

Review on Strengthening and Toughening Approaches in Ceramic Materials

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Abstract: Structural ceramic materials have many advantages, such as high strength, high hardness and wear resistance. However, the disadvantage of high brittleness leads to the instability and inconsistency of the ceramic materials, which restricts its wide applications. In order to reduce the restrictions of brittleness and expand its application ranges, it is necessary to effectively improve the fracture toughness of ceramic materials. Several kinds of strengthening and toughening methods have been used to obtain ceramic materials with high reliability, which in turn extended the service fields and service life of ceramic materials. In this paper, the strengthening and toughening approaches of structural ceramic materials and their mechanisms are introduced, including phase transformation toughening, second-phase (particle, whisker and fiber) toughening, nano-phase toughening and the combination of aforementioned approaches. The research status and future development direction of strengthening and toughening technology are also discussed.

1. Introduction

Structural ceramic materials have excellent properties such as high temperature stability, high strength, high hardness, chemical corrosion resistance, wear resistance, low density and thermal expansion coefficient. Therefore, structural ceramic materials have played more and more important role in recent years in the fields of energy storage, automobile, aerospace, machinery, chemical industry and so on [1]. But at the same time, ceramic materials are usually brittle, which leads to the poor reliability and damage resistance. The brittle characteristic of ceramic materials restricts the wider application and industrialization of structural ceramics in engineering [2].

Ceramic materials are polycrystalline materials composed of grains, and the chemical bonds are mainly ionic and covalent bonds. The microstructure and chemical bond not only promise the high strength of ceramics, but also make them very sensitive to microcracks. Once the microcracks formed, the ceramic materials show little resistance to the occurrence and development of cracks. During the fracture process, ceramics do not have the plastic deformation ability like metals. Thus there is almost no other mechanism to absorb energy except to produce a new fracture surface, which is the essential reason for the brittleness of ceramics [3]. Therefore, the strengthening and toughening of ceramic materials has become an inevitable problem. After decades of development, researchers have found several ways to strengthen and toughen ceramics, including fiber toughening, whisker toughening, particle toughening, phase transformation toughening, nano-phase toughening, self-toughening ceramics and so on [4]. With the applications of these strengthening and toughening methods, the toughness of ceramic materials has been greatly improved, which promote the application of ceramic materials in more fields as structural materials, e.g. next generation of deep-sea equipment materials [5].

2. The strength of ceramic materials

2.1. Influence factors on strength

Material strength refers to the maximum stress value of a material when it is damaged under a certain load. Unlike metal materials, the brittle fracture of ceramic materials occurs immediately after elastic deformation stage, and no plastic deformation stage is shown. Therefore, only fracture strength σ_f appears in ceramics, no yield strength σ_s or ultimate strength σ_b exists. Moreover,

ceramics are sensitive to tensile stress. The tensile state makes cracks expand rapidly in ceramics, causing the failures of materials. The theoretical value of fracture strength differs greatly from the measured value, and the actual breaking strength of ceramic materials is only a few fractions of the original value [6]. Although ceramic materials should have high fracture strength in theory, the actual fracture strength is often lower than that of metals. The compressive strength of ceramics is much greater than that of tensile strength, and the difference is much greater than that of metals. Compared with metal materials, ceramic materials have almost no open slip system at room temperature. Meanwhile the slip and proliferation of dislocation are difficult to occur too. Thus, ceramics are easy to break under the stress concentration caused by surface or internal defects.

Factors affecting the strength of ceramic materials mainly include porosity, grain size, grain shape and the nature of grain boundary phase. Commonly speaking, the higher the porosity, the lower the strength of the ceramic is. The smaller the grain size, the higher the strength is. The presence of grain boundary glass phase is detrimental to the strength. For single phase polycrystalline ceramic materials, uniform isometric grains are not easy to cause stress concentration, so that the strength is fully developed. Generally, increasing the toughness of ceramics will affect the strength, because the stronger the bond between ceramic grains, the more difficult it is to cause crack deflection or fiber bridging. However, particles, whiskers or fibers are unfavorable for the strength, because these phases exist as defects in the ceramic, and release fracture energy through the crack deflection induced by the defects. Therefore, increasing the fracture toughness of ceramics is based on the premise that the strength meets the requirements of use.

