

Article

Phase Transformation Behavior, Mechanical Properties Under Thermal Stress, and Slag-Induced Erosion of 2–4 mol% CeO₂-Doped CaO-Stabilized Zirconia

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Abstract: We investigated the phase transitions, mechanical properties, and chemical durability of a composition of 9 mol% CaO-stabilized zirconia (9CSZ) doped with 2–4 mol% CeO₂ under thermal stress against molten slag. The monoclinic phase fraction of 9CSZ was 7.14% at room temperature, and CSZ doped with 2–4 mol% CeO₂ showed a slightly lower value of 5.55–3.72%, with only a minor difference between them. The microstructure of 9CSZ doped with 2–3 mol% CeO₂ was similar to that of undoped 9CSZ, whereas the microstructure of 9CSZ doped with 4 mol% CeO₂ exhibited noticeable grain refinement. The mechanical properties of CSZ at room temperature tended to improve as the CeO₂ doping concentration increased. The Vickers hardness increased from 1088.4 HV to 1497.6 HV when the CeO₂ doping amount was 4 mol%, and the specific wear amount decreased from 1.5941 to 1.1320 × 10⁵ mm³/Nm. This tendency remained similar even after applying thermal stress. The monoclinic phase fraction of 9CSZ increased from 7.14% to 67.71% after the erosion experiment with the CaF₂-based slag. CeO₂-doped CSZ had a lower monoclinic phase fraction than CSZ after the erosion experiment, but as CeO₂ content increased from 2 to 4 mol%, the fraction rose to 4.07%, 30.85%, and 77.11%.

Keywords: partially stabilized zirconia; phase stabilization; phase transition; slag-induced erosion; mechanical properties; erosion resistance



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1. Introduction

Zirconia (ZrO₂) has been widely studied due to its excellent mechanical, thermal, and chemical properties, even under extremely harsh conditions. Notably, zirconia exhibits high toughness on par with metals, despite being a ceramic material, which makes it an ideal candidate for a wide range of material development applications, both structural and functional [1–4]. Molten slag in steelmaking processes is a highly basic and alkaline substance that causes significant chemical erosion of refractory materials. Therefore, zirconia (ZrO₂), with high mechanical properties and chemical durability under extreme conditions, is used as the refractory material in areas that come into contact with molten slag. Zirconia can exhibit significant changes in crystal structure and mechanical properties depending on the

temperature. The monoclinic phase is stable below 1170 °C, the tetragonal phase is stable between 1170 °C and 2370 °C, and the cubic phase is stable above 2370 °C. The transition from the tetragonal to the monoclinic phase involves volume expansion, which causes cracks and grain boundary fractures, leading to a rapid decrease in strength [5–7]. Therefore, various research projects have been conducted to improve the mechanical and thermal properties of zirconia used in high-temperature environments by using compounds such as Y_2O_3 , MgO , Al_2O_3 , Bi_2O_3 , and CaO as phase stabilizers [8,9]. Doping with these stabilizers reduces the transformation of the tetragonal phase, resulting in a structure with lower residual stress within the lattice [10,11]. The type and concentration of stabilizers determine whether zirconia becomes partially stabilized zirconia (PSZ) or fully stabilized zirconia (FSZ) at high temperatures. PSZ and FSZ absorb the stress generated when cracks occur by transforming into the monoclinic phase, which enhances mechanical properties. Therefore, the type and amount of stabilizers affect the phase stabilization of zirconia [12–14]. CaO -doped zirconia exhibits superior mechanical properties under high-temperature conditions, such as higher hardness and better high-temperature oxidation resistance, compared to zirconia doped with other stabilizers. Due to these properties and relatively low cost, CaO -doped zirconia is primarily used in structural ceramics like refractories [15–17]. CaO -PSZ demonstrates outstanding mechanical and thermal properties, but prolonged use at temperatures exceeding 1500 °C can cause destabilization due to the instability of Ca . Therefore, research is necessary to prevent the destabilization of CaO -PSZ and to improve its mechanical and thermal properties at high temperatures.

Previous research confirmed the trend in the mechanical properties of CaO -PSZ with an increase in CaO doping from 5 to 10 mol%, identifying that 9 mol% CSZ exhibited the most superior mechanical properties [18]. K.H. Heussner demonstrated that doping ZrO_2 with CeO_2 in nitrogen or oxygen atmospheres can enhance its mechanical strength [19]. Y. Nigara confirmed that doping CSZ with CeO_2 improves oxygen permeability [20]. However, studies have not yet explored the changes in mechanical and chemical properties resulting from the additional doping of CeO_2 in zirconia that has been enhanced through CaO doping.

To further improve the properties and chemical stability of CSZ, we doped 9 mol% CSZ with CeO_2 , which is chemically more stable than CaO and can substitute larger Ce^{4+} ions (97 pm) for Zr^{4+} ions (84 pm) in the lattice, investigating the resulting changes in properties and chemical stability against molten slag.

