Review on Recent Advancements in Severe Plastic Deformation of Oxides by High-Pressure Torsion (HPT)

Kaveh Edalati

1. Introduction

Severe plastic deformation (SPD) of oxides has been of interest in mineralogy and geology for many decades, but oxides have ionic or covalent bonds with brittle nature and can hardly be deformed at ambient temperature. SPD processing of oxides is first realized in 1930s, when Percy W. Bridgman introduce the principles of high-pressure torsion (HPT) method. Although the method is widely used nowadays to produce ultrafine-grained (UFG) metals, the application of method for SPD processing of oxides is quite limited. This article reviews some of the recent publications on the application of HPT method to oxide ceramics (Al₂O₃, ZrO₂, TiO₂, Y₂O₃, ZnO, and BaTiO₃) and summarizes their major findings: powder compaction and partial consolidation, nanograin formation, formation of different kinds of lattice defects such as dislocations and oxygen vacancies, strain and grain size dependence of phase transformations, and improvement of functional properties such as bandgap narrowing, photoluminescence, photocatalytic activity, and dielectricity.

Despite significant activities on SPD processing of metallic materials within this century,[1−4] there have been very limited works on SPD processing of oxides to achieve microstructural modifications and enhanced functional properties. In 2010, our group started working on SPD processing of oxides to develop nanostructured functional oxides. The first publication on α-Al₂O₃[29] together with a few following studies on other oxides such ZrO₂,[30] BaTiO₃,[31] TiO₂,[32,33] Y₂O₃,[34] ZnO,[35] and γ-Al₂O₃[36,37] proved significant effect of HPT processing on microstructure, phase transformation, and functional properties of oxides. In this paper, after a brief introduction of some old publications on the application of HPT to oxides, recent advancements reported by the author’s group in Kyushu University are reviewed and compared with metals by focusing on six main issues: 1) partial consolidation, 2) nanograin formation and dislocation activity, 3) oxygen vacancy formation, 4) phase transformation and size effect, 5) bandgap narrowing, and 6) functionality enhancement.

2. Early Studies on HPT Processing of Oxides

As mentioned earlier, SPD processing of oxides has been of interest for many decades in mineralogy and geology. Boeker is

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one of the first scientists that tried to combine high pressure and torsional shear to deform oxides, but pressure ranges at that time were not high enough for SPD processing. Real SPD processing of oxides was realized in Harvard University in 1935, when Bridgman introduced the principles of HPT by increasing the pressure to 5 GPa. Bridgman applied his method to different kinds of metallic and non-metallic materials and recognized that unlike metals, HPT processing of oxides was noisy due to snapping in the anvils during yielding the oxides. He suggested that this snapping behavior of oxides under high pressure simulates the mechanism of deep-seated earthquake in the earth (see a press release of his work in Figure 1b). In 1937, Bridgman applied the HPT method to a wide range of inorganic compounds including oxides and reported accelerated phase transformation, reduction or chemical decomposition in several compounds including Bi-based, Pd-based and Hg-based oxides. Moreover, he reported possible phase transformations and changes in the color in some other oxides such as MnO₂, Sb₂O₃, BCrO₄, and PbCrO₄. In 1938, Larsen and Bridgman confirmed that phase transformations are accelerated and crystallite sizes are reduced in different minerals by HPT processing.

Following the pioneering works of Bridgman, some other groups investigated the HPT processing of oxides, started with the work of Griggs on HPT processing of rocks at room temperature in 1936 and continued with the modern work of Paterson and Olgaard at very high temperatures in 2000. Bell (1963), Bates et al. (1963), Dachille and Roy (1964), and Vereshchagin et al. (1971) reported effectiveness of shearing stress in accelerating solid-state phase transitions in several oxides in good agreement with the reports by Bridgman.

A few recent works focused on the changes in the properties of oxides after HPT processing: Absalyamov (2002) studied the magnetic properties of Fe₂O₃; Vitchenko et al. (2007) and Ubushaeva et al. (2011) studied the physical properties of ferroelectric oxides; and Kallaev et al. (2013) studies the heat capacity of BaTiO₃. All these studies suggest that HPT processing can be effectively used to control the structure of oxides which can further employed to achieve enhanced functional properties, as will be discussed in the following sections.

