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CeO_2-ZrO_2 TETRAGONAL CERAMICS (Ce-TZP): MECHANICAL PROPERTIES

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This work presents the development and the characterization of CeO_2-stabilized tetragonal ZrO_2 polycrystals (Ce-TZP ceramics), since it is considered candidate material for applications as structural high performance ceramics, and as substitute of some metalic materials. Ce-TZP ceramics attain remarkable increasing in strength and fracture toughness. Sintered ceramics were fabricated from mixtures of powders containing different CeO_2 content prepared by conventional mechanical technique. It were adopted the bending strength, Vickers hardness and fracture toughness techniques to the determination of the mechanical parameters. These results were discussed and compared to those published in international literature.

1. INTRODUCTION

The reliability of structural ceramics is limited by their brittleness, since they show a tendeny to fail catastrophically by growth of a single crack that originates from a very small structural deftct. The defects are introduced during either fabrication or surface preparation or exposure to agressive environments. These defects (e.g. pores, bulk and surface cracks) influence the reproductibility of mechanical properties, specially parameters such as the strength, hardness and toughness in ceramics materials [1], [2].

Garvie et al [3] indicated the possibility of attaining remarkable increases in strength and toughness of ceramic materials. Pure ZrO_2 presents phase transformations: monoclinic (m) $\xrightarrow{1170°C}$ tetragonal (t) $\xrightarrow{2370°C}$ cubic (c), where m and c are stable phases, and t is a metastable phase. The phenomenon of transformation toughned in ceramics relies on the volume expansion, 3-5%, and shear strain $\approx$7%, developed when tetragonal zirconia transforms to monoclinic phase.

Toughning of zirconia and zirconia-based ceramics is attained by retention of the tetragonal zirconia in a metastable state. This phase changes to monoclinic form being initiated by the tensile stress field of an advancing crack. Any metastable tetragonal zirconia will transform if to exist a elastic stress field in the vinicity of the crack tip. As a result of this, the volume expansion due to t$\rightarrow$m transformation and accommodating shear strains exerts a back stress on the crack. This mechanism introduces the concept of a process zone around a crack tip (Fig.1). A number of other mechanisms associated with the second phase zirconia particles have been used to explain the enchanced mechanical properties in these kinds of ceramics. Phenomenons of great technological importance are the crack branching (Fig.2a) and the development of a grinding-induced surface transformation which develops a compressive surface stress (Fig. 3b) [4].

Tetragonal zirconia polycrystals (TZP ceramics) show the metastable tetragonal phase at room temperature. In CeO_2-ZrO_2 system exists an extensive solid solution region with tetragonal phase which is stable at near room temperature (Fig.4), that is must possible fabricate ceramics composed of the tetragonal phase containing widely different amount of CeO_2 content [5], [6]. Y_2O_3-stabilized tetragonal ZrO_2 polycrystals (Y-TZP

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The commercial application of ZrO_2-based ceramics is well under way: i) cutting tool tips of Al_2O_3-ZrO_2, ii) wear resistant as tappet heads, valve guides, valve seatings, piston crowns, scissors ans scalpels and iii) internal combustion engine and turbine parts (in experimental development programmes)[7].

In the present study we are reporting the Ce-TZP mechanical properties dependence on CeO_2 content , microstructure and fraction of tetragonal-to-monoclinic stress-induced transformation.

2. EXPERIMENTAL PROCEDURE

Several CeO_2-ZrO_2 mixtures containing different amounts of CeO_2 were prepared by conventional mechanical mixtures of these two powders. Commercial grade ZrO_2 (ZS2 from Von Mel, England) and CeO_2 (from Nuclemon, Brazil) were used.

In the Fig.3 is shown the experimental procedure adopted in this study.