2. Materials and Methods

The 9 mol% CSZ was synthesized using ZrO_2 (99%, Daejung Chemicals & Metals Co., Siheung-si, Republic of Korea) and CaO (98%, Junsei Chemical Co., Tokyo, Japan) as starting materials through a solid-state method. The synthesized 9CSZ was then doped with CeO_2 (99.9%, Junsei Chemical Co., Tokyo, Japan) according to the ratios specified in Table 1. The mixture was ball-milled with zirconia balls and ethanol for 24 h, dried at 90 °C for 24 h, and then calcined at 1200 °C with a heating rate of 5 °C per minute for 2 h.

Table 1. The composition of the 9CSZ specimens with different amounts of CeO_2 .

Compound	Composition	
	9CSZ	CeO_2 (mol%)
9CSZ	Balance	0
9CSZ_2 CeO_2		2
9CSZ_3 CeO_2		3
9CSZ_4 CeO_2		4

The test specimens were prepared by uniaxially pressing the synthesized powder at a pressure of 1 ton/cm³ to form cylindrical (20 mm diameter) and rod-shaped (5 mm width, 35 mm length) bodies. These formed bodies were then sintered in a box-type furnace, with a heating rate of 5 °C per minute, at 1600 °C for 6 h, followed by furnace cooling. The thermal shock test for the specimens involved heating the sintered samples in an air atmosphere to 1300 °C at a rate of 5 °C per minute, holding them at that temperature for 5 min, and then allowing them to cool naturally to 900 °C. This cycle was repeated 40 times to apply thermal shock.

Erosion tests were performed to evaluate the chemical stability of each specimen in the slag. Five grams of CSZ powder was pressed into pellets using a cylindrical mold with a diameter of 15 mm under a pressure of 1 ton/m². The formed CSZ specimens were placed in a graphite crucible, and 500 g of slag, as specified in Table 2, was added. The crucible was then maintained at 1550 °C for 3 h and subsequently cooled in the furnace. Since the slag dissolves in Al₂O₃, SiO₂, and MgO, a graphite crucible, which does not react with the slag, was used for the reactivity test. After cooling was completed following the melting process, the crucible was broken to retrieve the CSZ specimens from within the slag. The inner parts of the specimens, which were free from slag contamination, were then crushed and subjected to XRD analysis.

Table 2. Chemical composition of slag powder.

Slag Powder	SiO ₂	CaO	Na ₂ O	MgO	Al ₂ O ₃	F	C
Composition (wt%)	33.30	31.60	11.10	1.44	2.38	9.10	11.08

To evaluate the chemical stability of each specimen, we conducted reactivity tests with slag. The pellet-shaped specimens were placed in a graphite crucible, and the slag specified in Table 2 was added. The samples were then maintained at 1550 °C for 3 h, followed by furnace cooling. Since the slag has solubility in Al₂O₃, SiO₂, and MgO, a graphite crucible, which does not react with the slag, was used for the reactivity tests.

A crystal structure analysis was performed using X-ray diffraction (XRD, Rigaku, Ultima-IV, Japan) with measurements taken from 20° to 80° at a step size of 0.02°/2θ and a scanning speed of 2°/min. The XRD peaks and phase fractions were analyzed using the Rietveld refinement method with Highscore Plus software (version 3.0c) with a reference pattern for monoclinic ZrO₂ (m-ZrO₂, ICSD 98-006-0900) and tetragonal ZrO₂ (t-ZrO₂, ICSD 98-007-0014). And the monoclinic phase fraction was double-checked for integrated intensity by using ISO 5803 [21].

$$X = \frac{I(\bar{1}11)_m + I(111)_m}{I(\bar{1}11)_m + I(111)_m + I(101)_t} \quad (1)$$

$$X = \frac{I(\bar{1}11)_m + I(111)_m}{I(\bar{1}11)_m + I(111)_m + I_{ttc}} \quad (2)$$

Equation (1) is for a two-phase system (monoclinic and tetragonal phases), and Equation (2) is for a multi-phase system (a mixture of monoclinic, tetragonal, and cubic). X is the integrated intensity ratio, where $I(\bar{1}11)_m$ and $I(111)_m$ refer to the integral intensity of the monoclinic X-ray diffraction pattern. $I(101)_t$ refers to the integral intensity from the (101) plane of the tetragonal and I_{ttc} is the total integrated intensity of the tetrago-

nal phase (101) and cubic phase (111) reflections. The volume fraction of the monoclinic phase was calculated using Equation (3):

$$f_m = \frac{PX}{1 + (P - 1)X} \quad (3)$$

f_m is the volume fraction of the monoclinic phase and P is the intensity factor. In the monoclinic-tetragonal ZrO_2 system, $P = 1.219$ was used, while in the multiphase system, $P = 1.265$ was used.

