JOURNAL OF MATERIALS SCIENCE 17 (1982) 240–246

Transformation toughening

Part 3 *Experimental observations in the ZrO_2-Y_2O_3 system*

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Materials in the ZrO_2-Y_2O_3 system (with $\leqslant$7.5 mol % Y_2O_3) were fabricated to investigate the conditions required to retain the metastable, tetragonal phase and to determine the contribution of the stress-induced martensitic reaction to fracture toughness. Retention of the tetragonal phase was optimized by minimizing porosity and maintaining the grain size below a critical valve. The critical grain size increased from 0.2 to 1 μm for compositions ranging between 2 and 3 mol %, respectively. These results are consistent with the theories developed regarding the thermodynamics of the martenistic reaction in a constrained state. In the tetragonal plus cubic phase-field (compositions between 3.0 and 7.5 mol % Y_2O_3), the critical stress-intensity factor decreased from 6.3 to 3.0 MPa $m^{1/3}$ as the volume-fraction of the retained, tetragonal phase decreased to zero. Theoretical results, derived from the concept that the stress field of the crack does work to unconstrain the transformation, are in good agreement with the experimental results.

1. Introduction

Part 1 [1] of this series of papers presented a thermodynamic analysis to explain the size-effect associated with a constrained phase transformation. It was shown that a critical inclusion (or grain) size exists, below which the constrained transformation is thermodynamically unfavourable. The size effect arise from surface phenomena associated with the transformation, for example, twinning and/or microcracking, which relieve constraint. These surface phenomena can be avioded when material is fabricated with an inclusion size less than the critical size. It was further shown that the critical size could be increased by either increasing the elastic modulus of the constraining matrix or alloying to lower the chemical free-energy change associated with the transformation. From a practical viewpoint, increasing the critical size can relax the constraints imposed on the fabricator who must contend with inclusion coarsening and grain growth during heat-treatment and/or sintering. In Part 2 [2] the contribution of the constrained inclusions to the fracture toughness was analysed. It was shown that the energy absorbed in the fracture process was equivalent to the work performed by the loading system to stress-induce the transformation. The contribution of the stress-induced transformation was thus shown to be related to the chemical free-energy change associated with the transformation, the volume of material that remains in the transformed state during crack extension and the elastic modulus of the composite.

In the present part experimental work with materials in the ZrO_2–Y_2O_3 system is reported, concerned with both retention of the high-temperature tetragonal structure of ZrO_2 and its effect on fracture toughness. Fig. 1 illustrates [3, 4] that Y_2O_3 forms a solid solution with ZrO_2 and lowers the tetragonal → monoclinic transformation temperature from about 1200° C to about 565° C at a Y_2O_3 content of approximately 3.5 mol%. Thus, effects concerned with changing the chemical free-energy could be studied with Y_2O_3 additions up to about 3.5 mol% Y_2O_3 content. Fig. 1 also shows that a two-phase, tetragonal plus cubic phase-field exists between about 3.5 and about 7 mol% Y_2O_3, in which a two-phase material could be fabricated to determine the effect of the tetragonal phase content on

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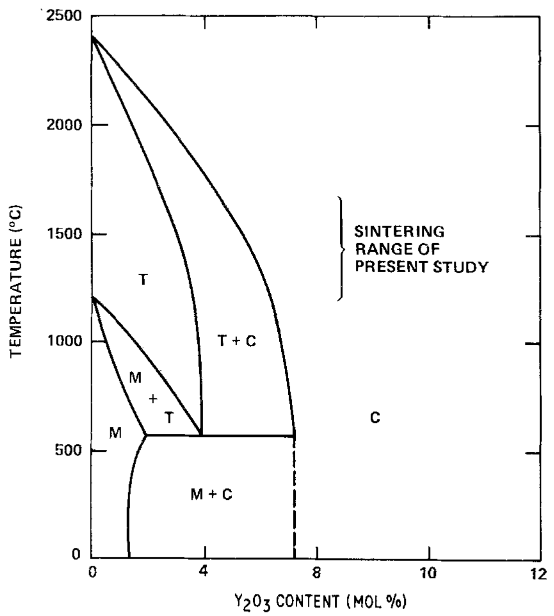

Figure 1 The portion of the ZrO_2–Y_2O_3 system used in the present work [3, 4].

fracture toughness. The ZrO_2–Y_2O_3 system appeared to be useful in obtaining data that may support some of the theoretical predictions made in Parts 1 and 2. In addition, Gupta *et al.* [5] have already demonstrated that single-phase tetragonal ZrO_2 could be fabricated in this system. Experimental effort was thus concentrated in three areas (a) the effect of density on retention of the tetragonal phase, (b) the critical grain-size required for phase retention and (c) the relation between fracture toughness and composition.

