MERIT domestic internship report

Graduate school of engineering
Department of materials science and engineering
Ikuhara laboratory, D3, Merit 7th
Hiroaki Nakade

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Tosoh corporation

Overview

The content of this internship is divided into 3 sections: 1. Discussion on analytical calculation of transformation toughening mechanism of tetragonal zirconia, 2. Systematic survey of previous reports on transformation toughening of tetragonal zirconia, 3. Patent survey. The outline of each section is described below. Due to the COVID-19 situation these days, the survey and research were conducted by myself and the results were discussed online with Tosoh researchers.

1. Ceramic materials generally exhibit high toughness and chemical stability. On the other hand, they tend to have low fracture toughness. When the microcrack is induced in the bulk, it easily fractures because of the singular stress field is emerged around the crack tip. However, tetragonal zirconia shows excellent fracture toughness by transformation toughening mechanism, which is explained as below. Phase transformation from the tetragonal to the monoclinic phase in zirconia is martensitic transformation accompanied volume expansion. This transformation is induced by the stress field around the tip. As a result, compressive force is applied to the crack and prevent from crack propagation. A quantitative toughening effect of transformation around the crack tip is studied by continuous linear-elastic model. In this internship, I studied this model and compared with my experimental results. To quantitatively evaluate the toughening effect, mainly three assumptions must be applied. First, the specimen is regarded as isotropic, continuous, and linear-elastic model. Second, the shape of the transformation zone perfectly follows stress distribution around the crack tip. Third, the volume expansion by transformation is isotropic without any shear deformation. Under these conditions, the degree of toughening ΔK_C by transformation around the crack tip is calculated to be

$\Delta K_C = 0$, which means that no toughening effect is obtained. Then, further crack propagation in transformed zone is taken into consideration. When the crack propagates into transformation zone, ΔK_C exhibits positive value as a function of $\Delta a/w$, where Δa is a crack length in transformation zone and w is a width of the transformation zone. To compare this analysis and experimental results, I measured ΔK_C by performing in-situ TEM mechanical test on tetragonal yttria stabilized zirconia thin film. As a result, the ΔK_C exhibited the higher value when transformation was taken place, while comparable value was obtained in other measuring time. Therefore, transformation toughening is suggested to be not only originated from static mechanism stated above, but also from dynamic transformation process.

2. In 1975, Garvie et al. revealed that the zirconia which contains the tetragonal phase exhibit high fracture toughness because of the tetragonal-monoclinic martensitic phase transformation[1]. In this internship, I systematically surveyed previous studies on tetragonal zirconia so far. In terms of microscopic observation, Hayakawa et al. (1989) conducted detailed transmission electron microscopy (TEM) observation[2]. Deville et al. (2002) used atomic force microscopy (AFM) to analyze crystallographic aspects of tetragonal-monoclinic phase transformation[3]. Further improvement in microscopy have made it possible to observe samples at the atomic level, as in Kasatkin et al. (2004)[4] and Wu et al. (2011)[5]. Despite these reports, the interface between the tetragonal and the monoclinic phase has not been clearly observed, and its atomistic structure is still unknown so far. For the mechanical properties, Eichler et al. (2006) controlled the grain sizes and measured fracture toughness to elucidate the relationship between fracture toughness and microstructure[6]. Chevalier et al. (1999) investigated the phenomenon of the degradation of the tetragonal zirconia under high temperature and high humidity atmosphere[7]. Next, I will introduce some theoretical studies. Several analytic studies using linear-elastic models were published around 1980, motivated from rapid development of fracture mechanics since the 1950s. Among those reports, the most influential one is considered to be the work done by McMeeking et al. (1982)[8]. From the viewpoint of crystallographic theory, Kelly et al. (2002) published important results including the prediction of habit plane and lattice correspondence[9]. Recently, with improvement of computer performance, a lot of efforts have been devoted to computational calculations, such as molecular dynamics simulation conducted by Zhang et al. (2016) revealed that the dynamic behavior of the transformation at the atomic level[10]. Phase field modeling was also used to discuss the dynamic behavior of phase transformation. Mamivand et al. (2014) reported the transformation behavior around the crack in the single crystal[11], and Moshkelgosha et al. (2021) reported the transformation behavior with polycrystal[12].

3. I conducted patent survey with the help from the Tosoh researcher. Here, we conducted a patent search in the setting of "developing cubic yttria stabilized zirconia with high ionic conductivity for application as a solid electrolyte". The search was conducted using J-PlatPat, a patent information platform administered by the Japan Patent Office, and the search formula was "'Title: ジルコニア(Zirconia) or ZrO2' & 'Description: 固体電解質(Solid electrolyte)' & 'Description: イオン伝導性(Ionic conductivity)' & 'Description: 部分安定化(Partially stabilized) or 立方晶(cubic)' & 'Description: イットリア(Yttria) or Y2O3'. There were 41 search results, which were classified from the following three perspectives. First of all, we classified the results into those containing yttria as a stabilizer and those without yttria, because those containing yttria as a stabilizer would be competitor in the setting of this study. The number of the former was 16 and the number of the latter was 25. Next, the classification was conducted based on the type of patent. There were 19 substance patents, 19 manufacturing patents, and 3 application patents. The patent status was also categorized: 8 patents had been granted, 4 had expired, 10 had been rejected, 9 had not yet been examined, 1 had been withdrawn, and 9 had been cancelled. In the end, the number of substance patents that contained yttria and were still in force was eight. The above search results were summarized and submitted to the Tosoh.

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Reference

[1] R.C. Garvie, R.H. Hannink, and R.T. Pascoe, Nature **258**, 703 (1975).

[2] M. Hayakawa, N. Kuntani, and M. Oka, Acta Metall. **37**, 2223 (1989).

[3] S. Deville and J. Chevalier, J. Am. Ceram. Soc. **86**, 2225 (2003).

[4] I. Kasatkin, F. Girgsdies, T. Ressler, R.A. Caruso, J.H. Schattka, J. Urban, and K. Weiss, J. Mater. Sci. **39**, 2151 (2004).

[5] Y.-C. Wu and Y.-T. Chiang, J. Am. Ceram. Soc. **94**, 2200 (2011).

[6] J. Eichler, M. Hoffman, U. Eisele, and J. Rödel, J. Eur. Ceram. Soc. **26**, 3575 (2006).

[7] J. Chevalier, C. Olagnon, and G. Fantozzi, J. Am. Ceram. Soc. **82**, 3129 (1999).

[8] R.M. McMeeking and A.G. Evans, J. Am. Ceram. Soc. **65**, 242 (1982).
[9] P.M. Kelly and L.R. Francis Rose, Prog. Mater. Sci. **47**, 463 (2002).
[10] N. Zhang and M. Asle Zaeem, Acta Mater. **120**, 337 (2016).
[11] M. Mamivand, M. Asle Zaeem, and H. El Kadiri, Acta Mater. **64**, 208 (2014).
[12] E. Moshkelgosha and M. Mamivand, Eng. Fract. Mech. **241**, 107403 (2021).