We used a high-resolution scanning electron microscope (HR-SEM, SU8230, Hitachi, Tokyo, Japan) to observe the microstructural changes on the specimen surfaces. The mechanical properties were assessed using a micro Vickers hardness tester (Wilson, VH1102, Lake Bluff, IL, USA) under test conditions of 20 N load and a dwell time of 15 s. Each measurement was repeated 10 times, and the Vickers hardness was calculated using the average value. Wear resistance was measured by determining the specific wear rate (m^3/N) under the conditions of a sliding distance of 1000 m, a load of 9.6 N, a velocity of 0.1 m/s, and an operating type of ball-on-disk. The measurements were conducted in accordance with the ISO 20808 testing method [22]. The flexural strength of each specimen was measured using a universal testing machine from the United States, with a lower support-point distance of 20 mm and a crosshead speed of 0.5 mm/min in a three-point bending test.

3. Results and Discussion

The results of the phase analysis after doping CeO_2 at 2–4 mol% into 9 mol% CSZ are shown in Figure 1. The monoclinic fraction (V_m) of zirconia was 7.14% for 9CSZ, while under doping conditions of 2–4 mol% CeO_2 , it decreased slightly to 5.55% and 3.72%, respectively, compared to CSZ, without showing any abrupt change. CeO_2 doping has a lesser effect on improving phase stability at room temperature because the Ce^{4+} ion has the same charge state as the Zr^{4+} ion, resulting in no formation of oxygen vacancies due to charge compensation. Phase stabilization is induced by lattice stress caused by the ionic radius difference between Zr^{4+} (84 pm) and Ce^{4+} (97 pm). The doping of Ce^{4+} , which has a larger ionic radius than Zr^{4+} , leads to lattice contraction, which is observed as a low-angle shift in the XRD pattern. In particular, the peak splitting between 30° and 30.5° observed in 4 mol% CeO_2 -doped CSZ suggests the formation of a cubic phase.

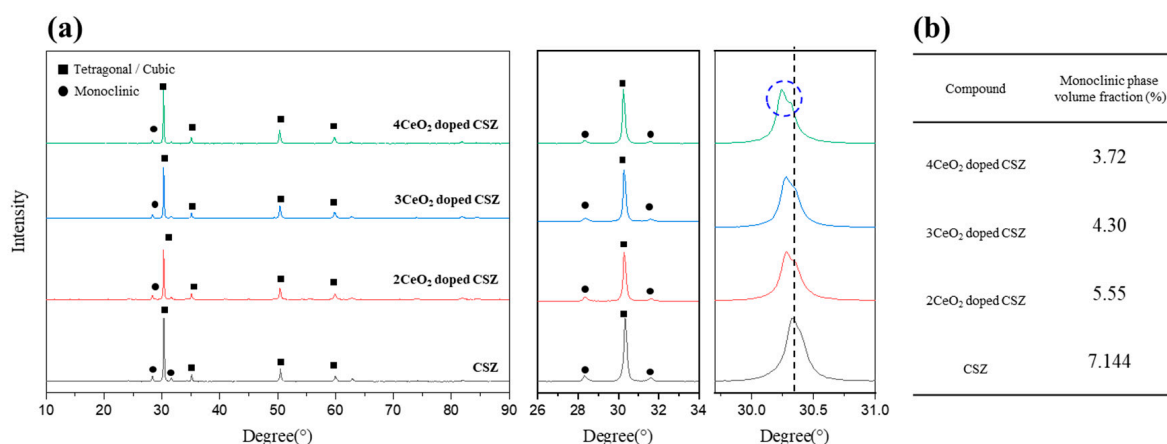


Figure 1. (a) XRD diffraction patterns of CeO_2 -doped 9CSZ powder calcinated at 1600°C (●: monoclinic phase, ■: tetragonal or cubic phase), (b) Phase fraction determined through Rietveld refinement.

Figure 2 shows the Ce 3d XPS spectrum of CeO₂-doped CSZ after wet ball milling and calcination at 1200 °C in an air atmosphere for 2 h. The sub-bands denoted as u' and v' in the XPS spectrum corresponded to the initial electron state of 3d₁₀4f₁ of Ce³⁺, while u, u'', u''', v, v'', and v''' represented the 3d₁₀4f₀ state of Ce⁴⁺ [23]. It is evident that Ce predominantly existed in the form of Ce⁴⁺ within the zirconia lattice, and with increasing CeO₂ doping, the proportion of Ce⁴⁺ increased from 73.98% in 1Ce_CSZ to 79.57% in 4Ce_CSZ. This trend indicates that local lattice tension increased with increased CeO₂ doping due to the ionic radius differences among Ce³⁺ (114 Å), Ce⁴⁺ (97 Å), and Zr⁴⁺ (86 Å). The proportion of Ce³⁺ decreased to alleviate local lattice tension induced by the difference in ionic size [24]. The stabilizing effect of CeO₂ doping is primarily due to lattice stress caused by the ionic radius difference between Zr⁴⁺ and Ce⁴⁺, not due to oxygen vacancy formation by charge compensation of Ce³⁺ [25]. CeO₂ doping leads to an increase in the tetragonal phase, which can lead to improving mechanical properties by transformation toughening under external mechanical stress [26,27].

