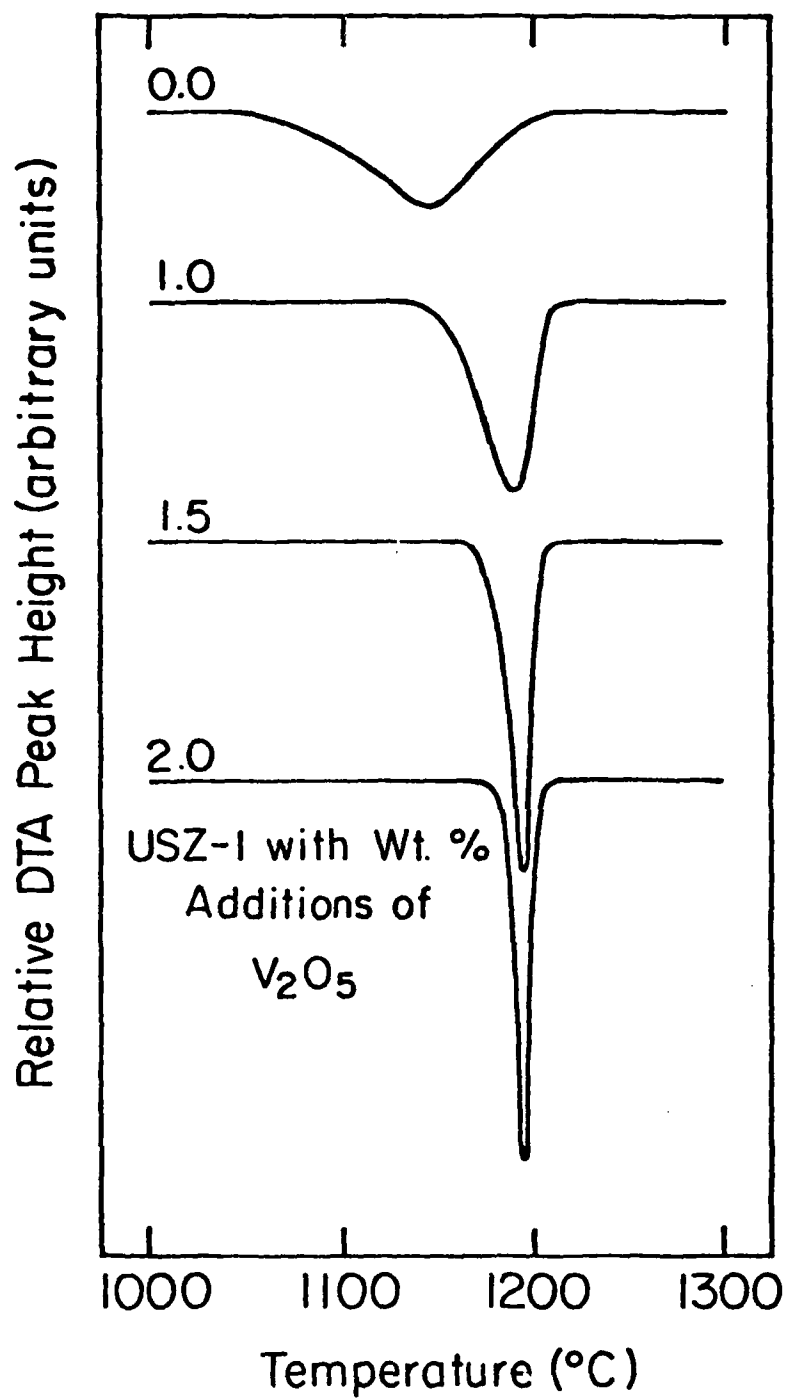


FIGURE 5. DTA heating curves for  $ZrO_2-V_2O_5$  samples (0-2 wt%  $V_2O_5$ ) showing a shift of the transformation temperature for the tetragonal phase with increasing  $V_2O_5$  content.

TABLE 1  
 Densification Data for  $\text{ZrO}_2\text{-V}_2\text{O}_5$  Samples  
 Sintered at 1100°C for 24 Hours

| Wt%<br>$\text{V}_2\text{O}_5$ | Th.                        | Forming  |     | Green           |       | Fired           |       |
|-------------------------------|----------------------------|----------|-----|-----------------|-------|-----------------|-------|
|                               | Density<br>$\text{g/cm}^3$ | Pressure |     | Density         |       | Density         |       |
|                               |                            | kpsi     | MPa | $\text{g/cm}^3$ | % ThD | $\text{g/cm}^3$ | % ThD |
| 1.5                           | 5.66                       | 35       | 241 | 3.78            | 66.8  | 4.89            | 86.4  |
|                               |                            | 50       | 345 | 3.87            | 68.4  | 5.06            | 89.4  |
| 2.0                           | 5.62                       | 35       | 241 | 3.78            | 67.3  | 5.00            | 89.0  |
|                               |                            | 50       | 345 | 3.89            | 69.2  | 5.15            | 91.6  |
| 5.0                           | 5.44                       | 35       | 241 | 3.72            | 68.4  | 4.71            | 86.6  |
|                               |                            | 50       | 345 | 3.83            | 70.4  | 4.71            | 86.6  |
| 8.0                           | 5.27                       | 35       | 241 | 3.79            | 71.9  | 4.80            | 91.1  |
|                               |                            | 50       | 345 | 3.87            | 73.4  | 4.81            | 91.3  |
| 12.0                          | 5.07                       | 35       | 241 | 3.77            | 74.4  | 4.88            | 96.3  |
|                               |                            | 50       | 345 | 3.85            | 75.9  | 4.89            | 96.4  |
| 15.0                          | 4.94                       | 35       | 241 | 3.59            | 72.7  | 4.85            | 98.2  |
|                               |                            | 50       | 345 | 3.67            | 74.3  | 4.86            | 98.4  |

also for the relationship between green density and forming pressure, dictating the use of high forming pressures in most cases. The data shown are for forming pressures of 35 and 50 kpsi (241 to 345 MPa), where it may be noted that for  $V_2O_5$  contents  $< 5.0$  wt%, the higher forming pressure and density resulted in significantly higher fired densities. However, for  $V_2O_5$  contents  $\geq 5\%$ , high green densities were evidently not as important due to the extensive particle rearrangement which took place during sintering.

The highest fired density ( $5.15 \text{ g/cm}^3$ ) was obtained for the 2 wt%  $V_2O_5$  addition and the highest theoretical density (98.4% ThD) for the 15.0 wt%  $V_2O_5$  addition. These latter samples were relatively fragile, however, owing to the low strength of the second phase and expansion mismatch between the solid phases. The theoretical density values were both measured pycnometrically and calculated from the expression given in Fig. 6 representing a series mixing relationship. Densities used were  $5.76 \text{ g/cm}^3$  for  $ZrO_2$  and  $3.36 \text{ g/cm}^3$  for  $V_2O_5$ . As is evident from Fig. 6, the relationship between calculated and measured values was very close. Densification data as a function of time are given in Fig. 7 for  $ZrO_2$  samples with 0.0, 1.5, 2.0 and 8.0 wt%  $V_2O_5$ . Comparison with the 0.0  $V_2O_5$  samples shows  $V_2O_5$  to be an effective sintering aid for  $ZrO_2$  at  $1100^\circ\text{C}$ . Densification generally increased with  $V_2O_5$  content, but because of the low sintering temperature, limited solubility of  $ZrO_2$  in the liquid phase, and moderately high dihedral angle ( $\sim 40^\circ$  at  $1100^\circ\text{C}$ ), much longer sintering times ( $\geq 8$  hrs) were needed than would normally be required for the liquid phase (sintering) systems. The magnitude linear shrinkage for the  $ZrO_2$ - $V_2O_5$  samples were typically in the range of 6-8 percent for reasonable dense samples. This reflects the relatively high initial pressed densities.