3. Recent Findings on HPT Processing of Oxides
3.1. Partial Consolidation

Application of HPT method to powders usually results in enhanced consolidation even at room temperature. While the powder consolidation for many metals, alloys, and metal-based composites is almost ideal and close to the bulk condition, the consolidation of oxide powders is only partial. This behavior of oxides, which is similar to that for intermetallic compounds including Bi-based, Pd-based and Hg-based oxides. Moreover, he reported possible phase transformations and changes in the color in some other oxides such as MnO₂, Sb₂O₃, BCrO₄, and PbCrO₄. In 1938, Larsen and Bridgman confirmed that phase transformations are accelerated and crystallite sizes are reduced in different minerals by HPT processing.

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Figure 1. HPT method for SPD processing of any kinds of materials. a) Illustration of HPT process (reproduced with permission. 2014, Elsevier); b) press release on first HPT facility with manual rotation designed by Bridgman in 1935 (title: scientist makes miniature earthquake) (taken from the archives of Harvard University and reproduced with permission. 2014).

Kaveh Edalati obtained a PhD degree in materials physics and chemistry from Kyushu University, Fukuoka, Japan, in 2010. He worked on development of nanomaterials by severe plastic deformation for his PhD study and continued this study for up to now. He is currently an assistant professor at the International Institute for Carbon-Neutral Energy Research, Kyushu University, Fukuoka, Japan. His current research field is the development of functional energy materials by engineering phase transformations and lattice defects via severe plastic deformation. He is currently the author of over one hundred journal papers.
components, is due to their high hardness, brittle behavior, and poor plasticity-induced consolidation. It was shown that when the HPT process is applied to fully dense samples of hard and brittle intermetallics such as TiFe[54] and Mg2Ni,[55] many cracks are formed and the consolidation is significantly destroyed. A behavior similar to intermetallics occurs during the HPT processing of oxides: partial consolidation of powders and reduced consolidation of bulk samples. Figure 2a shows the occurrence of compaction in Al2O3 powders when they are processed by HPT.[28] Analyzing the surface area using the pulsed nuclear magnetic resonance (NMR) and Bruanauer-Emmett-Teller (BET) methods,[56] as summarized in Figure 2b for TiO2,[32] ZnO[35] and Al2O3,[37] confirms that the surface area is reduced by HPT processing which is a clear indication for partial consolidation. This partial consolidation is unfavorable, when large surface area are required for an application such as photocatalysis.[33,35] However, this partial consolidation can lead to better sintering at lower temperature, as was shown for Al2O3,[29] BaTiO3,[31] and some kind of ceramic-based composites.[12]

3.2. Nanograin Formation and Dislocation Activity

It is currently well-known that the application of HPT to metallic materials results in significant grain refinement and formation of UFG microstructure with high-misorientation angles.[1–4] Grain sizes for metallic materials are usually at the submicrometer level and they are reduced with increasing the melting temperature[57] or by addition of solute atoms.[58] The grain sizes are reduced even more significantly to the nanometer level in intermetallics with a change in the atomic bonding from the metallic bonds to ionic or covalent bonds.[54,55] The grain refinement in oxides is also significant and nanograin with average sizes in the range of a few tenths of nanometers are formed, as shown in Figure 3 for (a) BaTiO3,[31] (b) TiO2,[32] (c) Y2O3,[34] and (d) ZnO[35] using transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Although the exact mechanism for the formation of nanograins with high-misorientation angles in oxides is not well-understood yet, the presence of high dislocation densities in the order of 1015 m−2 as shown in Figure 4 for (a) ZrO2[30] and (b) TiO2,[32] suggests that the formation of dislocations and their accumulation should play an important role in grain refinement. Another issue in HPT processing of oxides is the formation of nanograins with some steady-state sizes and not with the amorphous structure. The mechanism of the appearance of steady-state microstructure in metallic materials was investigated widely in recent years and it was attributed to strain-induced recovery,[59] dynamic recrystallization,[60] grain rotation,[61] and grain boundary migration.[4] Although the melting temperatures for oxides are significantly larger than those for metals, similar mechanisms such as dynamic recrystallization apparently contribute to grain refinement and the occurrence of steady state in oxides. The occurrence of enhanced dynamic recrystallization in oxides under high pressure and shear strain was reported decades ago by Larsen and Bridgman (1935),[19–21] Bennington (1956),[62] and Griggs et al. (1960).[63] It should be noted that when metastable oxides with very small nanograin sizes such as nanostructured γ-Al2O3 are processed by HPT,[36] an unusual grain growth occurs which is basically similar to the reported HPT-induced grain coarsening in nanograined metals with low stability.[64]