2. Experimental procedure

Composite powders (of composition 0 to 7.5 mol % Y_2O_3) were prepared by mixing in a mortar and pestle sub-micrometre-size ZrO_2 powder* with the appropriate amount of yttrium nitrate in methanol, after determining the conversion factor for the decomposition of yttrium nitrate to Y_2O_3. Prior to cold-pressing and sintering, the composite powders were calcined for 4 h at 400° C. Sintering experiments were performed in an air environment at temperatures between 900 and 1650° C. After sintering, densities† were obtained by either dimensional–weight measurements or a water displacement technique. X-ray diffraction analysis was used for phase identification. Monoclinic and tetragonal phase contents were determined from $(1\bar{1}1)$ and (111) diffraction peaks, using a planometer. The presence of the cubic phase was determined by both the (311) and the (400) diffraction peaks which would split the respective diffraction peaks of the tetragonal phase.

For selected materials the critical stress-intensity, factor, K_c, was determined at room temperature by using the idention technique developed by Evans and Charles [6]. Prior to using this technique, the surface of each specimen was finely polished and X-rayed to ensure that the surface was not noticeably altered by the preparation procedure. It should be noted that rough grinding will induce the tetragonal → monoclinic transformation at the surface, and the damaged layer can be removed (within current detectability limits of about $0.5\,\mu m$ [7]) by polishing. The intercept method was used to determine grain size on scanning electron micrographs of fracture surfaces.

3. Results and discussion

3.1. General fabrication observations

Approximately 80 % of the total shrinkage occurred rapidly (within 2 h) between 1150 and 1250° C; further shrinkage required temperatures greater than 1350° C. Densities of between 82 % and 87 % of the theoretical density could be achieved by sintering for 24 h at 1200° C followed by 2 h at 1400° C. Compositions containing $\geqslant 6$ mol % Y_2O_3 required sintering for an additional 2 h at 1550° C.

3.2. Retention of tetragonal ZrO_2: effect of density

Composite powders containing 2.5 mol % Y_2O_3 were uniaxially cold-pressed at different stresses to achieve green densities and were then sintered together for 2 h at 1500° C. Fig. 2 plots the results of this experiment in terms of the per cent of the tetragonal phase retained against the per cent of the theoretical density achieved during sintering. It can be concluded that the retention of the high temperature tetragonal phase at room temperature depends on the density achieved during fabrication. This conclusion shows that phase retention is directly related to the constraint imposed by neighbouring grains on one another. Porosity lowers the elastic modulus and introduces free surface. The effect of both of these factors would

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*Obtained from Zircar Corp., Florida, NY, USA.

†The theoretical densities of ZrO_2–Y_2O_3 materials were calculated from the lattice parameter data of Scott [4].

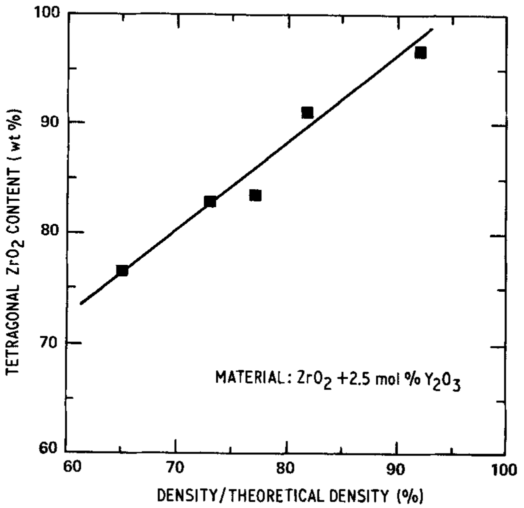

Figure 2 The effect of density on retention of tetragonal $ZrO_2 + 2.5\,mol\%\,Y_2O_3$.

reduce the strain energy associated with the transformation allowing larger grains and/or grains bounded by more free surface than neighbouring grains to undergo the transformation during cooling [1].