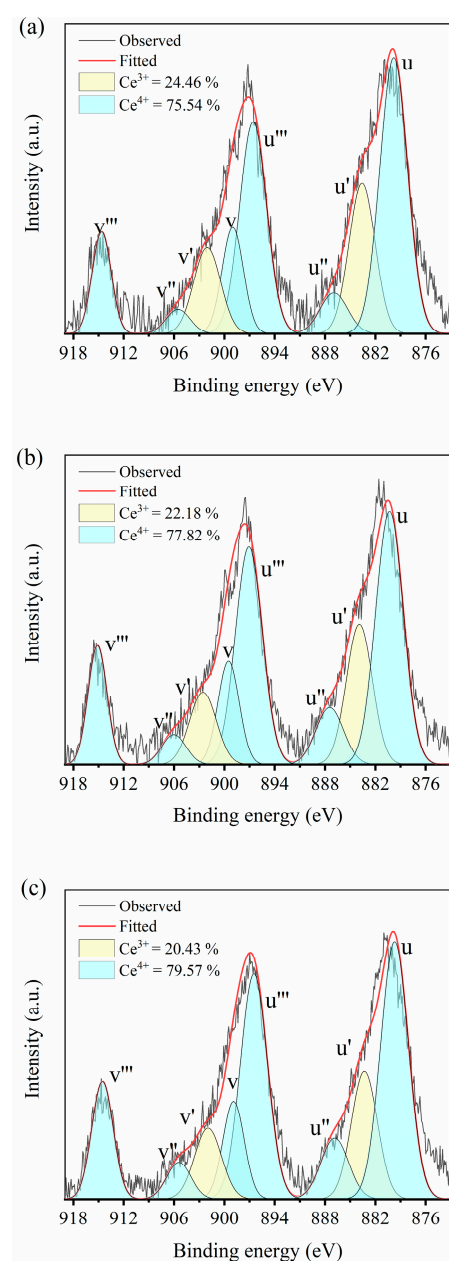


Figure 2. Ce 3d XPS spectrum and deconvoluted curves for Ce³⁺ and Ce⁴⁺ after background subtraction of (a) 2Ce_CSZ, (b) 3Ce_CSZ, and (c) 4Ce_CSZ.

Figure 3 shows the microstructures of each specimen. The grain size of 9CSZ doped with 2–3 mol% CeO_2 was comparable to that of 9CSZ, exhibiting a mixture of large grains ranging from 11.9 to 18 μm and small grains below 6 μm . In contrast, 9CSZ doped with 4 mol% CeO_2 showed only small grains below 5.8 μm . The changes in the microstructural distribution in 4 mol% CeO_2 -doped CSZ are thought to occur because the increased amount of CeO_2 doping, which does not sinter well, prevents grain growth during heat treatment.