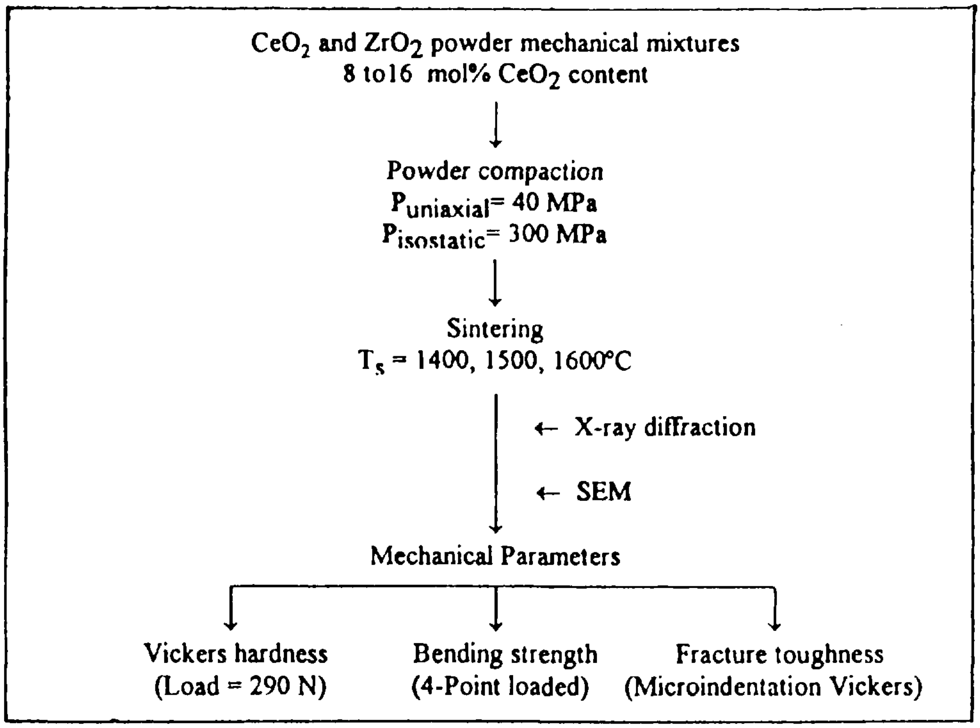

Fig. 3 Schematic cart flow of the experimental procedure for Ce-TZP preparation and mechanical parameters characterization.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. GRAIN SIZE IN SINTERED Ce-TZP CERAMICS

Scanning electron micrographs of Ce-TZP analyses indicated that the average grain size increased with the sintering temperature (Fig. 4). Results of SEM observation for these samples containing about 8 to 16 mol% CeO_2 revealed that shape and size of grains were invariable with changing CeO_2 content.

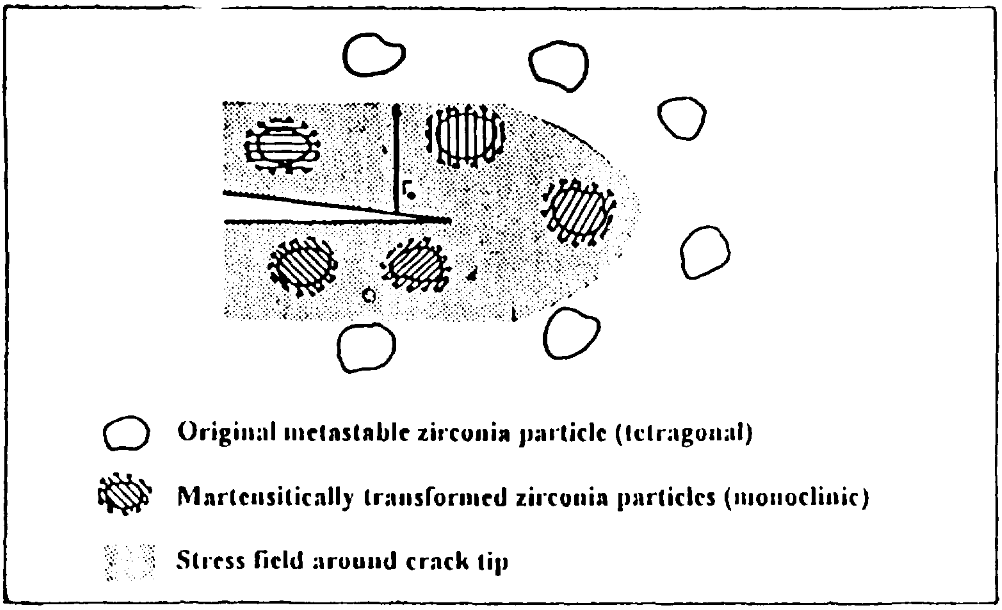

Fig. 1 Diagrammatic representation of a process zone around a crack tip in a material containing metastable tetragonal zirconia [4].