3.3. Oxygen Vacancy Formation

The continuous formation of vacancies up to supersaturated levels in HPT-processed metals is currently an accepted fact, which is believed to contribute to fast diffusivity in UFG metals and alloys.[65,66] Similar to metallic materials, formation of oxygen vacancies by HPT processing is another general features that can be observed in different oxides such as BaTiO3,[31] TiO2,[32] ZnO[35] and Al2O3,[37] Bridgman’s pioneering studies roughly indicated the reduction of some oxides by HPT processing, although he did not have access to advanced experimental tools to prove this issue.[19–21] Recent experiments using different techniques such as photoluminescence spectroscopy, as shown in Figure 5a for BaTiO3,[31] differential scanning calorimetry (DSC) as shown in Figure 5b for TiO2,[32] Raman spectroscopy, as shown in Figure 5c for ZnO,[35] and electron paramagnetic resonance (EPR) as shown in Figure 5d for ZnO,[35] provide clear evidence for the formation of oxygen vacancies in different oxides after HPT processing. The new peaks in Figure 5a–d clearly appear after HPT processing which correspond to oxygen vacancies. Other
characterization techniques such as X-ray diffraction, X-ray photoelectron spectroscopy and electron energy loss spectroscopy also provide extra evidence for the formation of oxygen vacancies.[31–37] The fraction of oxygen vacancies in HPT-processed oxides can reach up to 0.01% or even a few percent, which results in changes in the color of samples to darker forms after HPT processing (see the color of samples in Figure 6).[31–37] Since the formation of oxygen vacancies significantly influences the electronic structure of oxides,[67] it is expected that HPT-processed oxides exhibit special electrical and optical properties due to their modified electronic structures, as will be discussed below.

3.4. Phase Transformation and Size Effect

As mentioned earlier, the HPT method was widely used by Bridgman[19–21] and many other scientists[40–43] to control the phase transformations in different oxides. The method also exhibited high potential to achieve phase transformations in extremely hard materials such as silicon[13,14] and carbon polymorphs.[15,16] The method in a revised form of shear or rotational diamond anvil cell was successfully employed for in situ examination of phase transformation.[11,15,16] The method still receives significant attention in the SPD community to control the phase transformations in metals[68,69] and alloys.[27,28] Our studies on phase transformation of oxides by HPT processing reveal three main findings.

First, some oxides exhibit transition from metastable phases to stable phases such as tetragonal to monoclinic transition in ZrO₂ as in Figure 6a,[30] and γ-cubic to α-rhombohedral transition in Al₂O₃, as in Figure 6b.[36] These transitions are thermodynamically reasonable because strain can reduce the activation barrier for phase transformation and accelerate the kinetics for metastable-to-stable transitions.[69] However, some oxides exhibit transition from stable phases to high-pressure metastable phases such as tetragonal to cubic transition in BaTiO₃,[31] anatase-tetragonal to orthorhombic TiO₂-II transition in TiO₂ as in Figure 6c,[12,33] cubic to monoclinic transition in Y₂O₃ as in Figure 6d,[32,33] and wurtzite-hexagonal to rocksalt-cubic transition in ZnO.[35] The formation of these high-pressure metastable phases, which usually occur at pressures lower than the reported critical pressure for static compression,[12–37] should have a close connection with the formation of nanograins and lattice defects. The presence of large fractions of nanograin boundaries and dislocations during HPT processing provides numerous sites for the nucleation of new phases. It was suggested that the large fraction of these lattice defects and their
interactions (especially interaction between the dislocations and grain boundaries) lead to enhanced localized pressure which finally results in the formation of high-pressure phases under lower pressures. Recent theoretical studies by phase field approach and finite elements method confirmed that a dislocation pile-up under shearing creates strong stress concentration and significantly increases the local thermodynamic driving force for pressure-induced phase transformation at significantly low pressures. It should be noted that the reduction of pressure by shearing was also reported in some other phase transformations such as α-ω transition in ZrO2 and hexagonal-wurtzite transition in BN.

Second, as shown in Figure 6, the fraction of new phases increases significantly with increasing the shear strain (i.e., increasing the number of HPT turns) at early stages of straining, but finally saturates to steady-state-like levels at large strains. The variations of phase fraction versus strain in Figure 6 is similar to the hardness-strain behavior of many metallic materials, in which a saturation appears due to a balance between the strain-induced hardening and softening mechanisms. The reason for apparent saturation of phase fractions of oxides at some certain stationary levels (below 100%) was attributed to a balance between the direct and reverse phase transformation, as plastic strain promotes both direct and reverse transitions. Another possibility is the higher resistance of HPT-induced nanograins to plastic deformation which can make the kinetics of phase transformation slower. To clarify this issue, phase transformation should be examined after ultra-SPD processing with much larger number of HPT turns, as attempted earlier for some immiscible metallic systems.