2.2. Surface strengthening

As we all know, ceramics often need surface finishing to meet the application requirements of actual engineering products, which is due to its firing shrinkage and deformation caused by thermal stress and internal defects. However, the grinding process of abrasive and sample is often prone to machining damage, such as scratches, cracks, particle spalling, which in turn results in the decline of material strength. Experiments show that surface roughness, microstructure and surface residual stress had a comprehensive effect on the bending strength of Al_2O_3 ceramics, and the bending strength increased up to 528 MPa by decreasing the surface roughness and residual compressive stress of Al_2O_3 ceramics [7]. Besides the traditional grinding methods, surface defects of ceramics can be also eliminated by some technical methods recently emerged. For example, pulsed laser processing, as a non-contact processing technology with high material removal rate, has wide selectivity in preparation of complex ceramic structures compared with traditional machining technology. The surface of silicon nitride was treated by pulsed laser with different process parameters, and the surface morphology after ablation was observed, so as to illustrate the effect of pulsed laser on the surface of silicon nitride ceramic. It is found that the change of laser power has a significant effect on the surface quality of silicon nitride ceramics. The reduction of laser scanning speed also has a positive effect on the surface quality. The surface morphology will be improved with the reduction of laser scanning speed [8]. Figure 1 shows more surface treatment methods for silicon nitride ceramics [9].

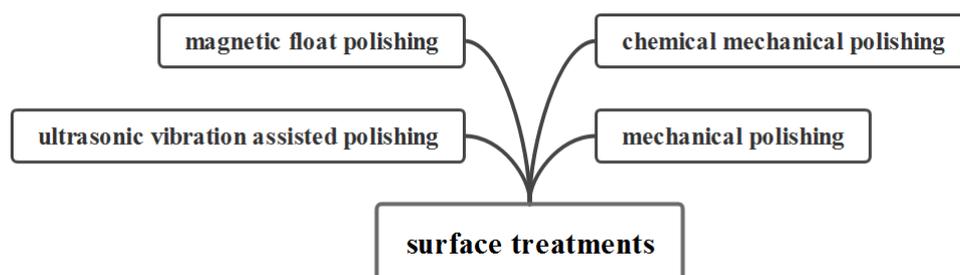


Figure 1 Different surface treatment methods for silicon nitride ceramics

3. Toughening approaches in ceramic materials

3.1. Second-phase materials toughening

By adding a second-phase material, such as particle, whisker and fiber, to the ceramic matrix, the energy to drive microcrack expansion is consumed. Moreover, the mismatch between the thermal expansion coefficient of the second-phase material and the matrix will induced stress within the ceramic matrix, which also can prevent crack expansion and improve the toughness. Other factors affecting the toughness of ceramic materials include microstructure, shape and size of internal defects, size and shape of sample itself, strain rate, environmental factors, stress state and so on. For example, when fibers are added into the ceramic matrix, the existence of high-strength fibers can not only share part of the external load, but also form a weak bonding interface between the fibers and the ceramic matrix. The failure of these weak interfaces can absorb a part of the external load and increase the fracture difficulty of the material, and the toughness of ceramic materials is improved. The toughening mechanisms of fibers in ceramic materials are mainly manifested in fiber pulling out, fiber bridging, crack deflection and microcrack generation [10]. For fiber toughening, a certain bonding force must be ensured between the interface of fiber and matrix, and the bonding force should not be too high. This is to ensure enough fiber pull-out length to form weak interface failure, so that the material will not be destructively deformed under the action of external load, which will lead to the failure of sample. The fibers can also form a bridging phenomenon between the fracture surfaces inside the ceramic material, which can prevent the crack from further spreading. Because of the existence of the second phases, cracks deflection and microcracks will occur in ceramic materials, which have toughening effect on ceramic materials.