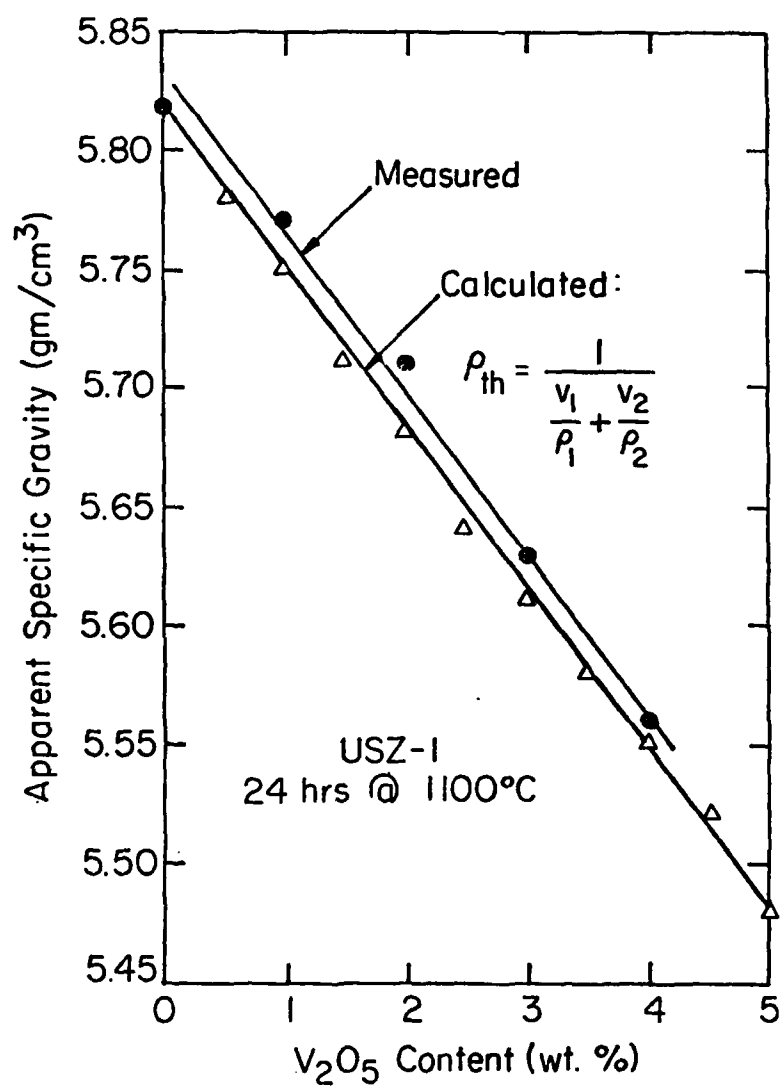


FIGURE 6. Comparison of measured and calculated theoretical density values for  $ZrO_2-V_2O_5$  samples.

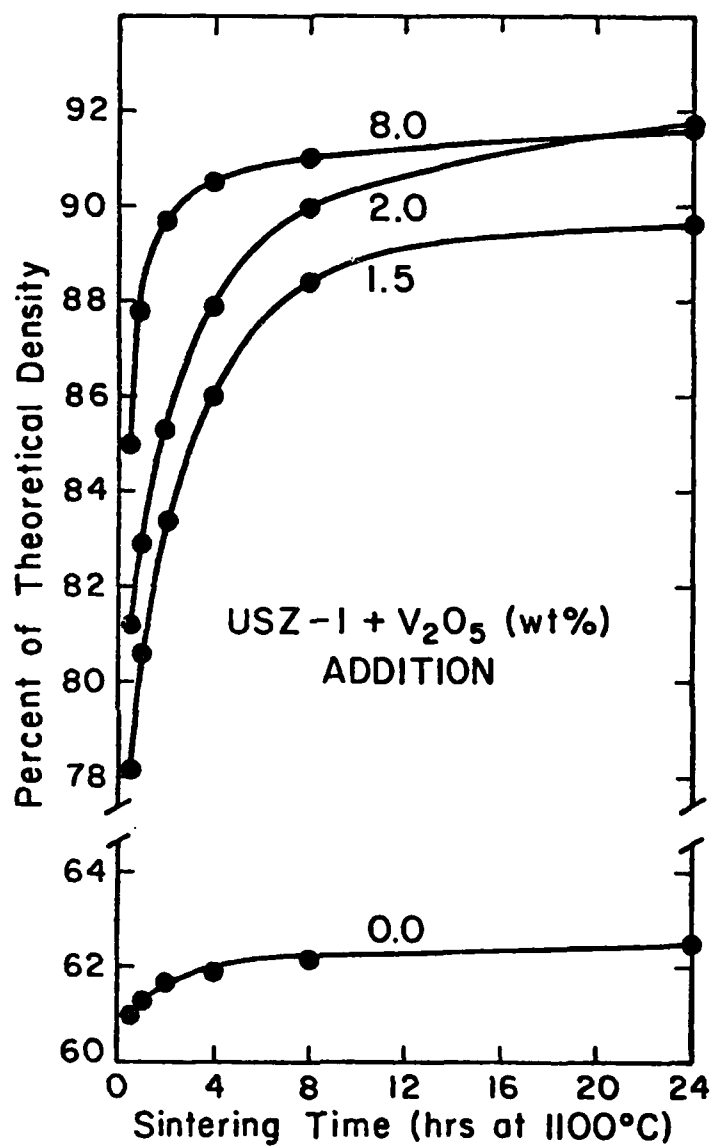


FIGURE 7. Percent of theoretical density vs. sintering time for ZrO<sub>2</sub> samples containing 1.5, 2.0, and 8.0 wt% V<sub>2</sub>O<sub>5</sub>.

Shrinkage data for some  $\text{ZrO}_2\text{-V}_2\text{O}_5$  samples are given in Fig. 8. These curves, as would be expected, show the same kinetic behavior as the densification. Figure 9 shows a plot of percent theoretical density as a function of  $\text{V}_2\text{O}_5$  content for samples formed at a pressure of 35 kpsi (241 MPa) and sintered at 1100°C for soak times up to 24 h. Two regions of relatively high densification were observed to occur as a function of  $\text{V}_2\text{O}_5$  content, especially noticeable for soak times in excess of 30 min. Density maxima occurred at  $\sim 2$  wt% and 12 wt%  $\text{V}_2\text{O}_5$ , giving a distinctly bimodal appearance to the densification curves. As the  $\text{V}_2\text{O}_5$  content was increased above 2 wt%, the density decreased until a minimum was reached at  $\sim 6$  wt%, above which the density increased again. This behavior was similar to that observed by Derebery and Kogut<sup>22</sup> as shown in Fig. 10, although in their study of the  $\text{ZrO}_2\text{-V}_2\text{O}_5$  system the fired densities obtained were somewhat lower and the maxima also occurred at lower  $\text{V}_2\text{O}_5$  additions.

An explanation for the observed bimodal densification behavior can be given with reference to Fig. 11, which shows the relative density versus  $\text{V}_2\text{O}_5$  content curve with regions I, II, and III representing different densification mechanisms.

The degree of densification obtained from rearrangement of spherical particles has recently been regarded as a direct function of the force existing between particles connected by a liquid bridge.<sup>23,24</sup> Calculations of the interparticle force indicate that the attractive forces are highest at low liquid contents and decrease as the liquid content increases. Experimental evidence supporting the results of these calculations was supplied by Huppmann and Riegger.<sup>24</sup> They found that the most pronounced rearrangement in arrays of spherical tungsten particles during sintering was obtained from particle rearrangement.

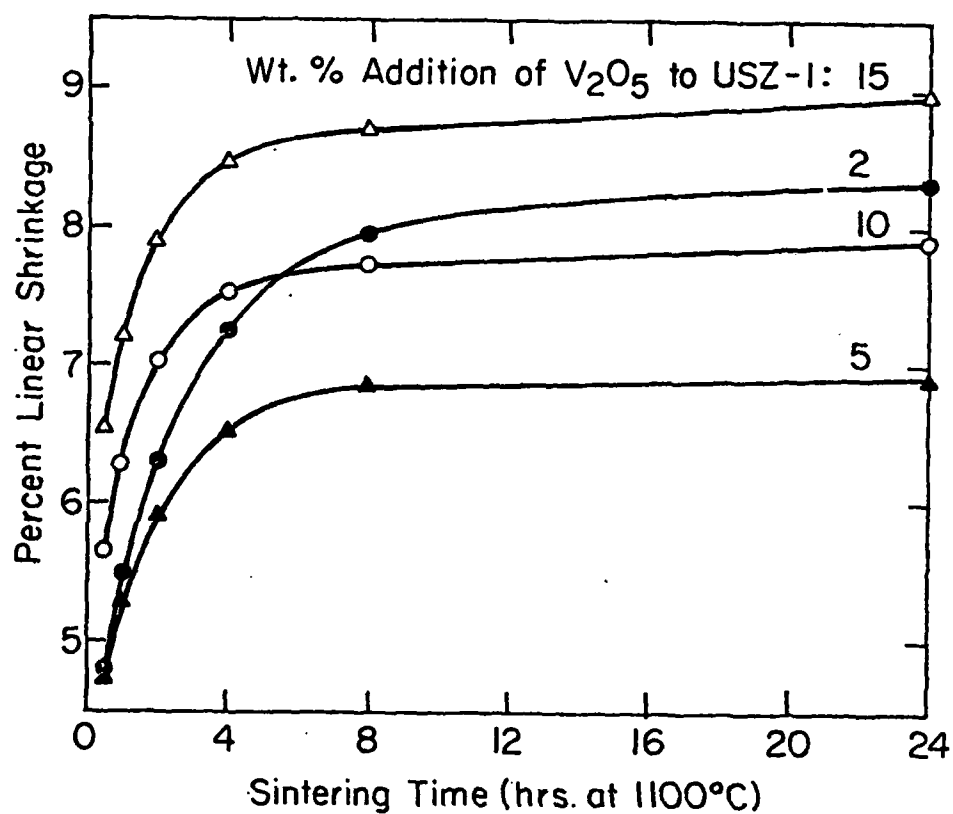


FIGURE 8. Percent linear shrinkage versus sintering time for  $ZrO_2-V_2O_5$  samples.