Third, the high-pressure phases remain stable in oxides for years after HPT processing. The stability of these high-pressure phases after releasing the pressure should be due to the large activation energy for nucleation of new phases on nanograin boundaries which makes the reverse phase transformation to the stable phases energetically unfavorable. Close examinations by high-resolution TEM confirm that high-pressure phases remain stable only when the grain sizes are smaller than a critical level (see Figure 7a for TiO2 and Figure 7b for Y2O3). It should be noted that the size effect on the stability of metastable phases has been widely reported for different oxides such as ZrO2, Y2O3, BaTiO3, Al2O3, TiO2, iron oxides, and so on. Moreover, the effect of size on phase stability is not limited to HPT-processed oxides, as a similar effect was reported in HPT-processed metals.

3.5. Bandgap Narrowing

The stability of high-pressure phases and large oxygen vacancy concentration after HPT processing can change the electronic structure of these oxides and results in bandgap narrowing of different oxides such TiO2, Y2O3, ZnO, and Al2O3. Figure 8 shows Kubelka-Munk plots of the UV-vis diffuse reflectance spectra of (a) TiO2 and (b) ZnO for the estimation of bandgap. The bandgap for the starting TiO2 powders with the anatase structure is 3.1 eV, but it reduces to 2.4 eV after HPT processing due to the formation of high-pressure TiO2-II phase and oxygen vacancies. Annealing of the samples leads to the disappearance of oxygen vacancies which results in increasing the bandgap. For ZnO, the bandgap of the starting powder which has a stable wurtzite structure is 3.1 eV. The bandgap is slightly reduced to 2.8 eV by HPT processing under 3 GPa due to the formation of oxygen vacancies in the wurtzite phase. After HPT processing under 6 GPa, the decrease in bandgap becomes more significant down to 1.8 eV because of the simultaneous effect of high-pressure rocksalt phase and oxygen vacancies, as discussed using the first principles calculations in ref. The change in the electronic structure of oxides by HPT processing and reduction in their bandgap (i.e., increasing light absorbance) is considered as a significant finding which contrast with the bandgap narrowing by addition of dopants.

3.6. Functionality Enhancement

Although the effect of microstructure and phase transformation on mechanical and functional properties of metals processed by HPT processing have been investigated widely (see reviews in refs. 25, 40), there are limited publications on functional
Figure 5. Formation of oxygen vacancies in oxides by HPT processing. a) Photoluminescence spectra for BaTiO₃ (reproduced under the term of the Creative Commons Attribution License,[31] 2015, Taylor and Francis Group), b) DSC profiles for TiO₂ (reproduced with permission.[33] 2016, ACS Publications), c) Raman spectra for ZnO (reproduced with permission.[35] 2017, RCS Publications), and d) EPR spectra for ZnO (reproduced with permission.[35] 2017, RCS Publications) before and after HPT processing.

Figure 6. Enhancement of phase transformation by straining via HPT processing. Phase fractions against shear strain after HPT processing for a) tetragonal to monoclinic transition in ZrO₂ (reproduced with permission,[30] 2011, Elsevier), b) γ → α transition in Al₂O₃ (reproduced with permission,[36] 2018, Elsevier), c) anatase to TiO₂-II transition in TiO₂ (reproduced with permission,[32] 2016, Elsevier) and d) cubic to monoclinic transition in Y₂O₃ (reproduced with permission,[34] 2017, ACS Publications). Inset: appearance of samples.
properties of HPT-processed oxides. Here, three functional properties which are of interest in the field of energy materials are discussed: photoluminescence, as shown in Figure 9 for TiO$_2$,\textsuperscript{[32]} photocatalysis as shown in Figure 10 for ZnO,\textsuperscript{[35]} and dielectricity as shown in Figure 11 for BaTiO$_3$.\textsuperscript{[31]}

Figure 9 shows the photoluminescence spectra of Al$_2$O$_3$ after HPT processing for 1/4 and 4 turns.\textsuperscript{[32]} The intensity of photoluminescence peaks significantly increases by HPT processing, and the increase becomes more significant with increasing the number of HPT turns. Such an increase in the photoluminescence intensity by HPT processing is due to the generation of oxygen monovacancies and vacancy pairs and their effect on electron/hole recombination.\textsuperscript{[90]} It should be noted that modification of photoluminescence properties is not limited to Al$_2$O$_3$,\textsuperscript{[37]} as we observed similar results for BaTiO$_3$,\textsuperscript{[31]} TiO$_2$,\textsuperscript{[32]} Y$_2$O$_3$,\textsuperscript{[34]} and ZnO\textsuperscript{[35]} due the formation of oxygen vacancies and/or phase transformations.