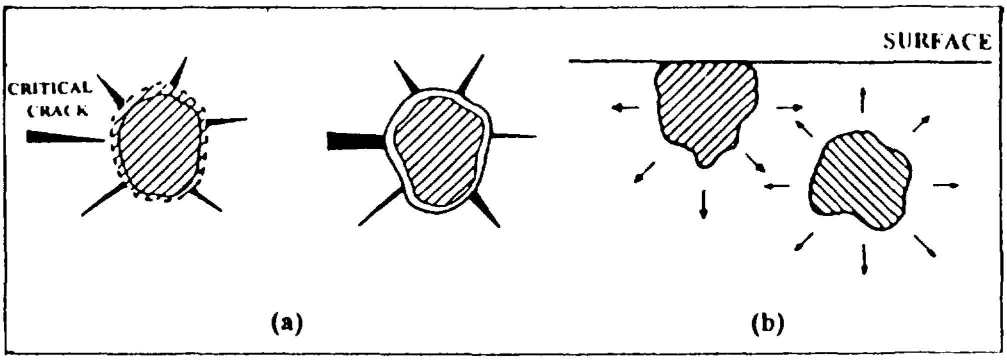

Fig. 2 Schematic representation of : (a) the more commum crack particle interaction (crack branching) and (b) the development of compressive surface layer by t → m transformation via martensitic shear process (grinding-induced transformation in a compressive surface layer) [4].

ceramics) is the representative toughned zirconia ceramic. Y-TZP ceramics containing 2 mol% Y_2O_3 possesses high fracture toughness (10 to 12 MPa.m$^{-1/2}$) and high bending strength (1300 MPa.m$^{-1/2}$) [4], [5]. Neverthless, it has been reported that strength and toughness degrade by low temperature aging below 500°C in water vapour and organic and inorganic gases. This undesirable degradation results from the tetragonal-to-monoclinic phase transformation. Thermal stability of this ceramic is influenced by grain size, Y_2O_3 content and aging atmosphere [6]. However, Ce-TZP ceramics containing 12 mol% CeO_2 possesses intermediate bending strength (600 MPa) and high fracture toughness (20 MPa.m$^{-1/2}$). This material is very resistent to t→m transformation during low temperature aging [5], [6].

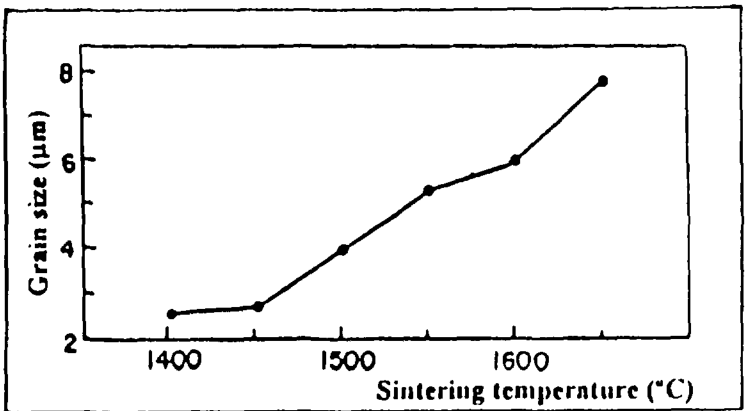

Fig. 4 Behaviour of sintering temperature-grain size curve.