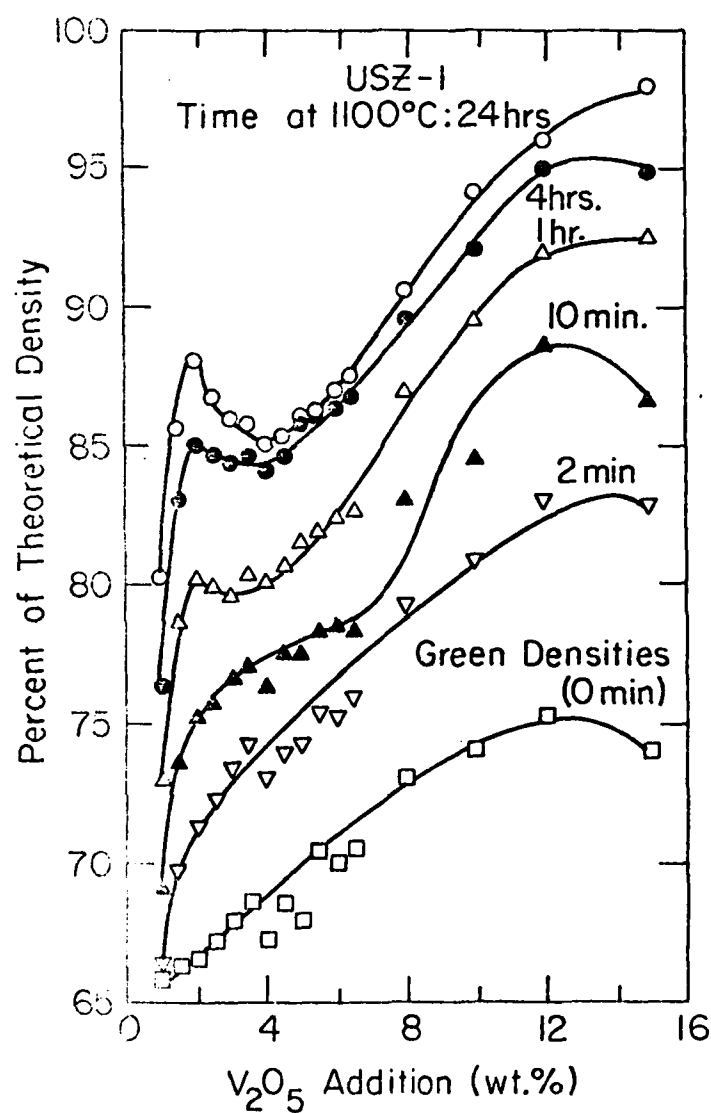


FIGURE 9. Percent theoretical density versus wt%  $V_2O_5$  and soak times for  $ZrO_2-V_2O_5$  samples sintered at 1100°C.

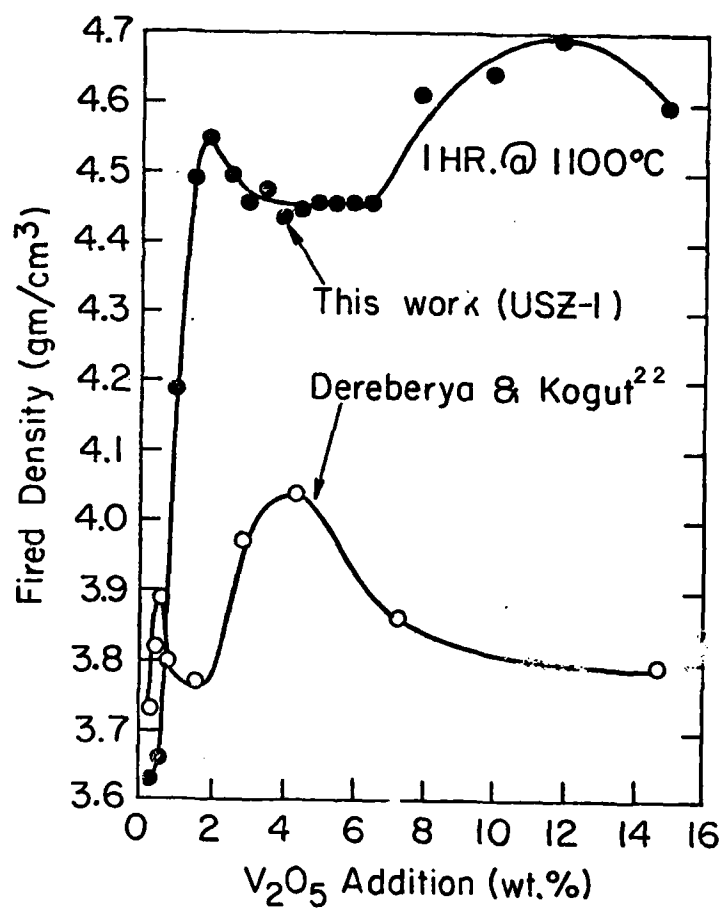


FIGURE 10. Comparison of fired density data showing density maxima as a function of V<sub>2</sub>O<sub>5</sub>.

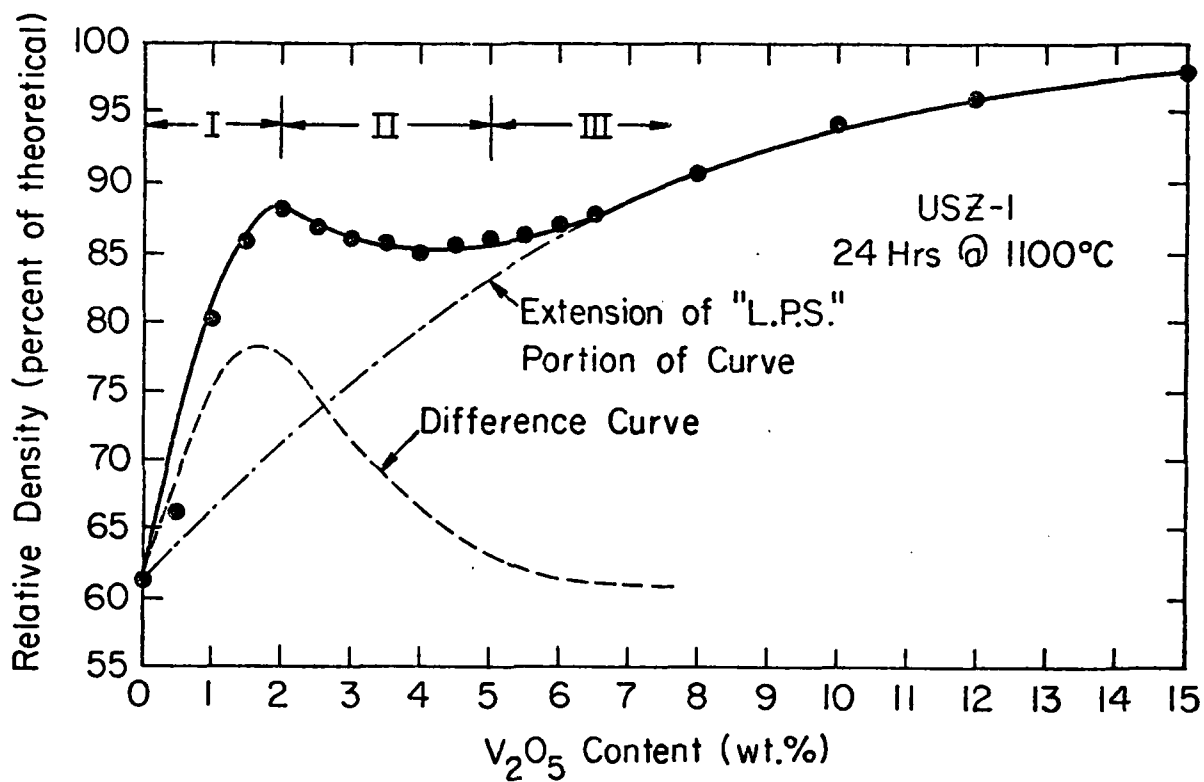


FIGURE 11. Relative density curve illustrating regions (I, II, III) of different densification mechanism as a function of  $V_2O_5$  content at 1100°C/24 h.

From this analysis, the densification for region I in Fig. 11, is attributable mainly to particle rearrangement due to the low liquid content ( $\sim 5$  vol% liquid for 2 wt%  $V_2O_5$ ) and resultant high hydrostatic forces. Region III, in contrast, would densify mainly by solution-precipitation processes since with  $> 15$  vol% liquid ( $> 6$  wt%  $V_2O_5$ ) the interparticle attractive forces would be relatively weak. Both regions I and III should show monotonic increases in density over the composition ranges to which they apply. In region II, both densification mechanisms evidently apply, except that with too little liquid for efficient solution-precipitation and too much for efficient particle rearrangement, particle bridging and solid-solid contact (resistive) conditions would predominate. This in turn would lead to a decrease in density. The density maximum (Fig. 11) at the 2 wt%  $V_2O_5$  addition, therefore, represent an optimum balance between the attractive forces (due to capillary action) and the resistive forces (due to frictional contact between particles).