3.3. Retention of tetragonal ZrO_2: critical grain-size

Composite powders containing 0, 1.5, 2.0, 2.5, 3.0 and 3.5 mol% Y_2O_3 were cold-pressed and sintered for 2 h at temperatures ranging from 1200 to 1600° C. Detailed grain-size measurements were made on the 2.0 mol% Y_2O_3 composition as a function of temperature; these results are shown in Fig. 3. Measurements on other selected compositions were in agreement with these data. The phase content of each specimen was compared to the grain-size measurement in order to determine the critical grain-size required to retain $\geqslant 90\%$ of the tetragonal phase. Since densitites between 80% and 90% of the theoretical density could only be achieved with the sintering conditions stated, monoclinic contents $\leqslant 10\%$ were neglected. (If full density could be achieved, the critical grain-size would be expected [1] to be somewhat smaller than those reported in Fig. 4.)

As shown in Fig. 4, a high tetragonal-phase content could not be achieved for the composition containing 1.5 mol% Y_2O_3, i.e., grain growth during sintering precluded an average grain size of less than 0.2 μm. The pure ZrO_2 was completely monoclinic under all conditions. More importantly, Fig. 4 shows that the average critical grain-size significantly increases between 2 and 3 mol% Y_2O_3. The composition containing 3.5 mol% Y_2O_3 contained a detectable amount of cubic phase, indicating that this composition lies in the tetragonal + cubic phase-field at temperatures greater than 1200° C (see Fig. 1).

The increase in the critical grain-size with increasing Y_2O_3 content is consistent with the

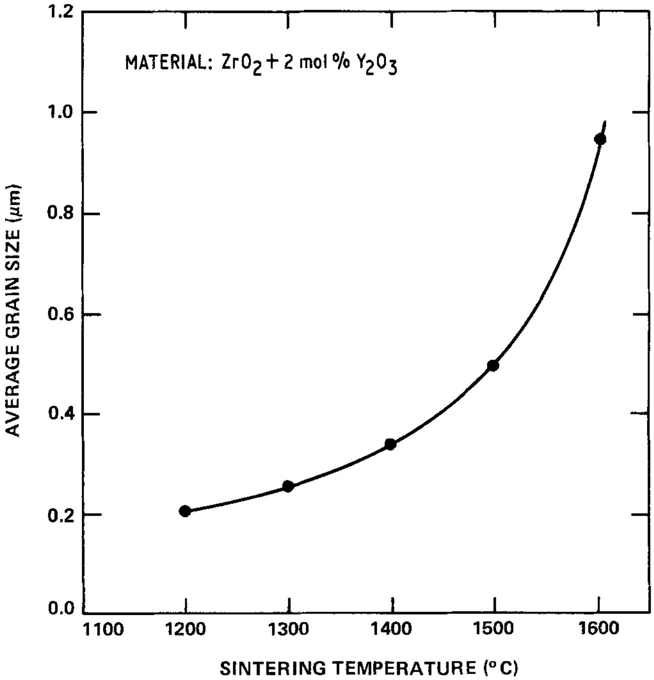

Figure 3 Average grain-size plotted against sintering temperature determined for the ZrO_2 material containing $2\,mol\%\,Y_2O_3$.

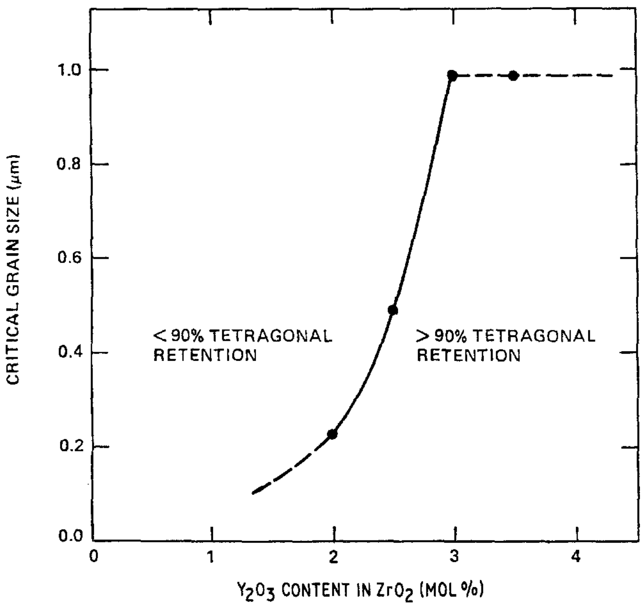

Figure 4 Critical grain-size plotted against Y_2O_3 content in tetragonal ZrO_2.

theortical prediction that the critical grain-size would increase as the magnitude of the change in chemical free-energy decreases (see Part 1 [1]).

