氏　　　　　名	皮（ぴー）　在（じぇ）　煥（ふぁん）
学 位 の 種 類	博士（工学）
学 位 記 番 号	甲第１５５号
学位授与年月日	平成１６年　３月２５日
学位授与の要件	学位規則第４条第１項該当
学 位 論 文 題 目	Isothermal and Athermal Martensitic Transformations in Yttria Doped Zirconia （イットリア添加ジルコニアにおける等温および非等温マルテンサイト変態）
学位論文審査委員	（主査）　早 川 元 造 （副査）　北岡征一郎　　音 田 哲 彦

学 位 論 文 の 内 容 の 要 旨

Zirconia and zirconia doped with a small amount of stabilizer, such as yttria and rare-earth oxides, are well known to exhibit martensitic transformation. The martensitic transformation plays an important role in both the toughening of zirconia based ceramics and the degradation of the same materials during aging. Nevertheless, the detail of the transformation mechanism is not well understood.

For zirconia doped with a small amount of yttria (<1.75 mol%), the metastable tetragonal phase can be obtained by rapid cooling to room temperature. The quenched metastable tetragonal phase readily transforms into the stable monoclinic phase by heating at around 500K (as expected from the isothermal nature of the transformation) and also undergoes a burst type martensitic transformation during subzero cooling to the liquid nitrogen temperature. The occurrence of both isothermal and athermal transformations in the sample of the same chemical composition is very rare and no other system is known to transform at so much different temperatures as in the present case. Thus the present work was initiated to investigate the characteristics of both types of transformation in yttria doped zirconia.

In Chapter 1, the basis of the present study is described. To deepen the comprehension of the phase transformations of zirconia alloys, crystal structure of zirconia, characteristics of martensitic phase transformation and transformation modes in zirconia-yttria alloys are briefly overviewed. And the objective of the present work is stated.

In Chapter 2, quantitative studies of the kinetics of the isothermal and athermal transformations of zirconia doped with a small amount of yttria are described. The amount of yttria and the grain size were found to give significant influence on the location of the C-curve, namely the stability against the transformation. The effect of aging during the incubation period was found to be cumulative. It was interpreted as suggesting the occurrence of the microstructural change during the pre-aging. However, it was pointed out that a caution was necessary to properly interpret the observation because of the limited sensitivity of the measurement of the transformation.

Metastable tetragonal phase of zirconia doped with 1.40~1.60mol% of yttria was also found to exhibit a burst type martensitic transformation at subzero temperatures. The transformation essentially occurred by a single large burst. The burst temperature was strongly dependent on the yttria content and grain size. The pre-aging within the incubation time was not effective for the athermal transformation behavior, suggesting the microstructural change during pre-aging does not affect the athermal transformation. There was a relatively large temperature gap between the isothermal and athermal transformations as described in Chapter 2. This suggested a possibility of the presence of a microstructural difference between the products. Thus, a further study on the microstructure of the individual product unit and crystallographic feature was motivated.

In Chapter 3, the morphology and growth rate of the isothermally and athermally formed individual product units were studied on the optical microscopic level. The habit planes of both products were also identified. Although the grain size of polycrystalline specimens prepared by the usual sintering condition is normally submicron size and too small for optical microscopic analysis, coarse grains of a single phase can be obtained by annealing at a high temperature. A full retention of the tetragonal phase with coarse grains was possible with the specimens ZrO_2-1.9mol% Y_2O_3. In these coarse grains, $\{101\}_t$ annealing twins are frequently observed, although they don not exist in the usual fine grained specimens. In these coarse grains, well-defined thin plate and lenticular martensite were observed to nucleate at a grain boundary and isothermally grow into a grain. The growth rate in their longitudinal direction was found quite slow and temperature dependent. Two-surface trace analyses identified the habit plates near $\{013\}_c$ in agreement with previously reported results obtained for an arc-melted specimens by TEM studies.

On the other hand, when a coarse grain specimen underwent a burst type transformation, it shivered on the cooling stage. Lens and pyramid shape martensite units appeared simultaneously and instantly. Habit planes of both products were formed to be different even in the same grain.

In Chapter 4, the characteristics of the products from the isothermal and athermal transformations were compared in detail. The reverse transformation temperature of athermal transformation was found about 20K lower than the isothermal transformation. The behavior of weight increase at around 600K during heating in the air appeared to make a variation in the individual products, indicating athermally transformed samples should absorb more oxygen than isothermally transformed ones. However, The difference in the lattice parameters was too small to be detected, suggesting the oxygen content does not influence the lattice parameter so much. Furthermore, Rietveld analysis revealed that the isothermal and athermal products were found to be essentially the same structure. From these observations, it was concluded that both isothermal and athermal transformations are indeed martensitic transformations.

Finally, in Chapter 5, experimental results and discussions given in the previous chapters are summarized.

論 文 審 査 の 結 果 の 要 旨

ジルコニアのマルテンサイト変態は、ジルコニア系セラミックスの靱化機構を担う現象であるとともに、低温時効による劣化の原因ともなるので工業的に重要な現象である。また、セラミックスのマルテンサイト変態という希有な現象であるとともに、近年発見された「等温変態と非等温変態の二面性」のため変態機構の解明に役立つ系であることが期待され、興味深い研究課題となっている。

本研究では、この二面性に注目し、等温変態と非等温変態の共通点や相違点を明確にすること及び両者の本質を明らかにすることを目的としている。

まず、等温変態の速度論的研究においては微小球状試料を用いた高感度な変態量測定より、時間－温度－変態線図において明確なＣ曲線を描くことを明らかにし、これに対するイットリア添加量や結晶粒径の影響を明らかにしている。また、予時効が変態開始時間に及ぼす効果の測定より、変態開始前の潜伏期においても変態のエンブリオが成長しつつあることを明らかにしている。非等温型についても変態温度の組成依存性や結晶粒径依存性を定量的に求めている。

つぎに、等温および非等温型マルテンサイトについて光学顕微鏡および電子顕微鏡レベルでの詳細な組織観察を実施し、等温型については板状マルテンサイト、非等温型についてはレンズ状とピラミッド型の二種類のマルテンサイト形態が存在することを明らかにした。等温マルテンサイトに関してはその場観察より個々のマルテンサイト板の成長速度を測定し、板状およびレンズ状マルテンサイトについて現象論的解析に必要な晶癖面の測定にも成功している。

さらに、従来からジルコニアの等温変態生成物はベイナイト的であり、マルテンサイトとは異なるという説も提唱されているが、本研究ではＸ線回折法による詳細な構造解析や熱分析法による逆変態温度の比較より､等温変態生成物は本質的に非等温 マルテンサイトと同一の相であることを明らかにしている。

これら一連の成果は、ジルコニア系セラミックスのマルテンサイト変態の解明に大きく貢献するものであり、本論文は博士（工学）の学位論文に値するものと認める。