#### B. Microstructural Analysis

SEM photomicrographs of the fracture surfaces of sintered  $ZrO_2$  samples containing 1.0, 1.5, 2.0, and 8.0 wt%  $V_2O_5$  are shown in Fig. 12. Intergranular fracture is clearly indicated by the presence of second phase areas on the surfaces of the  $ZrO_2$  grains. The second phase was not as evident for the 1.0 wt%  $V_2O_5$  samples, and as expected, the quantity of second phase observed increased with  $V_2O_5$  content. In addition, the grain size increased substantially with  $V_2O_5$  content.

SEM photomicrographs of polished, thermally etched surfaces of sintered samples containing 1.5, 2.0, 4.0, and 8.0 wt%  $V_2O_5$  are shown in Fig. 13. The  $ZrO_2$  grains show a flattened polyhedral shape typical of many liquid phase sintering systems for which the content of liquid phase is relatively

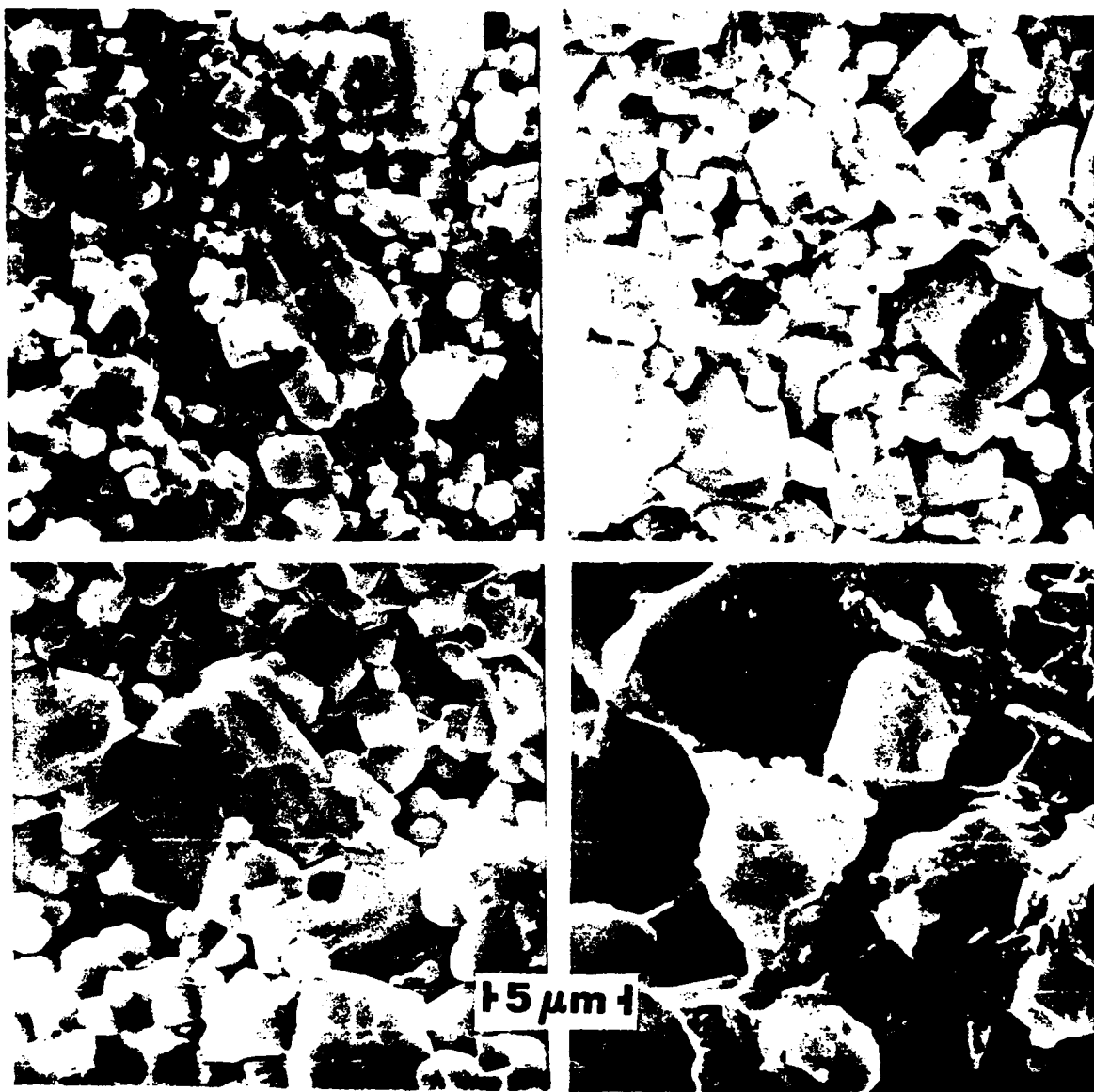


FIGURE 12. SEM photomicrographs of fracture surfaces of  $\text{ZrO}_2$  samples containing: a) 1.0, b) 1.5, c) 2.0, and d) 8.0 wt%  $\text{V}_2\text{O}_5$ .

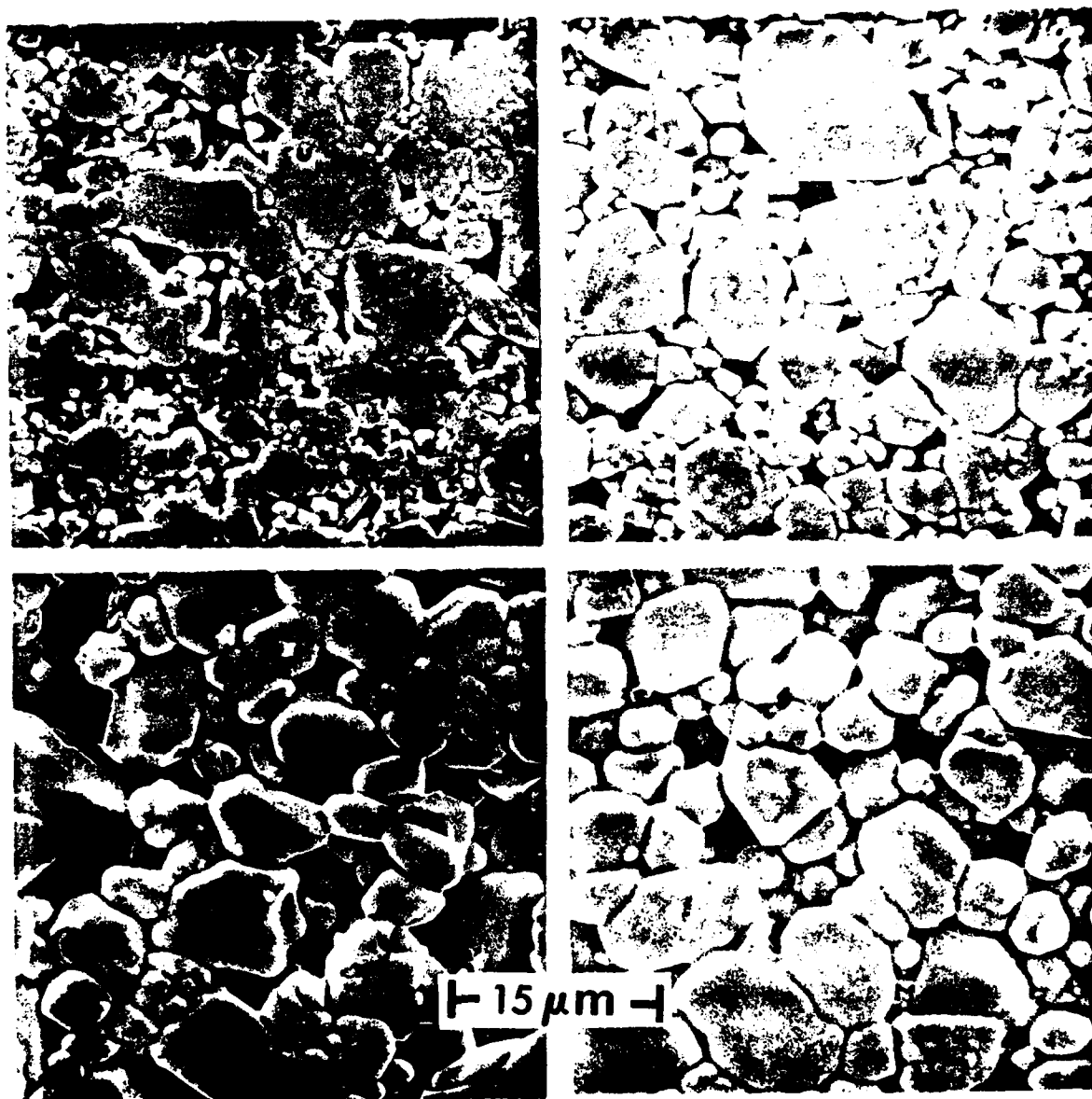


FIGURE 13. SEM photomicrographs of polished, thermally etched surfaces of  $\text{ZrO}_2$  samples containing: a) 1.5, b) 2.0, c) 4.0, and d) 8.0 wt%  $\text{V}_2\text{O}_5$ .

low. The large  $\text{ZrO}_2$  grains in the 1.5 wt% sample (Fig. 13a) appear to be composite grains formed from particles comparable in size to those of the milled, unfired powder ( $\sim 1.0 \mu\text{m}$ ). This subgrain structure indicated that grain growth in samples containing small amounts of  $\text{V}_2\text{O}_5$  occurred mainly by a particle agglomeration mechanism.<sup>25</sup> As the  $\text{V}_2\text{O}_5$  content of the samples increased from 1.5 to 8.0 wt%, the average size of the grains increased. However, this increase in average size was due mainly to a decrease in the number of smaller grains, indicating that larger grains grew at the expense of smaller grains (Ostwald ripening). Grain growth, therefore, most likely occurred by a combination of particle agglomeration (dominant at low liquid contents) and Ostwald ripening (dominant at high liquid contents).