3.4. Fracture toughness

The object here was to measure fracture toughness as a function of the retained tetragonal phase. Composite powders containing 1.5 to 7.5 mol% Y_2O_3, in increments of 0.5 mol% Y_2O_3 were prepared. According to Fig. 1, compositions with $\geqslant$ 3 mol% Y_2O_3 should contain increasing contents of the cubic phase. Sintering schedules were optimized (see Section 3.1.) to produce materials with densities in the range of 88% to 93% of the theorotical density. Phase indentification results were consistent with the concepts required for retention of the tetragonal phase and and the phase diagram for this system (Fig. 1).

A two-phase, tetragonal + cubic, material was produced between 3 mol% Y_2O_3 and 7 mol% Y_2O_3; the volume-fraction of the tetragonal phase decreased from one at 3.0 mol% Y_2O_3 to zero at 7.0 mol% Y_2O_3. Only the 1.5 mol% Y_2O_3 composition contained an appreciable amount (> 10%) of the monoclinic phase, because the average grain-size was in excess of the critical value. The monoclinic phase was not detectable in compositions containing $\geqslant$ 3 mol% Y_2O_3.

Results of the stress-intensity factor, K_c, measurements are shown in Fig. 5. as a function of the Y_2O_3 content and the volume-fraction of the tetragonal phase. Three identations were used to determine K_c for each composition; data scatter illustrates high and low values. Fig. 5. shows that K_c drops from 6.5 MPa m$^{1/2}$ to 3.0 MPa m$^{1/2}$ as the volume-fraction of the tetragonal phase decreases to zero. The 1.5 mol% Y_2O_3 composition had a relatively low K_c value due, appearently, to the large amount of monoclinic phase.

The solid line in Fig. 5. was obtained from the calculated effect of the tetragonal volume-fraction on K_c by using [2]

$$K_c = \left[K_0^2 + \frac{2(|\Delta G^c| - \Delta U_{se} f) E_c V_i R}{(1 - \nu_c^2)}\right]^{1/2}, \qquad (1)$$

where K_0 is the fracture toughness of the cubic phase (3.0 MPa m$^{1/2}$), $|\Delta G_c|$ is the magnitude of the chemical free-energy change associated with the transformation, $\Delta U_{se} f$ is the residual strain energy associated with the transformed grains near the fracture surface, E_c and ν_c are the elastic modulus and Poisson's ratio of the composite, respectively, R is the depth of the transformation zone from the fracture surface and V_i is the volume-fraction of the tetragonal phase. Equation 1 can be rewritten as

$$K_c^2 - K_0^2 = C V_i, \qquad (2)$$

where the constant, C, can be evaluated for V_i = 1.0 and used to predict the effect of volume-fraction. As shown, the predicted effect of the tetragonal phase volume-fraction on K_c is in perfect agreement with the experimental values.