Figure 10 shows the photocatalytic degradation rate of Rhodamine B under visible light on ZnO powder before HPT processing and after HPT processing for 3 turns under 3 and 6 GPa\textsuperscript{[35]} (see the bandgap estimations for these three samples in Figure 8). The powder sample does not show any photocatalytic activity under visible light which is due to its large bandgap as 3.1 eV. It should be noted that for visible-light photocatalytic activity under sunlight, a photocatalyst should have a bandgap below 3 eV and ideally close to 2 eV.\textsuperscript{[88,91]} The sample processed by HPT under 3 GPa shows enhanced photocatalytic activity due to the effect of oxygen vacancies on bandgap narrowing.

Figure 8. Bandgap narrowing of oxides by HPT processing. Kubelka-Munk plots of UV-vis diffused reflectance spectra for a) TiO$_2$ powder before HPT (anatase phase), after HPT (oxygen vacancy and TiO$_2$-II formation) and after HPT + annealing (TiO$_2$-II formation) (reproduced with permission\textsuperscript{[33]} 2016, ACS Publications); and b) ZnO powder before HPT (wurtzite phase) and after HPT under 3 GPa (oxygen vacancy formation) and 6 GPa (oxygen vacancy and rocksalt phase formation) (reproduced with permission\textsuperscript{[35]} 2017, RCS Publications). $h$: absorption coefficient; $k$: Planck’s constant, $\nu$: light frequency.
However, the best photocatalytic activity is achieved for the samples processed by HPT under 6 GPa, containing the high-pressure rocksalt phase and large concentration of oxygen vacancies with a bandgap of 1.8 eV. It should be noted that TiO$_2$-II phase stabilized by HPT also exhibit visible-light photocatalytic activity for hydrogen generation from water.\textsuperscript{[33]} Here, it worth mentioning that the HPT process not only contributes to the photocatalytic hydrogen production on TiO$_2$ semiconductors, but also contributes to the improvement of hydrogen storage properties of metals\textsuperscript{[92,93]} and intermetallics.\textsuperscript{[54,55]} These results on ZnO and TiO$_2$ clearly show that the HPT processing can be considered as a new route for production of new visible-light-active photocatalysts for effective usage of solar energy.\textsuperscript{[91]}

4. Conclusions

Severe plastic deformation of oxides through the high-pressure torsion process is effective to stabilize high-pressure phases, produce nanograinned oxides, and generate dislocation and oxygen vacancies. These structural and microstructural features of severely deformed oxides make them potential candidates as functional and energy materials.

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Conflict of Interest

The author declares no conflict of interest.

Keywords

functional ceramics, nanostructured oxides, phase transformation, severe plastic deformation (SPD), ultrafine-grained (UFG) materials

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\textsuperscript{[1]} R. Z. Valiev, R. K. Islamgaliev, I. V. Alexandrov, \textit{Prog. Mater. Sci.} \textbf{2000}, \textit{45}, 103.

\textsuperscript{[2]} R. Z. Valiev, Y. Estrin, Z. Horita, T. G. Langdon, M. J. Zehetbauer, Y. T. Zhu, \textit{JOM} \textbf{2006}, \textit{58}, 33.

\textsuperscript{[3]} A. P. Zhilyaev, T. G. Langdon, \textit{Prog. Mater. Sci.} \textbf{2008}, \textit{53}, 893.

\textsuperscript{[4]} R. Pippan, S. Scheriau, A. Taylor, M. Hafok, A. Hohenwarter, A. Bachmaier, \textit{Annu. Rev. Mater. Res.} \textbf{2010}, \textit{40}, 319.

\textsuperscript{[5]} P. Li, Q. Lina, X. Wang, Y. Tian, K. M. Xue, \textit{Int. J. Refract. Met. Hard Mater.} \textbf{2018}, \textit{72}, 367.