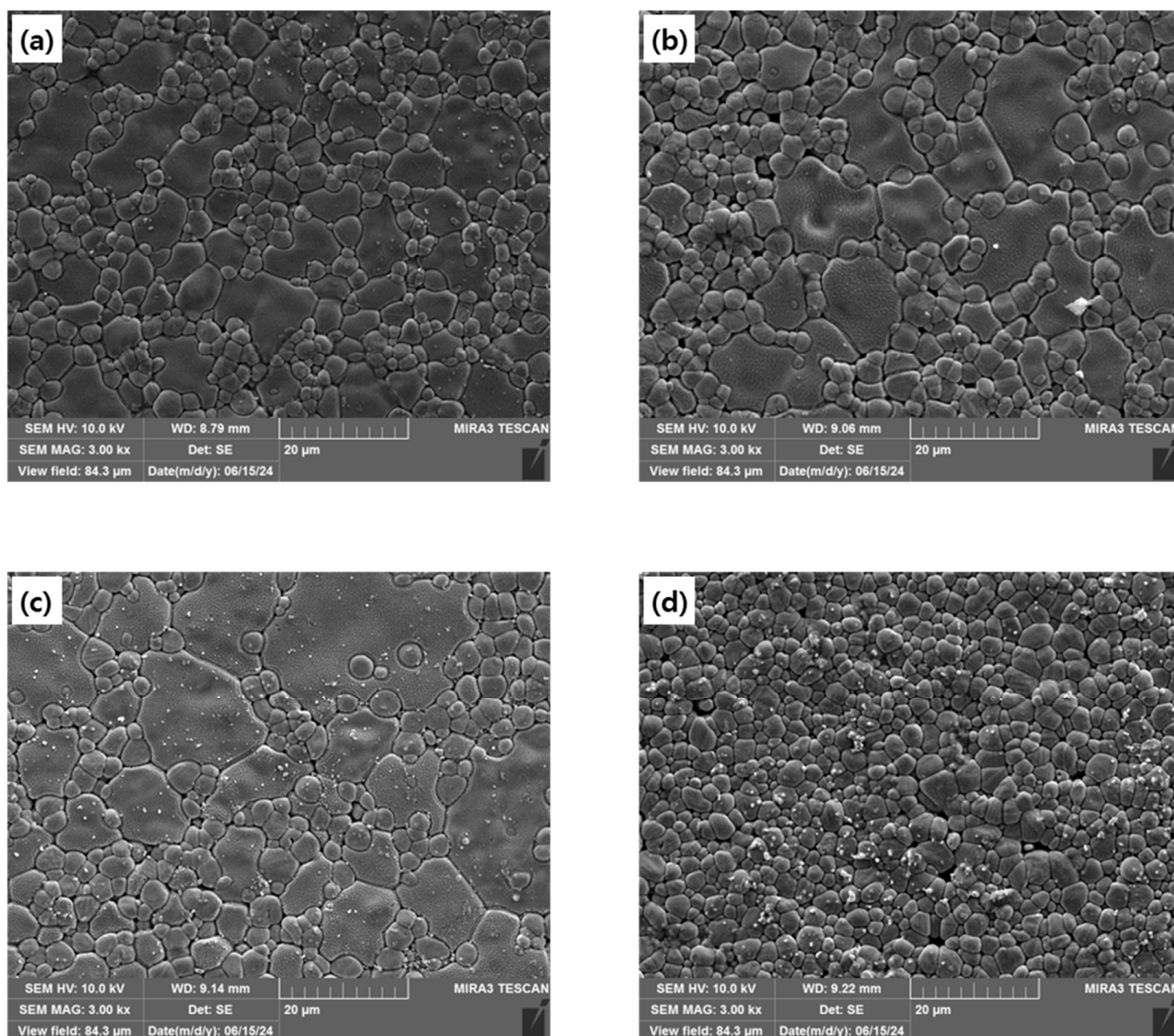


Figure 3. FE-SEM images and average grain sizes of (a) 9CSZ, (b) 2CeO₂-CSZ, (c) 3CeO₂-CSZ, and (d) 4CeO₂-CSZ specimens after sintering.

The phase analysis results after applying thermal stress to 2–4 mol% CeO_2 -doped CSZ are shown in Figure 4. The monoclinic phase fraction (V_m) of zirconia was significantly increased from 7.14% to 23.26% in the case of 9CSZ, whereas under the 2–4 mol% CeO_2 doping conditions, it was relatively less changed to 10.91%, 10.03%, and 9.15%, respectively. These results indicate that the phase stability of 9CSZ with CeO_2 improved under thermal stress. The reduction in oxygen vacancies and the minimization of lattice structure distortion are believed to be caused by the substitution of Ce^{4+} , which has the same electric valence state as Zr^{4+} and a similar ionic size.

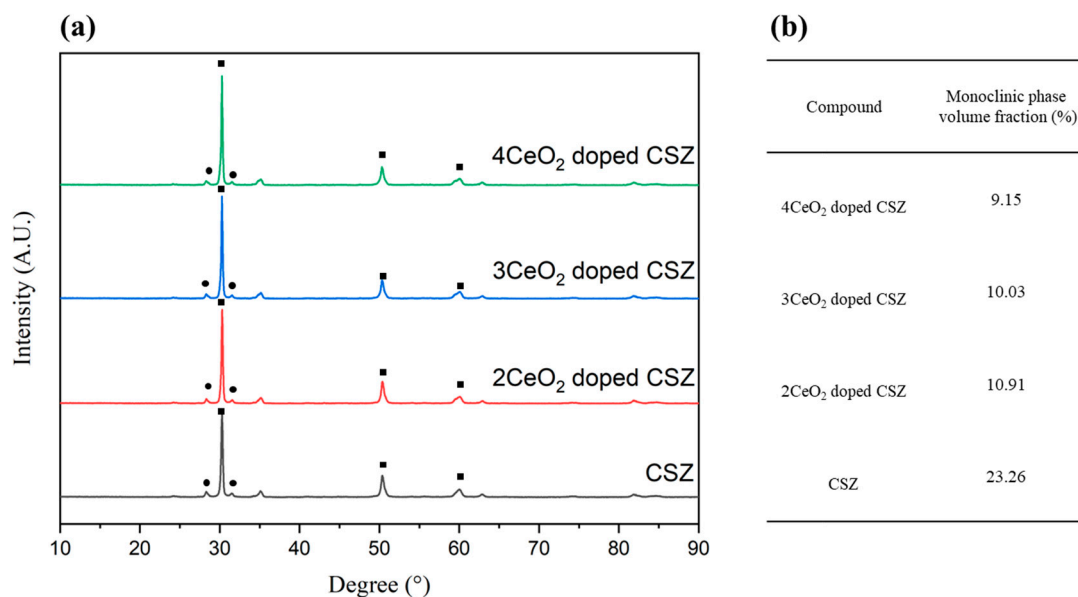


Figure 4. (a) XRD diffraction patterns of CeO₂-doped 9CSZ after thermal shock ($\Delta 400$ °C) (●: monoclinic phase, ■: tetragonal or cubic phase), (b) Phase fraction determined through Rietveld refinement.