3.2. Self-toughening

Self-toughening, also known as *in-situ* toughening, is an ideal ceramic toughening method. The rod-shaped grains similar to whiskers are produced in the sintering process of the material via controlling of sintering factors. Its mechanism mainly depends on the pull-out of *in-situ* reinforcement, bridging and crack deflection mechanism. The most typical *in-situ* toughened ceramic material is *in-situ* toughened Si_3N_4 ceramic. $\beta\text{-Si}_3\text{N}_4$ rod grains with certain size and aspect ratio could highly improves the strength and toughness of the material. $\beta\text{-Si}_3\text{N}_4$ rod grains can be obtained in the Si_3N_4 ceramics through the optimization of composition and process. Changing the sintering process parameters of ceramic materials or introducing sintering additives are effective means for the formation of $\beta\text{-Si}_3\text{N}_4$ rod grains, which can produce the toughening effect similar to whisker. For example, introducing of La_2O_3 can increase the aspect ratio of $\beta\text{-Si}_3\text{N}_4$ grains, and the Si_3N_4 ceramic with a flexural strength of 686 MPa and a fracture toughness of $7.42 \text{ MPa}\cdot\text{m}^{1/2}$ is obtained [11].

3.3. Phase transformation toughening

A classical phase transformation toughening is the phase change properties of ZrO_2 . Pure ZrO_2 has three crystalline forms: cubic (c- ZrO_2), tetragonal (t- ZrO_2) and monoclinic (m- ZrO_2), which are stable at high, medium and low temperatures, respectively. The transformation of ZrO_2 from t- ZrO_2 to m- ZrO_2 is a Martensitic phase transition, usually accompanying with 3%~5% volume increase. The transition temperature from t- ZrO_2 to m- ZrO_2 could be adjusted by adding additives such as CeO_2 or Y_2O_3 into the ZrO_2 ceramic matrix. Stress-induced phase change toughening means that t- ZrO_2 grains, which are in a sub-stable state within the ceramic matrix, will undergo a t-m phase transformation when external forces is applied (such as crack tip stress). The phase transformation causes volume expansion, which generates compressive stress on the expanding cracks and hinders the crack expansion. The phase transformation and volume expansion can also absorb or consume the energy of crack tip expansion, resulting in a significant increase in material strength and fracture toughness. The flexural strength and fracture toughness of partially stabilized zirconia ceramics could be more than 1500 MPa and $15 \text{ MPa}\cdot\text{m}^{1/2}$ [12]. However, the method is based on the characteristics of ZrO_2 , but many brittle ceramic materials do not have such characteristics. So the phase transformation toughening method can not be widely used.

3.4. Nano-phase toughening

Nanomaterials have small particle sizes and high surface energy. Experiments show that the materials processed to nanometer scale will show some special effects compared with the normal materials. Due to the large surface area, high surface energy and surface bonding energy of nano-particles, the nano-particles show high chemical activity which comes from the surface effect. By the addition of nanomaterials, the sintering temperature of ceramic materials can be effectively decreased, resulting in grain refinement and an increase in the number of grain boundaries, which also reduces the size of pores and defects in ceramics, resulting in a significant increase in the strength and toughness of nanoceramics. Part of the reasons is that it is an effective way to reduce the sintering temperature of ceramics through reducing the original size of the raw material particles. The particle size of the ceramic material is an important factor which affects the sintering temperature. The smaller the particle size, the more contact points between the stacked particles, and the shorter the transport distance of the material molecules, and then the entire sintering period and the sintering temperature could be reduced. The sintering of ceramic materials at a lower temperature is beneficial for the preparation of ceramic composites and the inhibition of grain growth. For example, Al₂O₃/ZrO₂ nanocomposite ceramics were obtained by combustion synthesis assisted rapid water cooling, and their nanoprecipitation mechanism and microstructure evolution were studied. The ceramic with 15 mol% Al₂O₃ contains high-density nano-particles and supra-nano-particles. The fracture toughness and the flexural strength of the ceramic can reach up to $12.63 \pm 0.36 \text{ MPa}\cdot\text{m}^{1/2}$ and $1026 \pm 59 \text{ MPa}$ [13].

Several mechanisms are considered to be effective after the introduction of nano-phase into the nanoceramic matrix. One theory is that it can make the matrix structure more uniform and finer, and the abnormal growth of the matrix grains can be suppressed. Another theory is that it leads to the densification between nano-particles and matrix particles, and the matrix particles encapsulate the nano-particles inside, forming a special structure, which can consume more crack expanding energy and improve the toughness of nanocomposite ceramics. And one theory is that the nano-particles introduced in the grain boundaries of the matrix can limit the grain boundary slip, also prevent the generation of pores and creep, thus improving the strength and toughness of nanocomposite ceramics.