The average fired grain size is shown plotted as a function of  $\text{V}_2\text{O}_5$  content in Fig. 14. Essentially no grain growth occurred until the  $\text{V}_2\text{O}_5$  content exceeded 1 wt%. Above 4 wt%  $\text{V}_2\text{O}_5$ , the grain growth was relatively insensitive to the quantity of liquid present. Since grain growth for high  $\text{V}_2\text{O}_5$  contents had been attributed mainly to solution-precipitation, it follows that the rate-controlling step in this process was solution of  $\text{ZrO}_2$  at the solid-liquid interface.

Figure 15a is a TEM photomicrograph of a  $\text{ZrO}_2$ -2 wt%  $\text{V}_2\text{O}_5$  sample showing a multiple-grain intersection containing a second phase (region A) which extends into an adjacent grain boundary (region B). This boundary region is shown at a higher magnification in Fig. 15b. A microdiffraction pattern of region A and EDAX spectra of regions A, B, and C (taken from the  $\text{ZrO}_2$  grain at a distance of  $\sim 400 \text{ \AA}$  from the edge of the intergranular phase) are shown in Figs. 15c, d, e, and f, respectively. The microdiffraction pattern indicated that the second phase was amorphous. The EDAX spectrum from region A (Fig. 15d) shows that the second phase contained mainly vanadium,

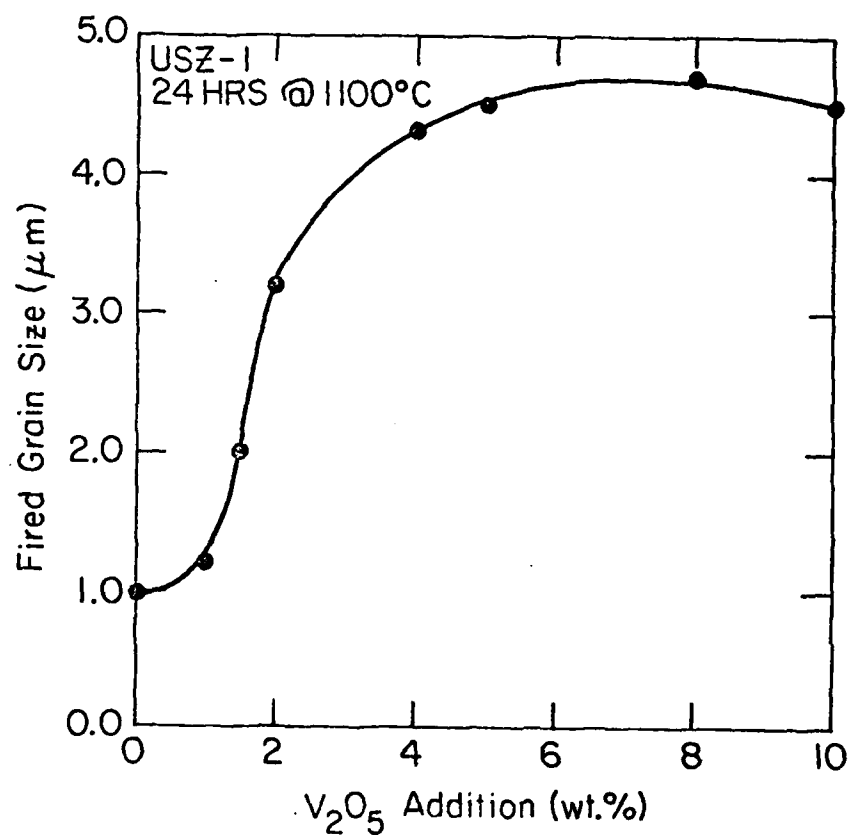
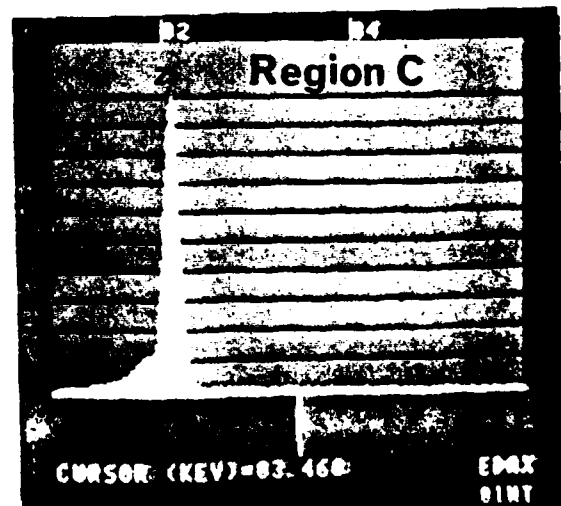
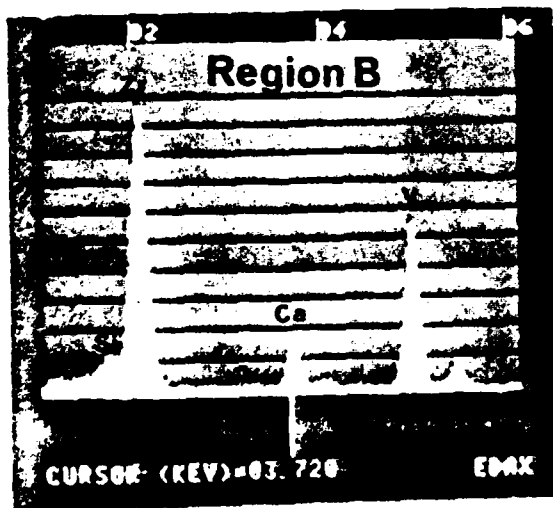
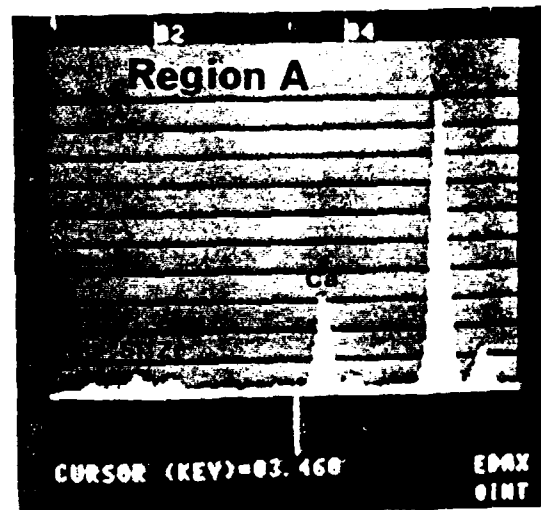
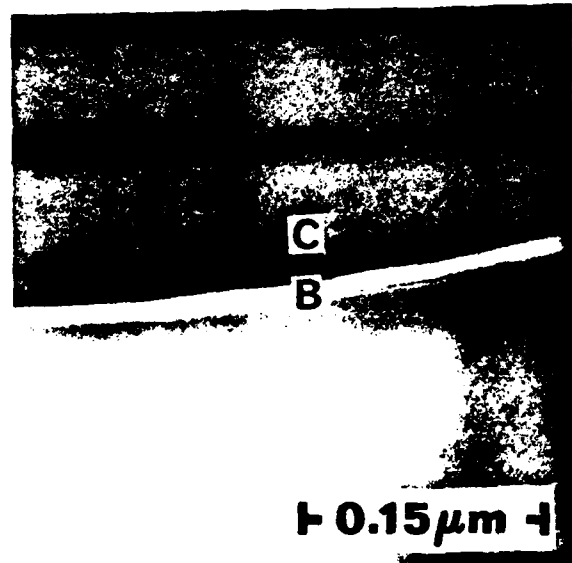
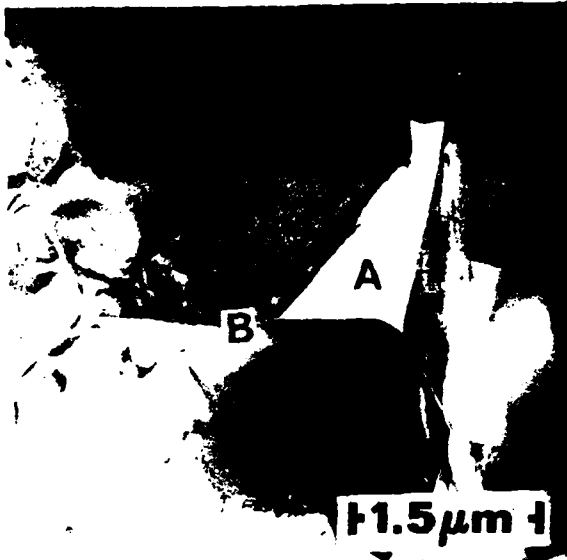


FIGURE 14. Fired grain size vs  $V_2O_5$  content of  $ZrO_2$  samples.