The mechanical properties of each specimen were observed after subjecting 2–4 mol% CeO₂-doped CSZ to thermal shock under $\Delta 400$ °C (1300 and 900 °C) conditions. Figure 5 shows the changes in Vickers hardness before and after thermal shock, indicating that the Vickers hardness gradually increased with an increasing amount of CeO₂ doping. The Vickers hardness of all specimens decreased after applying thermal shock. Specifically, 2–4 mol% CeO₂-doped CSZ showed a decrease of 20.3% (1254.9 → 1000.1 HV), 17.5% (1303.4 → 1077.9 HV), and 22.8% (1497.6 → 1156.7 HV), respectively. In contrast, 9CSZ exhibited a relatively larger decrease of approximately 41.5% (1088.4 → 637.0 HV).

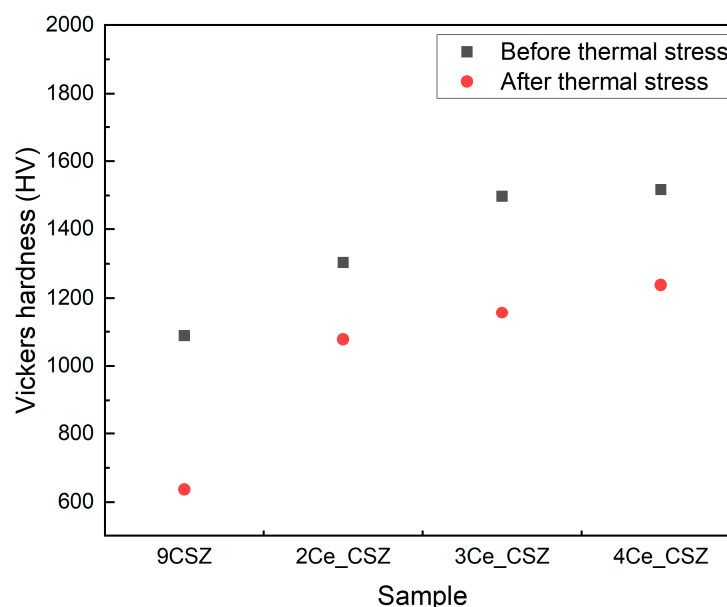


Figure 5. Vickers hardness of CeO₂-doped CSZ before (black scattered point) and after (red scattered point) post-heat treatment.

The flexural strength before and after thermal shock is shown in Figure 6. The flexural strength gradually increased with an increase in CeO₂ doping content, and the flexural

strength of all specimens decreased after thermal shock. Specifically, the flexural strength of 9 mol% CSZ before the thermal shock test was 100.23 MPa, while the flexural strength of 2–4 mol% CeO₂-doped CSZ was 115.9 MPa, 123.1 MPa, and 123.8 MPa, respectively. After thermal shock, the flexural strength of 9 mol% CSZ was 88.2 MPa, and the flexural strength of 2–4 mol% CeO₂-doped CSZ was 91.38 MPa, 99.3 MPa, and 98.3 MPa, respectively. The decrease in flexural strength of CeO₂-doped CSZ after the thermal shock was greater compared to 9 mol% CSZ, but it still exhibited higher values than 9 mol% CSZ even after the thermal shock. The increase in flexural strength for 4 mol% CeO₂-doped CSZ was smaller compared to 3 mol%-doped CSZ, which was consistent with the trends observed in the Vickers hardness results.

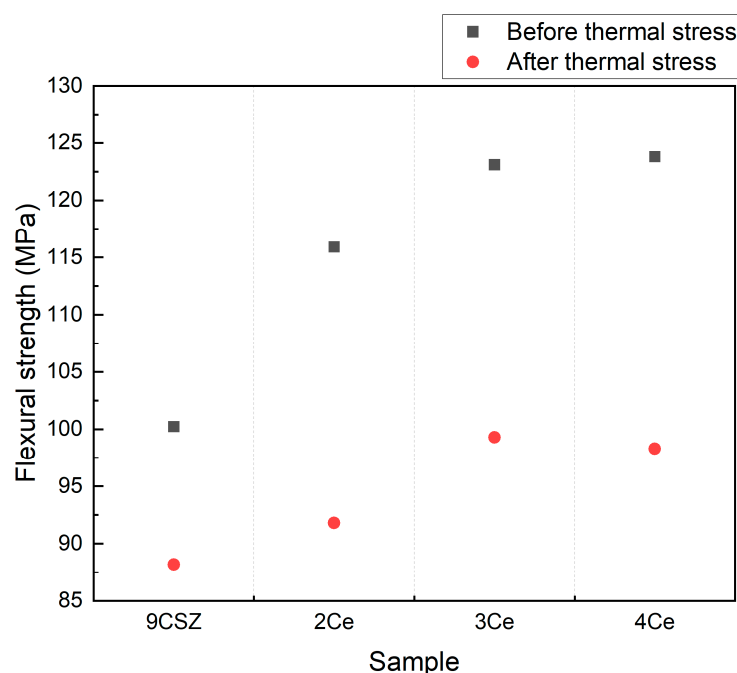


Figure 6. Flexural strength of CeO₂-doped CSZ before (black scattered point) and after (red scattered point) post-heat treatment.