3.2. STRESS-INDUCED TRANSFORMATION TOUGHNING BY T→M PHASE CHANGE

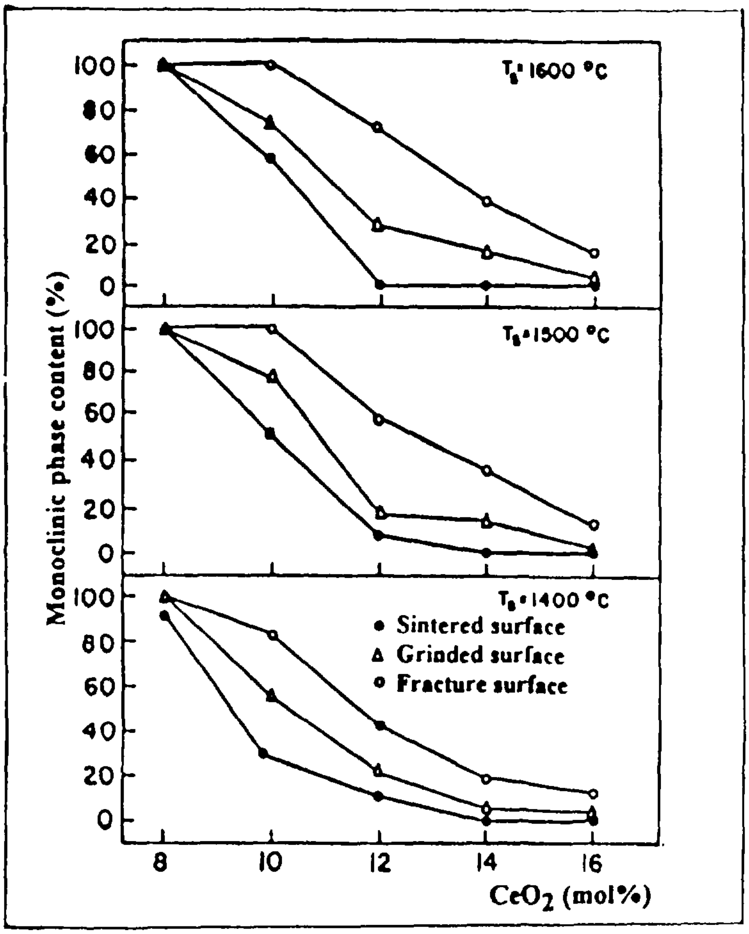

Fig.5 Dependence of stress-induced transformation on CeO_2 content and grain size.

The fraction of tetragonal-to-monoclinic stress-induced transformation that occurred during surface grinding and fracture is shown in Fig.5. These curve behaviours indicate that amount of monoclinic phase formed under applied stress depends strongly on CeO_2 content and grain size. These results suggest that amount of energy due to stress applied influences the amount of t→m transformation.

3.3. BENDING STRENGTH

The results shown in Fig.6 indicate that fracture strength was higher when the Ce-TZP contained about 12 to 14 mol% CeO_2 content and sintered at 1600°C. Tsukuma and Shimada [5] reported that fracture strength depends on grain size and when it was smaller than 1 μm the values of this parameters can be about 800 MPa. They obtained stress-strain curves from 3-point bending strength measurement that showed a serrated region which was due to significant plastic deformation prior to failure (in a non-linear stress-strain relashionship under a higher stress field). They suggested that this plastic deformation was due to decreasing CeO_2 content and increasing grain size.

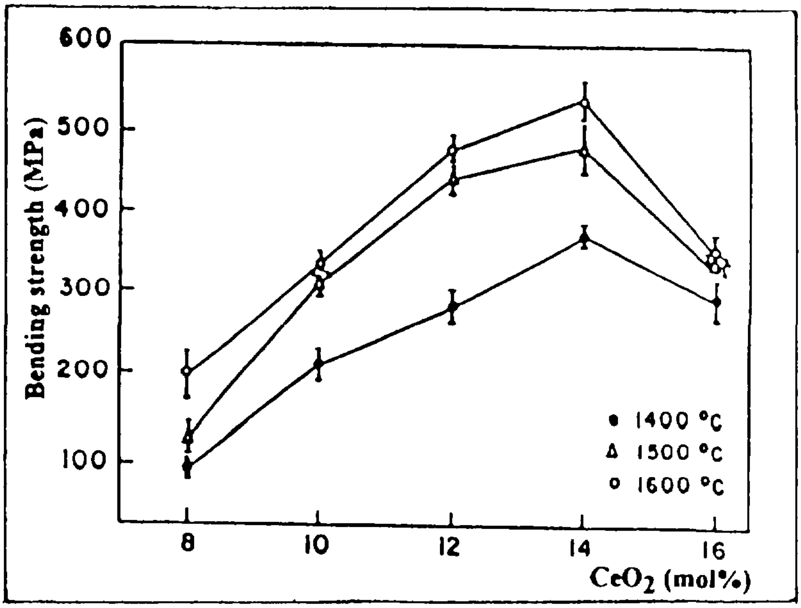

Fig.6 Bending strength of Ce-TZP ceramics containing different amount of CeO_2 content and sintered at several temperatures.