FIGURE 15.  $\text{ZrO}_2$  sample containing 2 wt%  $\text{V}_2\text{O}_5$ :  
a) TEM photomicrograph showing multiple-grain junction containing second phase (region A) which extends into an adjacent grain boundary (region B), b) higher magnification of boundary region (region B), c) microdiffraction pattern of second phase (region A), and EDAX spectra of: d) region A, e) region B, and f) region C (taken from  $\text{ZrO}_2$  grain  $\sim 400 \text{ \AA}$  from edge of second phase).



with a substantial amount of calcium and minor amounts of zirconium, silicon, and magnesium. The presence of zirconium was expected, due to the limited solubility of  $\text{ZrO}_2$  in the liquid phase. The calcium, silicon, and magnesium originated as oxide impurities in the  $\text{ZrO}_2$  powder which segregated to the intergranular regions. The EDAX spectrum from the grain boundary (Fig. 15e) shows the presence of the second phase. However, since the boundary phase was only  $\sim 150 \text{ \AA}$  wide, a large portion of the characteristic X-rays originated in the surrounding  $\text{ZrO}_2$  grains due to beam spreading. The sharpness of the composition gradient in the grain boundary region is shown by the EDAX spectrum (Fig. 15f) collected  $\sim 400 \text{ \AA}$  away from the edge of the intergranular phase (region C). With the possible exception of silicon, no impurities were detected within the  $\text{ZrO}_2$  grains.

Approximate elemental compositions, determined from the EDAX data for the second phase, are listed in Table 2 for  $\text{ZrO}_2$  samples containing 1.5 and 2.0 wt%  $\text{V}_2\text{O}_5$ . The equivalent oxide compositions, also given in Table 2, would be expected to form glassy second phases, which would account for the amorphous microdiffraction pattern observed.

DTA and hot-stage X-ray analysis showed that additions of  $\text{V}_2\text{O}_5$  up to 2 wt% increased the starting temperature of the monoclinic-tetragonal phase transformation from  $\sim 1050^\circ\text{C}$  for 0 wt% to  $\sim 1150^\circ\text{C}$  for 2 wt%. For  $\text{V}_2\text{O}_5$  additions  $> 2$  wt%, the starting temperature remained constant at  $\sim 1150^\circ\text{C}$ , indicating that a solubility limit of vanadium ions in the  $\text{ZrO}_2$  lattice had been reached. However, it was determined from emission spectrographic analysis of a  $\text{ZrO}_2$ -2 wt%  $\text{V}_2\text{O}_5$  sample (repeatedly milled and washed to remove the intergranular phase) that the vanadium content (Table 2) within the  $\text{ZrO}_2$  grains was  $\leq 0.2$  at.% ( $\sim 0.15$  wt%  $\text{V}_2\text{O}_5$  or  $\text{V}_2\text{O}_4$ ). The low vanadium content in the  $\text{ZrO}_2$  grains was consistent with the data obtained from the XRD

TABLE 2: Composition of Intergranular Phase  
(From EDAX Data)

| <u>1.5 wt% V<sub>2</sub>O<sub>5</sub></u> |      |                                      | <u>2.0 wt% V<sub>2</sub>O<sub>5</sub></u> |                                      |           |
|-------------------------------------------|------|--------------------------------------|-------------------------------------------|--------------------------------------|-----------|
| Element                                   | At.% | Equivalent                           | At.%                                      | Equivalent                           |           |
|                                           |      | Wt% Oxide                            |                                           |                                      | Wt% Oxide |
| V <sub>Kα</sub>                           | 65.7 | V <sub>2</sub> O <sub>5</sub> : 74.8 | 74.4                                      | V <sub>2</sub> O <sub>5</sub> : 81.4 |           |
| Ca <sub>Kα</sub>                          | 26.8 | CaO : 18.7                           | 19.6                                      | CaO : 13.2                           |           |
| Zr <sub>Kα</sub>                          | 2.1  | ZrO <sub>2</sub> : 3.2               | 2.1                                       | ZrO <sub>2</sub> : 3.0               |           |
| Si <sub>Kα</sub>                          | 2.9  | SiO <sub>2</sub> : 2.2               | 2.4                                       | SiO <sub>2</sub> : 1.7               |           |
| Mg <sub>Kα</sub>                          | 2.5  | MgO : 1.3                            | 1.5                                       | MgO : 0.7                            |           |

Vanadium Content of ZrO<sub>2</sub> Grains:

(From Emission Spectrographic Analysis)

Vanadium Content  $\leq$  0.2 At.%.

analysis, which showed no changes in the monoclinic lattice parameters as a function of  $V_2O_5$  content. With no change in the lattice parameters and only a small percentage of the vanadium in the  $V^{4+}$  state (qualitatively determined from EPR studies, Fig. 16), and taking into account charge and size considerations, it was concluded that  $V^{4+}$ , rather than  $V^{5+}$ , ions diffused into the  $ZrO_2$  lattice.

The percent weight loss of  $ZrO_2$ - $V_2O_5$  samples is shown in Fig. 17 as a function of  $V_2O_5$  content. The uniformly low loss for  $V_2O_5$  contents  $\leq 1.5$  wt% indicated that the  $V_2O_5$  was effectively tied up in the glassy second phase. However, as the  $V_2O_5$  content was increased above 1.5 wt%, the effects of the impurities were diluted and the properties of the second phase approached more nearly those of pure  $V_2O_5$  (which has a relatively high vapor pressure at  $1100^\circ C^{25}$ ).

### C. Fired Properties

The dc electrical conductivity data for  $ZrO_2$  samples containing 1.5 and 2.0 wt%  $V_2O_5$  are shown plotted in Fig. 18 as a function of the inverse absolute temperature. The conductivity of the 1.5 wt% sample was the same for heating and cooling; however, for the 2 wt% sample, the conductivity abruptly increased at  $\sim 450^\circ C$  during cooling. This behavior can be attributed to partial crystallization of  $V_2O_5$  from the intergranular phase, indicated by a DTA exotherm observed at  $\sim 450^\circ C$  and the increased conduction which would result from the crystallization of  $V_2O_5$ .<sup>3</sup> Crystallization of  $V_2O_5$  was, however, not confirmed by microdiffraction, possibly because the crystallites were extremely small. In contrast, the linear conduction behavior for samples with  $\leq 1.5$  wt%  $V_2O_5$  would indicate the absence of crystalline  $V_2O_5$ , the added  $V_2O_5$  being tied up in the glassy intergranular phase.

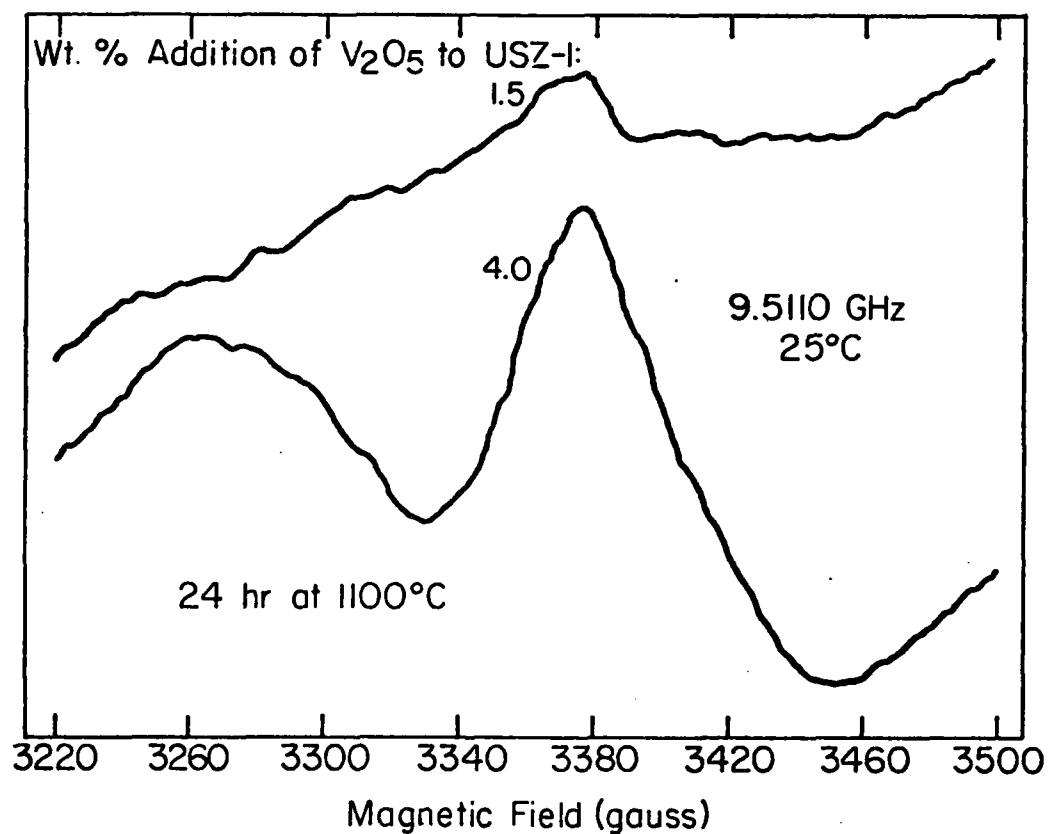


FIGURE 16. EPR data showing  $V^{4+}$  paramagnetic peaks in fired  $ZrO_2$  samples with 1.5 wt% and 4.0 wt%  $V_2O_5$ .