The results of the wear resistance evaluation of the specimens before and after thermal shock are shown in Figure 7. The wear amount of the specimens decreased with increasing CeO₂ doping levels, and all specimens exhibited an increase in wear amount after thermal shock, which was consistent with the trend observed in Vickers hardness. The specific wear amount of 9CSZ increased by 136.2% ($1.5941 \rightarrow 3.7650 \times 10^5 \text{ mm}^3/\text{Nm}$) before and after thermal stress. CeO₂-doped 9CSZ exhibited specific wear amount changes of 125.4% ($1.4265 \rightarrow 3.2160 \times 10^5 \text{ mm}^3/\text{Nm}$), 136.7% ($1.2512 \rightarrow 2.9610 \times 10^5 \text{ mm}^3/\text{Nm}$), and 173.4% ($1.1320 \rightarrow 3.0951 \times 10^5 \text{ mm}^3/\text{Nm}$) before and after thermal stress as the CeO₂ doping level increased from 2 to 4 mol%. As the CeO₂ doping level increased, the increase in the wear amount before and after thermal stress also increased, with a particularly sharp change observed in the 4 mol% CeO₂-doped CSZ. The sharp increase in the wear amount before and after thermal stress in the 4 mol% CeO₂-doped CSZ is believed to be related to the formation of the cubic phase, as indicated by XRD analysis.

The results of Figures 5–7 show that doping 9CSZ with CeO₂ can further enhance the mechanical properties of CSZ. However, it was identified that doping with more than 4 mol% CeO₂ leads to a decrease in the property stability of CSZ after thermal stress.

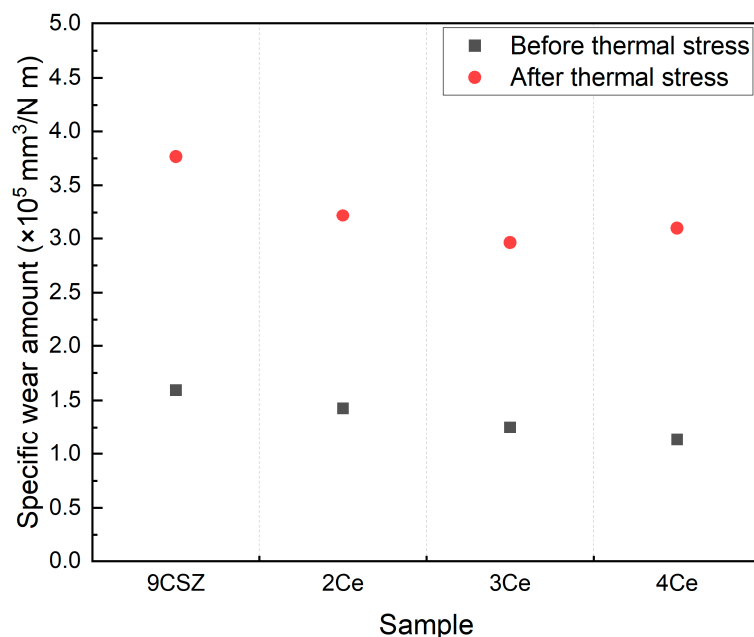


Figure 7. Specific wear amount of CeO₂-doped CSZ before (black scattered point) and after (red scattered point) post-heat treatment.

Figure 8 shows the phase transition of the CeO₂-doped CSZ after an erosion test with a highly basic CaF₂-based slag to examine the effect of CeO₂ doping on the erosion resistance of CSZ. The monoclinic phase fraction of 9CSZ increased significantly from 7.144% to 67.71% after the erosion test, while 2Ce_CSZ and 3 Ce_CSZ showed a relatively lower monoclinic phase fraction of 4.07% and 30.85%. The 4Ce_CSZ showed a higher monoclinic phase fraction of 77.12%. As the CeO₂ content increased, the monoclinic phase fraction also tended to increase, with the 2 mol% CeO₂ doping condition showing the lowest monoclinic phase fraction.