\textsuperscript{[6]} S. Lee, K. Edalati, Z. Horita, \textit{Mater. Trans.} \textbf{2015}, \textit{56}, 1072.

\textsuperscript{[7]} G. Rogl, D. Setman, E. Schaffer, J. Horky, M. Kerber, M. Zehetbauer, M. Falmbigl, P. Rogl, E. Royanian, E. Bauer, \textit{Acta Mater.} \textbf{2012}, \textit{60}, 2146.

\textsuperscript{[8]} M. Peterlechner, T. Waitz, H. P. Karnthaler, \textit{Scr. Mater.} \textbf{2008}, \textit{59}, 566.

\textbf{Figure 10.} Enhancement of visible-light photocatalytic activity by HPT processing. Photocatalytic Rhodamine B degradation under visible light on ZnO before and after HPT processing under 3 and 6 GPa ($\Delta C$: degraded amount of Rhodamine B; $C_0$: initial concentration of Rhodamine B). Reproduced with permission.\textsuperscript{[34]} 2017, ACS Publications.

\textbf{Figure 11.} Enhancement of dielectricity by HPT processing. Dielectric constant against temperature for BaTiO$_3$ before and after HPT processing. Reproduced under the term of the Creative Commons Attribution License.\textsuperscript{[31]} 2015, Taylor and Francis Group.
[78] K. Edalati, R. Uehiro, K. Fujiwara, Y. Ikeda, H. W. Li, X. Sauvage, R. Z. Valiev, E. Akiba, I. Tanaka, Z. Horita, Mater. Sci. Eng. A 2017, 701, 158.
[79] R. C. Garvie, J. Phys. Chem. 1965, 69, 1238.
[80] G. Skandan, C. M. Foster, H. Frase, M. N. Ali, J. C. Parker, H. Hahn, Nanostruct. Mater. 1992, 1, 313.
[81] M. H. Frey, D. A. Payne, Phys. Rev. B 1996, 54, 3158.
[82] J. M. McHale, A. Auroux, A. J. Perrotta, A. Navrotsky, Science 1997, 277, 788.
[83] A. A. Gribb, J. F. Banfield, Am. Mineral. 1997, 82, 717.
[84] A. Navrotsky, L. Mazeina, J. Majzlan, Science 2008, 319, 1635.
[85] K. Edalati, S. Toh, M. Arita, M. Watanabe, Z. Horita, Appl. Phys. Lett. 2013, 102, 181902.
[86] K. Edalati, T. Daio, M. Arita, S. Lee, Z. Horita, A. Togo, I. Tanaka, Acta Mater. 2014, 68, 207.
[87] P. Kubelka, F. Munk, Z. Tech. Phys. 1931, 12, 593.
[88] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 2001, 293, 269.
[89] R. Z. Valiev, M. J. Zehetbauer, Y. Estrin, H. W. Hoppel, Y. Ivanisenko, H. Hahn, G. Wilde, H. J. Roven, X. Sauvage, T. G. Langdon, Adv. Eng. Mater. 2007, 9, 527.
[90] B. D. Evans, J. Nucl. Mater. 1995, 219, 202.
[91] J. Nowotny, C. C. Sorrell, L. R. Sheppard, T. Bak, Int. J. Hydrogen Energy 2005, 30, 521.
[92] D. R. Leiva, A. M. Jorge, T. T. Ishikawa, J. Huot, D. Fruchart, S. Miraglia, C. S. Kiminami, W. J. Botta, Adv. Eng. Mater. 2010, 12, 786.
[93] T. Grosdidier, J. J. Fundenberger, J. X. Zou, J. C. Pan, X. Q. Zeng, Int. J. Hydrogen Energy 2015, 40, 16985.
[94] G. Aft, D. Hennings, G. de With, J. Appl. Phys. 1985, 58, 1619.
[95] T. Hoshina, J. Ceram. Soc. Jpn. 2013, 121, 156.
[96] R. Kulagin, Y. Zhao, Y. Beygelzimer, L. S. Toth, M. Shtern, Mater. Res. Lett. 2017, 5, 179.
[97] A. E. Medvedov, M. Y. Murashkin, N. A. Enikeev, R. Z. Vaviev, P. D. Hodgson, R. Lapovok, Adv. Eng. Mater. 2018, 20, 1700867.
[98] K. Edalati, T. Daio, S. Lee, Z. Horita, T. Nishizaki, T. Akune, T. Nojima, T. Sasaki, Acta Mater. 2014, 80, 149.