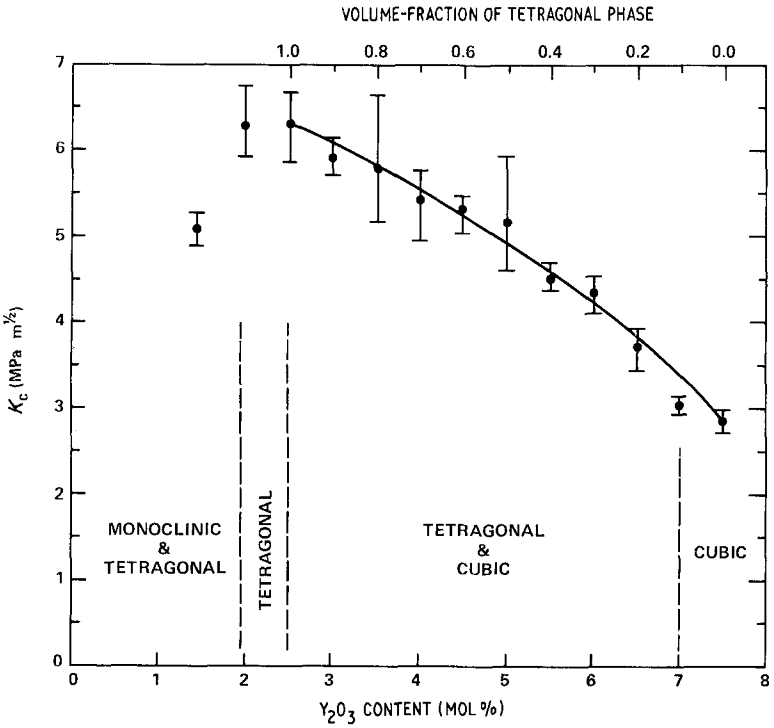

Figure 5 Fracture toughness, plotted against mol% of Y_2O_3 in ZrO_2.

By assuming that the depth of the transformation zone is approximately equivalent to the grain size [2] one can use Equation 1, the experimental values of K_c and K_0, and the expected elastic properties of the material to determine the factor $(|\Delta G^c| - \Delta U_{se}f)$. This factor is the work per unit volume loss during the stress-induced transformation [2]. Using the values E_c = 165 GPa*, ν_c = 0.25 and $R = 0.5\,\mu$m, the work done per unit volume of transformed material was calculated to be 176 MJ m^{-3}.

3.5. Fractography

Fig. 6 illustrates the typical fracture-surface topography of four compositions sintered at 1600° C for 2h. Intergranular fracture (Fig. 6a) was typical of the highly monoclinic materials, suggesting that the crack path followed the intergranular microcracks produced during fabrication as a result of the phase transformation. Such materials were quite friable. Irregular, transgranular fracture was typical of tetragonal materials (Fig. 6b). The irregular fracture topography of individual grains may be a result of the crack interacting with the complex internal structure of the twinned monoclinic grains which transformed ahead of the propagating crack. Fig. 6b also indicates that intergranular microcracks were not produced ahead of the crack front, because of the stress-induced transformation, i.e., if microcracks were present, the fracture surface would resemble that shown in Fig. 6a. A smooth transgranular fracture surface was typical for the cubic materials (Fig. 6c). The porosity (~ 15%) associated with these materials is easily recognized in the cubic material because of the near-planar topography of the fracture surface. Since both the tetragonal and cubic phases produce different fracture topographies, it was relatively easy to recognize tetragonal grains surrounded by cubic grains for two phase compositions such as the 5 mol% Y_2O_3 composition shown in Fig. 6d. This observation suggests that the two phases in such compositions (3 mol% $\leqslant Y_2O_3 \leqslant$ 6.5 mol%) are present as separate grains, instead of as tetragonal precipates within a cubic matrix such as are produced by fabricating in the cubic phase field and quenching into the tetragonal + cubic phase field [9].

4. Conclusions

Retention of the tetragonal phase was found to depend on both density and grain size. The depen-

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*The elastic modulus of dense ZrO_2 (t) is 207 GPa [8]; the value of 165 GPa was calculated for a material with 10% porosity.