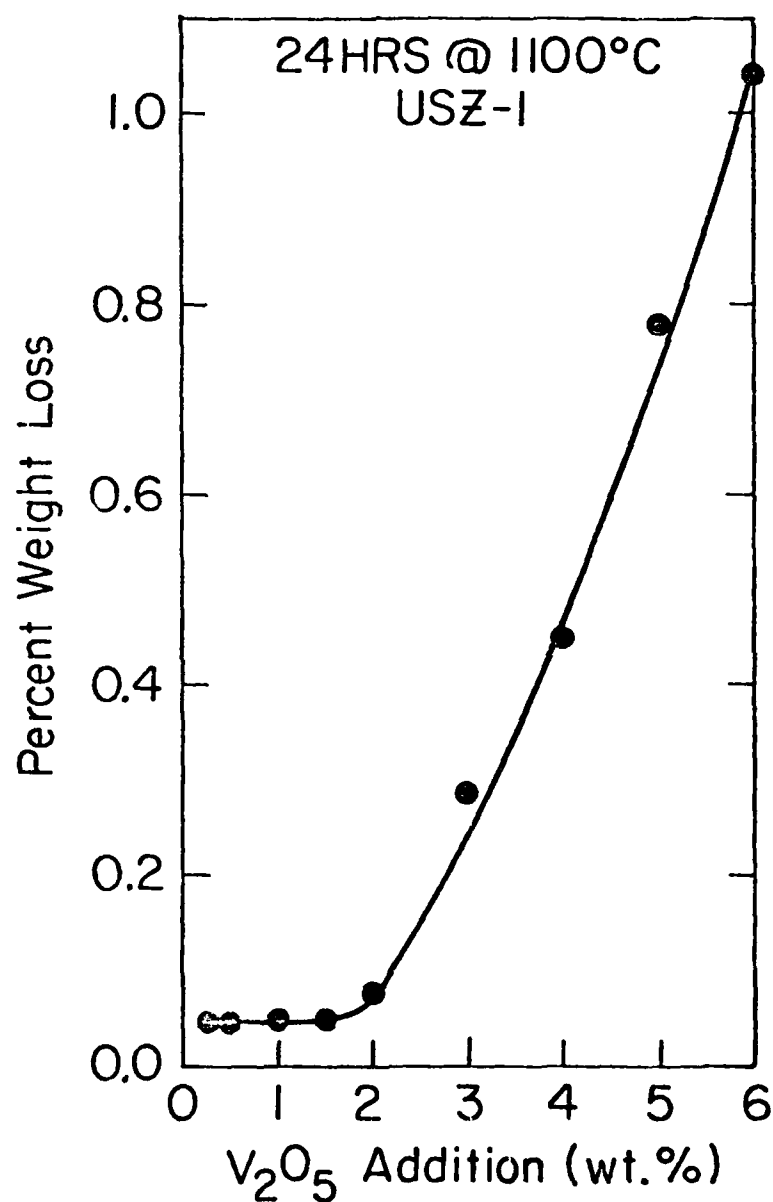


FIGURE 17. Percent weight loss as a function of  $V_2O_5$  content of  $ZrO_2$  samples.

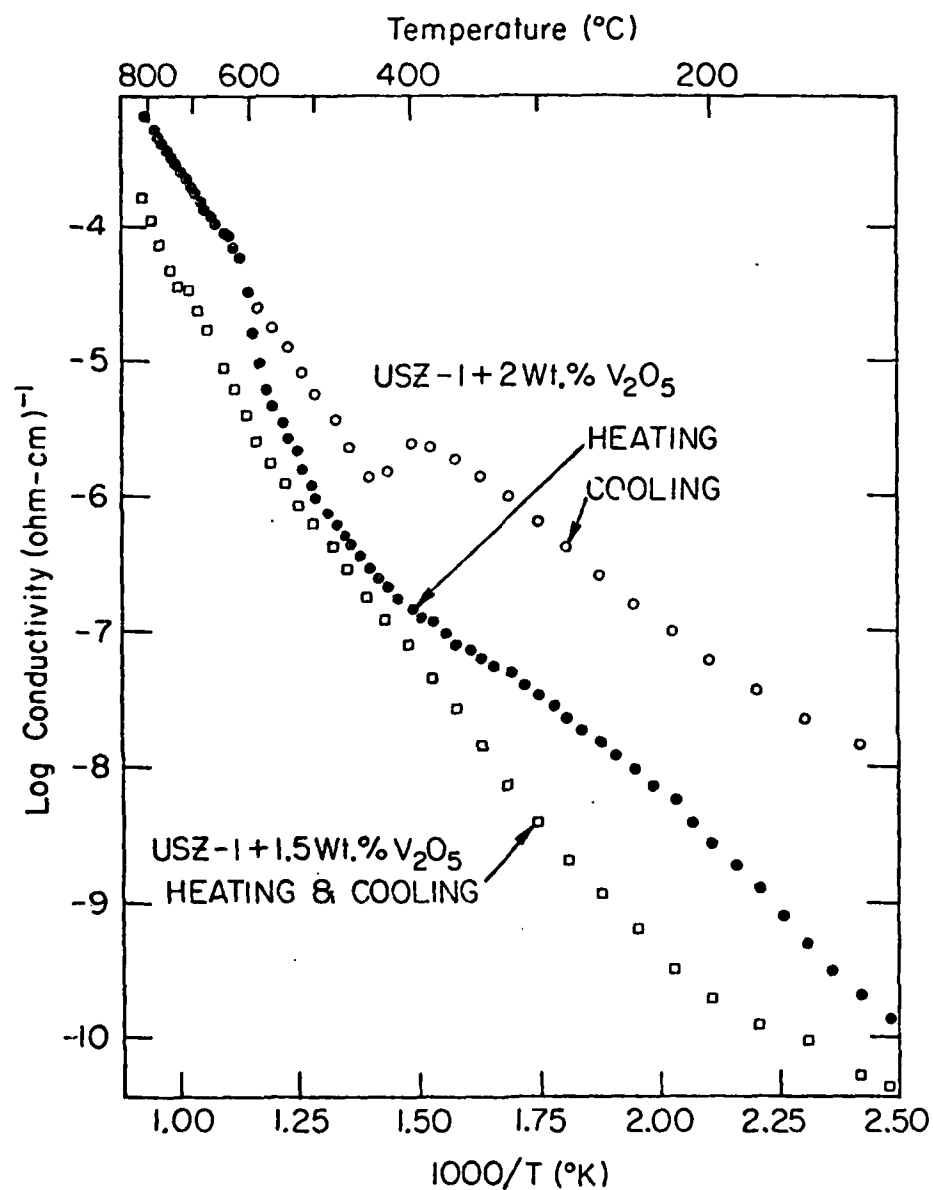


FIGURE 18. Log conductivity vs inverse absolute temperature for ZrO<sub>2</sub> samples containing 1.5 and 2.0 wt% V<sub>2</sub>O<sub>5</sub>.

The thermal expansion (up to 950°C) of a  $\text{ZrO}_2$ -1.5 wt%  $\text{V}_2\text{O}_5$  sample is shown in Fig. 19. The expansion was linear with the relatively low expansion coefficient of  $5.6 \times 10^{-6}/^\circ\text{C}$ , which is consistent with the existence of a glassy intergranular phase of relatively low expansion. For greater  $\text{V}_2\text{O}_5$  contents, the expansion became nonlinear due to the large ( $\sim 30$  vol%) expansion of  $\text{V}_2\text{O}_5$  upon melting.<sup>3</sup>

Table 3 summarizes the fired properties for  $\text{ZrO}_2$  samples containing 1.5, 2.0, and 8.0 wt%  $\text{V}_2\text{O}_5$ . The 1.5 wt% samples exhibited the best overall fired properties. The 1.5 wt% addition evidently produced a sufficient quantity of liquid ( $\sim 4.0$  vol%) to cause a high degree of densification. The presence of impurities resulted in the formation of a glassy second phase. This aided sintering and essentially determined the characteristics of the fired properties. As the  $\text{V}_2\text{O}_5$  content was increased above 1.5 wt%, the properties became increasingly dominated by the intergranular phase. In general, larger quantities of  $\text{V}_2\text{O}_5$  increased the thermal expansion and electrical conductivity and decreased the strength of the samples, as would be expected.