3.4. VICKERS HARDNESS

Vickers hardness of Ce-TZP ceramics decreased extensively with decreasing CeO_2 content and grain size (Fig.7). In Fig.8 is shown that Vickers hardness decreased linearly with the amount of monoclinic phase formed by stress-induced transformation.

Hannink and Swain [8] reported that the hardness decreased with an increasing of amount of stress-induced transformation due to the plastic deformation zone formed around the indent in Mg-PSZ. In this case, the result suggests that the plastic deformation, which is introduced by stress-induced transformation, is responsible for the decrease of hardness. However, on the surface of the zirconia ceramic exists a compressive stress due to the volume expansion that occur during t→m transformation.

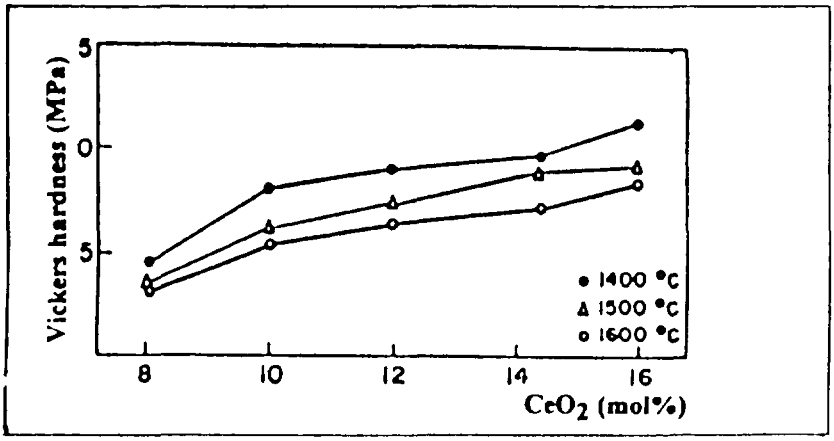

Fig.7 Relation between Vickers hardness, CeO_2 content and grain size.

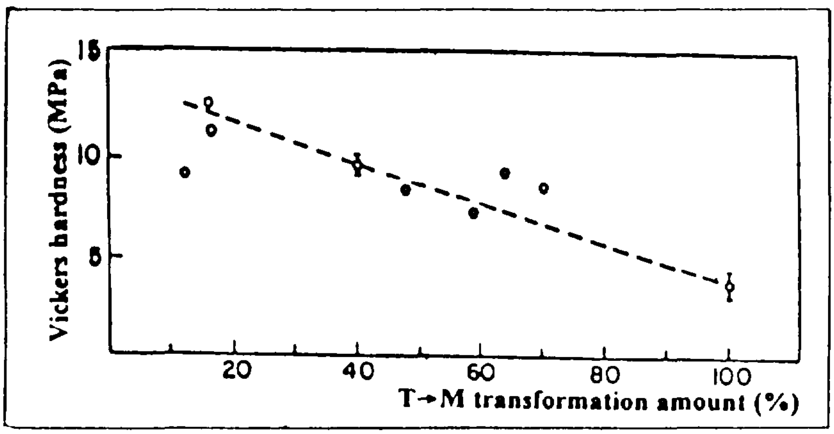

Fig.8 Dependence of Vickers hardness on the amount of monoclinic phase formed by stress-induced transformation.

3.5. FRACTURE TOUGHNESS (K_{IC})

The results of fracture toughness indicate that there is a composition range (about 10 to 12 mol% CeO_2 content) with the better K_{IC} values (about 16 to 17 MPa.m) (Fig. 9). The curve behaviours show the influence of grain size on fracture toughness data. Neverthless, these Ce-TZP ceramics were exhibited a maximum strength at the intermediate value of fracture toughness (Fig 10).

In previous studies [6] and [9] were suggested that the strength of transformation-toughned zirconia (such as Mg-PSZ, Y-TZP and Ce-TZP) is governed by two factors, i.e. flaw size and tranformation limited stress. The curve region when exist a proportional relation between strength and toughness the strength is limited by the flaw size, and the region of inverse relation the strength is limited by the critical stress required for iniciate the t→m transformation.