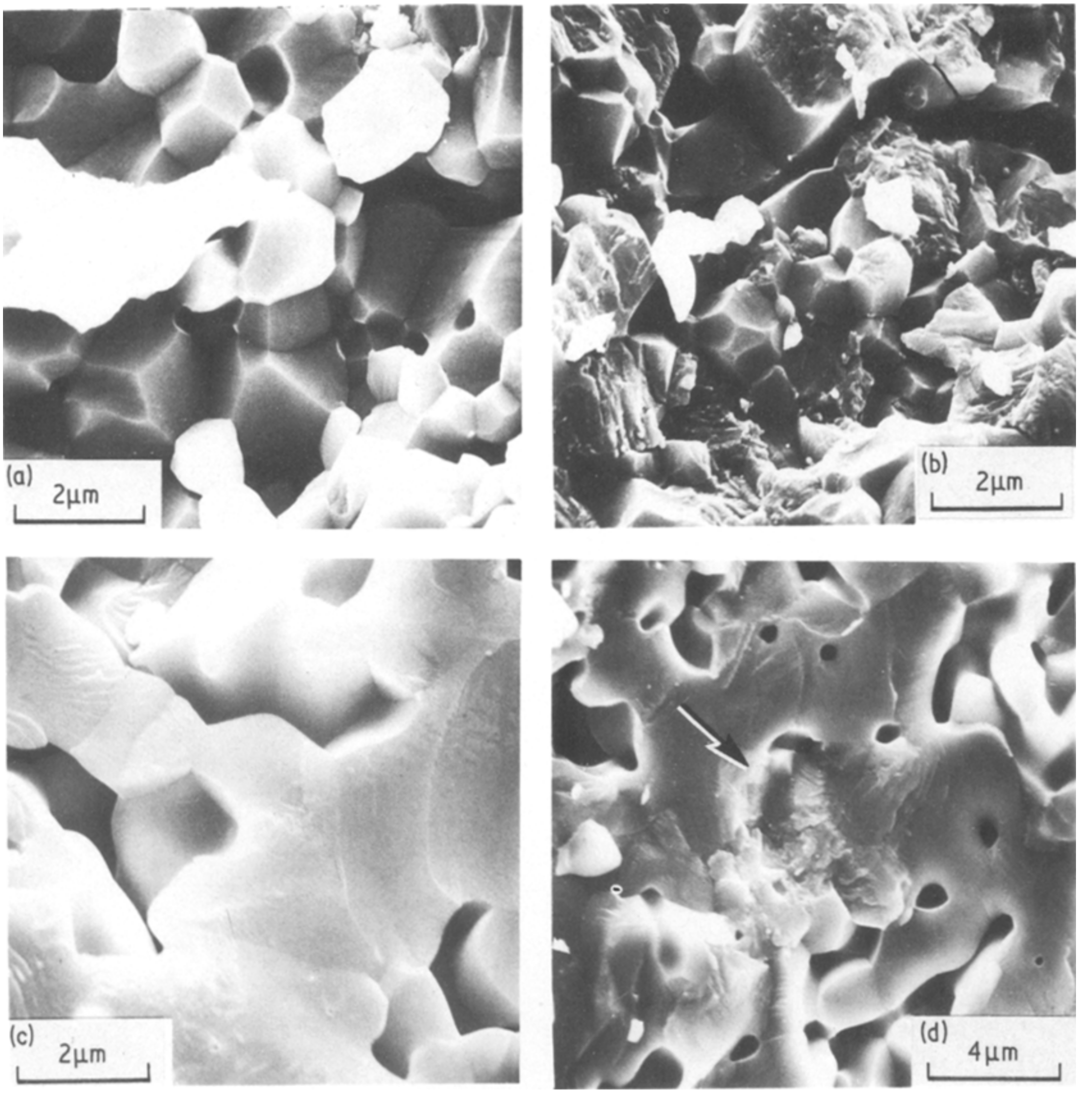

Figure 6 Fracture surfaces of (a) monoclinic ZrO_2 + 2 mol% Y_2O_3 composition, (b) tetragonal ZrO_2 + 3.5 mol% Y_2O_3 and (d) mixed tetragonal + cubic ZrO_2 + 5 mol% Y_2O_3. All sintered at 1600° C for 2 h.

dence on density is consistent with the need for self-constraint and with the concepts developed regarding the thermodynamics of the martenistic reaction in an elastically-constrained matrix. The effect of Y_2O_3 on the critical grain-size is consistent with the theory relating the chemical free-energy change to the size-effect produced by surface phenomena (e.g., twinning and microcracking) that can accompany the transformation.

The contribution of the stress-induced transformation to the fracture toughness is significant and is directly related to the volume-fraction of the retained tetragonal phase. A theoretical approach developed to explain this contribution is in good agreement with experimental data validating the concept that the contribution of the transformation lies with the work done to unconstrain the martensitic reaction. Fractography indirectly supports this concept.

Acknowledgement

The author wishes to thank Mr M. G. Metcalf for technical services. This work was supported by the Office of Naval Research, under Contract number N00014-77-C-0441.

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Received 12 May
and accepted 18 June 1981