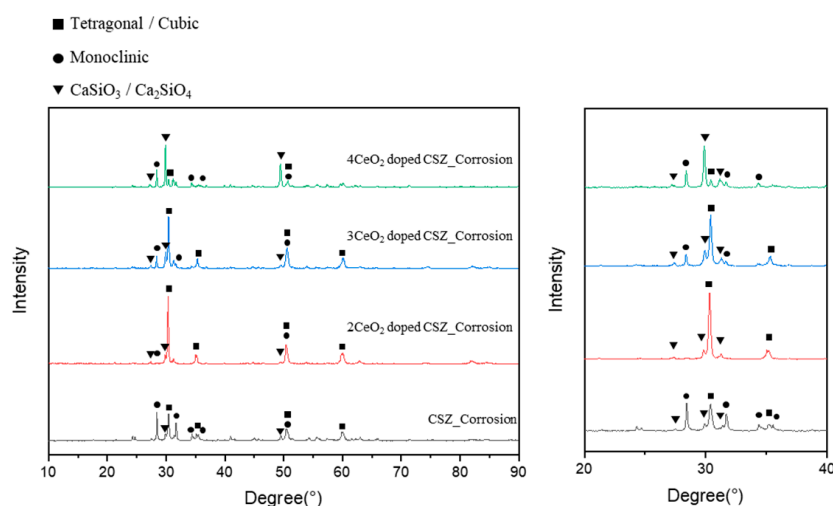


Figure 8. X-ray diffraction patterns of CeO₂-doped 9CSZ after erosion experiment in slag.

The higher phase stability of CeO₂-doped CSZ after chemical erosion with CaF₂-based slag is considered to be due to the very low solubility of CeO₂ in the slag, unlike CaO, which prevents the dopant from chemically dissolving into the slag at high temperatures. However, excessive CeO₂ doping can lead to structural instability in CSZ, so it is important to investigate the optimal doping concentration.

4. Conclusions

We doped 9 mol% CaO-stabilized ZrO₂ with 2–4 mol% CeO₂ to investigate the mechanical and chemical changes due to CeO₂ doping. The mechanical property changes under thermal stress and the behavior of the CSZ composition and phase changes after an erosion test in CaF₂-based slag were then observed. The monoclinic phase fraction (V_m) of zirconia was 7.14% for 9CSZ, while under doping conditions of 2–4 mol% CeO₂, it decreased slightly to 5.55% and 3.72%, respectively, compared to CSZ, without showing any abrupt change. The Ce⁴⁺ ion had the same charge state as the Zr⁴⁺ ion, resulting in no formation of oxygen vacancies due to charge compensation. Phase stabilization was induced solely by lattice stress caused by the difference in the ionic radii between Zr⁴⁺ (84 pm) and Ce⁴⁺ (97 pm). Therefore, doping with a small amount of CeO₂ is presumed to have a lesser effect on improving phase stability at room temperature. In particular, the peak splitting between 30° and 30.5° observed in 4 mol% CeO₂-doped CSZ suggested the formation of a cubic phase. The grain size of 9CSZ doped with 2–3 mol% CeO₂ was comparable to that of 9CSZ, while 9CSZ doped with 4 mol% CeO₂ exhibited finer microstructure. This is presumed to be due to the cubic phase formed at 4 mol% doping.

The Vickers hardness increased from 1088.4 HV to 1497.6 HV as the CeO₂ doping amount in 9CSZ increased. Even after applying a thermal shock of $\Delta 400$ °C (1300→900 °C), the CeO₂-doped 9CSZ showed relatively higher values, increasing from 637.0 HV to 1156.7 HV, compared to 9CSZ. The specific wear amount before thermal stress decreased to 1.4265×10^5 mm³/Nm, 1.2512×10^5 mm³/Nm, and 1.1320×10^5 mm³/Nm with the addition of 2–4 mol% CeO₂ doping, compared to the specific wear amount of CSZ, which was 1.5941×10^5 mm³/Nm. The specific wear amount of 9CSZ increased by 136.2% ($1.5941 \rightarrow 3.7650 \times 10^5$ mm³/Nm) before and after thermal stress. CeO₂-doped 9CSZ exhibited specific wear amount changes of 125.4% ($1.4265 \rightarrow 3.2160 \times 10^5$ mm³/Nm), 136.7% ($1.2512 \rightarrow 2.9610 \times 10^5$ mm³/Nm), and 173.4% ($1.1320 \rightarrow 3.0951 \times 10^5$ mm³/Nm) before and after thermal stress as the CeO₂ doping level increased from 2 to 4 mol%. As the level of CeO₂ doping increased, the increase in wear amount before and after thermal stress also increased, with a particularly sharp change observed in CSZ doped with 4 mol% CeO₂. The sharp increase in wear amount before and after thermal stress in CSZ doped with 4 mol% CeO₂ is believed to be related to the formation of the cubic phase generated in 4 mol% CeO₂-doped CSZ.

Doping CeO₂ into 9CSZ resulted in a lower formation of the monoclinic phase compared to 9CSZ, even under the chemical reaction conditions with CaF₂-based slag at 1550 °C. These results suggested that CeO₂ doping in CSZ can enhance phase stability under high temperature and high alkalinity conditions. However, the monoclinic phase fraction was lowest at 2 mol% CeO₂ doping, and it showed an increasing trend as the doping concentration increased beyond that.

As a result, CeO₂ doping was found to improve the mechanical properties of 9 mol% CSZ and enhance its stability against CaF₂-based slag at high temperatures. However, doping with more than 4 mol% CeO₂ can cause a decrease in mechanical properties under thermal stress conditions of 1300–900 °C due to the formation of the cubic phase. Therefore, it is important to optimize the CeO₂ doping concentration according to the operating conditions.

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