#### IV. Conclusions

1. Addition of  $\text{V}_2\text{O}_5$  (1.5-2.0 wt%) to monoclinic  $\text{ZrO}_2$  powders (avg ps  $\sim 1 \mu\text{m}$ ) resulted in dense ceramic compacts (90-92% ThD) when sintered in air at 1100°C for 24 h.
2. Densification and grain growth were determined by rearrangement and solution-precipitation processes for which the rate-controlling step was found to be solution of  $\text{ZrO}_2$  at the solid-liquid

Table 3. Summary of Fired Properties  
for  $\text{ZrO}_2\text{-V}_2\text{O}_5$  Samples

| Wt%<br>$\text{V}_2\text{O}_5$ | Average<br>Fired           |      | Expansion<br>Coeff.<br>$10^{-6}/^\circ\text{C}$ | Elec. Cond.<br>$800^\circ\text{C}$<br>$10^{-4}(\text{ohm-cm})^{-1}$ | Calc. Flex.      |     |
|-------------------------------|----------------------------|------|-------------------------------------------------|---------------------------------------------------------------------|------------------|-----|
|                               | Density<br>$\text{g/cm}^3$ | %ThD |                                                 |                                                                     | Strength<br>kpsi | MPa |
| 1.5                           | 5.06                       | 89.5 | 5.6                                             | 2.0                                                                 | 22               | 152 |
| 2.0                           | 5.15                       | 91.6 | 6.0                                             | 6.5                                                                 | 23               | 159 |
| 8.0                           | 4.81                       | 91.3 | 6.9                                             | 120.0                                                               | 18               | 124 |

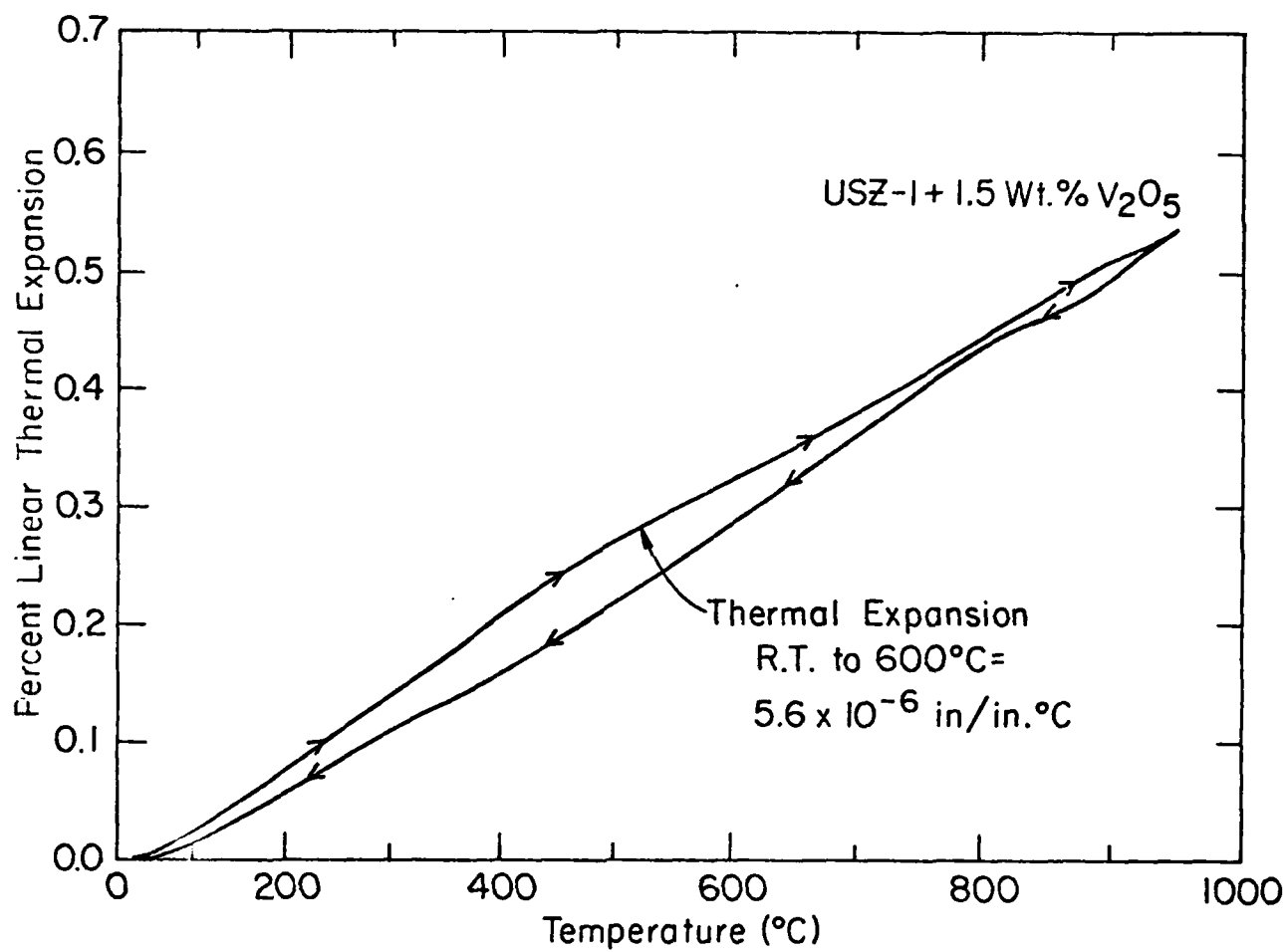


FIGURE 19. Thermal expansion to  $950^{\circ}C$  of  $ZrO_2$  sample containing 1.5 wt%  $V_2O_5$ .

interface. Solubility of vanadium (as  $V^{4+}$ ) in the  $ZrO_2$  phase was low.

3. For  $V_2O_5$  contents  $< 2$  wt%, an amorphous intergranular phase, observed from the microstructures, essentially determined the properties of the fired compacts. For  $V_2O_5$  contents  $> 2$  wt%, crystallization of  $V_2O_5$  from the intergranular phase tended to degrade the properties.
4. Properties measured for sintered compacts (1.5 wt%) were:  
 $\alpha = 5.6 \times 10^{-6}/^{\circ}C$ ;  $\sigma(800^{\circ}C) = 2.0 \times 10^{-4} \text{ (ohm-cm)}^{-1}$ ;  
and  $S_R = 152 \text{ MPa}$ , comparable to those of bulk  $ZrO_2$ .

#### V. Acknowledgements

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VII. Summary of Work Accomplished  
Under Contract No. US Navy-N-00014-78-C-0279

1. Reports

Reports issued under this contract include the following:

- a. D. E. Wittmer and R. C. Buchanan, "Densification of PZT Ceramics with  $V_2O_5$  Additive," (ONR Report # 1), University of Illinois, Urbana, IL (Jan. 1979).
- b. H. D. DeFord and R. C. Buchanan, "Low Temperature Densification of  $ZrO_2$  with Vanadate Additive," (ONR Report # 2), University of Illinois, Urbana, IL (July 1979).
- c. A. Sircar and R. C. Buchanan, "Densification of Zirconia with Borates," (ONR Report # 3), University of Illinois, Urbana, IL (Jan. 1980).
- d. R. C. Buchanan and H. D. DeFord, "Densification of Monoclinic  $ZrO_2$  with Vanadate Additives," (ONR Report # 4), University of Illinois, Department of Ceramic Engineering, Urbana, IL (July, 1982).

2. Thesis

- a. D. E. Wittmer, "Low Temperature Densification of Lead Zirconate Titanate with Vanadium Pentoxide Additions," Ph.D. Thesis, University of Illinois, Urbana, 1980.
- b. G. Wolter, "Properties of Hot Pressed  $ZrV_2O_7$ ," M.S. Thesis, University of Illinois, Urbana, 1981.
- c. H. D. DeFord, "Low Temperature Densification of Zirconium Dioxide with Vanadate Additives," M.S. Thesis, University of Illinois, Urbana, 1982.

3. Papers

- a. D. E. Wittmer and R. C. Buchanan, "Low Temperature Densification of Lead Zirconate Titanate with Vanadium Pentoxide Additive," J. Am. Ceram. Soc., 64[8] 485-90 (1981).
- b. A. F. Grandin de l'Eprevier and R. C. Buchanan, "Preparation and Properties of  $Ca_2V_2O_7$  Single Crystals," J. Electrochem. Soc., (1982).
- c. R. C. Buchanan, H. D. DeFord, and R. W. Doser, "Effects of Vanadate Phase on Sintering and Properties of Monoclinic  $ZrO_2$ ," Advances in Ceramics, Vol. II, [Grain Boundary Phenomena in Electronic Ceramics] American Ceramic Society (1982).
- d. A. Sircar and R. C. Buchanan, "Densification and Phase Changes in  $CaO$ -stabilized  $ZrO_2$  with Borate Additives," J. Am. Ceram. Soc., (submitted) (1982).

#### 4. Patents

a. "Low Temperature Densification of PZT Ceramics," by Relva C. Buchanan and Dale E. Wittmer, US Patent #4,283,228, August, 1981.

b. "Low Temperature Densification of Zirconia Ceramics," by Relva C. Buchanan, H. Dale DeFord, and Anup Sircar, US Patent # 4,303,447, December 1, 1981.