4. Conclusion

The brittleness of ceramics is determined by the nature of covalent bond and ionic bond, but there are still many factors affecting the toughness of ceramics. In order to obtain the best toughening effect, we should solve the problems of material optimization design and process optimization design. The combination of several toughening mechanisms mentioned above are usually applied in ceramic materials, such as multi-phase particles synergistically toughening, particle-whisker synergistically toughening, phase transformation and whisker synergistically toughening. When these toughening methods are used synergistically, if the factors can be coordinated, it will show a synergistic effect and the fracture properties of ceramic materials will greatly improve. However, if the factors can not be well coordinated, the toughening effect may decrease. There are still many problems need to be solved in the research of strengthening and toughening of ceramic materials. Based on recent research progress, it can be found that there are two mainstream directions for the development of strengthening and toughening of ceramic materials. One direction is to reduce the grain size from micron level to nano level, and the other direction is to control the interface between the matrix phases and the reinforcement phases. Ceramic materials are the representative products of the advanced materials and manufacturing processes thereof. With the further development of toughening and strengthening approaches of ceramic materials, the application of ceramic materials will be more and more widely used in engineering fields.

References

- [1] Liu Kun, Ma Beiyue, Ren Xinming, et al. Research progress of ceramic materials prepared by hot-press sintering [J]. *Refractories & Lime*, 2021, 46(6):16-22.
- [2] Bao Yiwang, Sun Yi, Kuang Fenghua, et al. Development and prospects of high strength pre-stressed ceramics [J]. *Journal of Inorganic Materials*, 2020, 35(4):399-406.
- [3] Xu Xiqing, Liu Jiachen, Research progress and development trend of deformable amorphous ceramics [J]. *Advanced Ceramics*, 2020, 41(3):134-147.
- [4] Zhang Guotao, Li Guangwei, Yang Jingqi. Application of multiphase toughening technology in building ceramics [J]. *Shandong Ceramics*, 2019, 42(1):13-16.
- [5] Gong Wen, Wu Chaofeng, Zhao Zhiping, et al. Next-generation high-strength ceramic materials for deep-sea equipment and structural analysis [J]. *Digital Ocean & Underwater Warfare*, 2020, 3(4):281-287.
- [6] Cui Jinping, Zhao Wei, Rao Pinggen. Research progress of single-edge V-notch beam method for measuring fracture toughness of structural ceramics [J]. *Advanced Ceramics*, 2021, 42(3):139-156.
- [7] Liang Jingjing, Zhang Xiangzhao, Zhao Guanghui, et al. Effect of grinding process on surface quality and mechanical properties of Al_2O_3 ceramics [J], *Materials Reports*, 2020, 34(8):16020-16024.
- [8] Chen Yongbiao, Yuchi Guangzhi, Li Si, et al. Effect of pulsed laser on surface morphology of silicon nitride ceramics [J]. *Journal of Hunan Institute of Science and Technology(Natural Sciences)*, 2021, 34(2):10-14.
- [9] Xiao Xiaolan, Yan Qiusheng, Lin Huatai, et al. Research progress of silicon nitride ceramic ball grinding and polishing technology[J]. *Journal of Guangdong University of Technology*, 2018, 35(4):18-23.
- [10] Wang Zhangwen, Zhang Jun, Fang Guodong, et al. Effect of interfacial layer on mechanical properties of fiber toughened ceramic matrix composites [J]. *Equipment Environmental Engineering*, 2020, 17(1):77-89.
- [11] Dou Gaoya. Study on preparation and properties of self-toughened silicon nitride ceramics [J]. *Ceramics*, 2019(09):53-62.
- [12] Zhang Wen, Xiang Yang, Peng Zhihang, et al. Research progress of continuous fiber reinforced ZrO_2 ceramic matrix composites [J]. *Advanced Ceramics*, 2021, 42(3):170-180.
- [13] Yongdong Yu, Fengyu Lin, Yongting Zheng, et al. High-density nanoprecipitation mechanism and microstructure evolution of high-performance Al_2O_3/ZrO_2 nanocomposite ceramics [J]. *Journal of the European Ceramic Society*, 2021, 41(10):5269-5279.