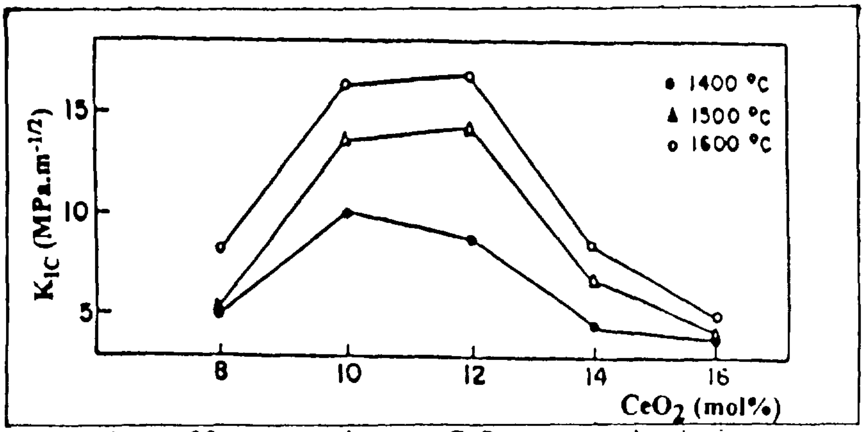

Fig.9 Dependence of fracture toughness on CeO_2 content and grain size

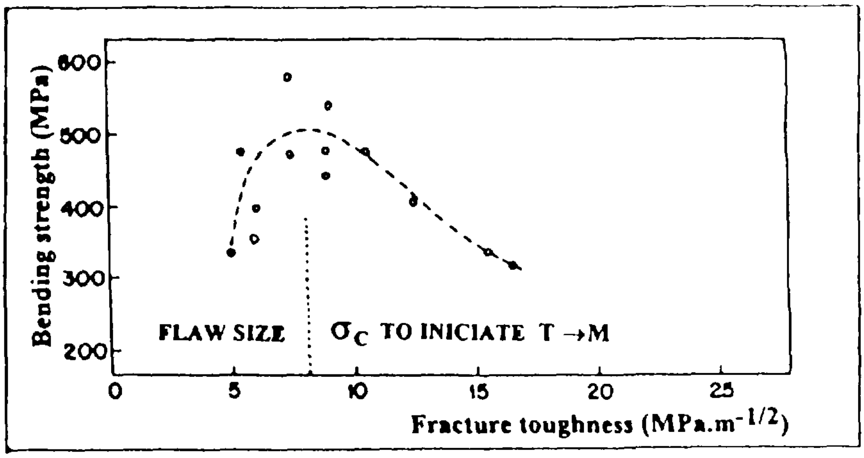

Fig.10 Relation between the fracture toughness and the bending strength for Ce-TZP ceramics.

3.6. STRUCTURAL DEFECTS

The powder characteristics (e.g. particle and agglomerate sizes) influenced strongly the microstructure voids (e.g. pores and cracks). The sintering temperature exerted an high influence the grain size too [1], [2].

These microstructural characteristics exert an essential influence on reability of mechanic parameters, as fracture strength, hardness and fracture toughness. Structural defects in polycrystalline ceramics have been identified and systematically eliminated by modifying and optimizing processing methods (powder preparation and densification processes, principally) [1], [10].

4. CONCLUSIONS

The present study revealed that the mechanical properties were strongly dependents on the amount of monoclinic phase formed by stress-induced transformation and structural defects.

Tetragonal monoclinic phase transformation in Ce-TZP ceramics was influenced by CeO_2 content and grain size. The bending strength, fracture toughness and Vickers hardness parameters were analysed on basis of the correlation with the amount of stress-induced transformation. The more adequate parameters obtained is shown in Tab. 1.

Tab 1 Mechanical parameters obtained in this study and from the literature [6] e [11].

CHARACTERISTICS AND PROPERTIES	TOSOH	TSUKUMA	NONO
Chemical composition (%)			
ZrO_2	88.0	88.0	88.0
CeO_2	12,0	12.0	12.0
Particle size (μm)	0.3	0.5	0.6
Density (g/cm^3)	6.2	6.2	5.9
Grain size (μm)	-	2.6	6.2
Bending strength (MPa)	500	800	490
Fracture toughness ($MPa.M^{-1/2}$)	20	10	17
Vickers hardness (MPa)	8.5	8.7	8.6

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