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Creep Deformation of Mg-PSZ under Compressive Loading

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Abstract: Mg-PSZ (magnesia-partially-stabilized zirconia) has been studied under compressive loading at room temperature. Mechanical strain was recorded continuously using strain gauges while the sample phase composition and microstructure has been recorded at regular intervals on the ENGIN-X pulsed-neutron facility at the Rutherford-Appleton Laboratory in Didcot, England. Diffraction pattern analysis has been accomplished using the GSAS II software. The observed mechanical strain is time dependent, and a correlation is established between the mechanical creep strain and the phase and microstructural changes observed. Deformation and associated microstructural changes have been observed for all applied loads but were most marked for the highest load which was -1,200 MPa. It is suggested that the ongoing deformation and microstructural changes after unloading the specimen, are on account of a stress within the sample.

Key words: Mg-PSZ, compressive loading, mechanical strain, neutron diffraction.

Nomenclature

E	Young's Modulus
T	timing window
d_{hkl}	interplanar spacing for the *hkl* crystal planes
Å	Angstrom unit
mm	millimetre
a_0, b_0, c_0	lattice parameters for a crystalline phase
P	phase
W_p	weight fraction of phase, p
N	number of phases
S_{pF}	phase fraction of phase, p
m_p	mass per unit cell of phase, p
V_p	volume fraction of phase, p
wR	data residual in GSAS II fit
T	time (in seconds)

Greek Letters

δ	a phase in Mg-PSZ, $Mg_2Zr_5O_{12}$
ν	Poisson's ratio
$\mu\varepsilon$	microstrain
μs	microseconds
β	angle in a monoclinic lattice
μm	microns
υ_p	volume per unit cell of phase, p
σ	stress
ε	strain

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1. Introduction

Pure zirconia, ZrO_2, is not a useful material because phase transformations as it cools after processing at high temperature, are accompanied by dilatational and shear strains that lead to cracking. The addition of oxides such as MgO, stabilizes the high-temperature phases and the resultant "partially-stabilized zirconia", Mg-PSZ (magnesia-partially-stabilized zirconia), is used in many applications [1]. Commercially available Mg-PSZ contains 8 to 10 mol % MgO, as illustrated in the phase diagram (Fig. 1). But, in addition, it is known to contain the δ phase ($Mg_2Zr_5O_{12}$) which is tetragonal [2] and a small amount of orthorhombic (o-ZrO_2) [3, 4]. At room temperature, Mg-PSZ is essentially a composite comprised of a mixture of cubic (c-ZrO_2), tetragonal (t-ZrO_2), monoclinic (m-ZrO_2) as well as the above two phases. Fig. 2 shows this composite microstructure at both the optical and electron microscope scales.

There are two, little-understood features of the material. First, the transformation t-ZrO_2 to m-ZrO_2

(which is martensitic) is time-dependent, causing creep under a constant stress [5]. Second, when the applied stress is removed, the creep strain reverses [6]. These effects occur under both tensile and compressive stresses, but at very different magnitudes.

In a presentation at the ICOMAT2017 (International Conference on Martensitic Transformations) [7], it was shown, as the result of an *in-situ* neutron diffraction experiment in which an Mg-PSZ sample was loaded in compression, that for applied loads in excess of ~1,200 MPa, the m-ZrO_2 content of the sample increased while the t-ZrO_2 content decreased. However, these workers did not look for these previously reported, time-dependent, "creep" effects.

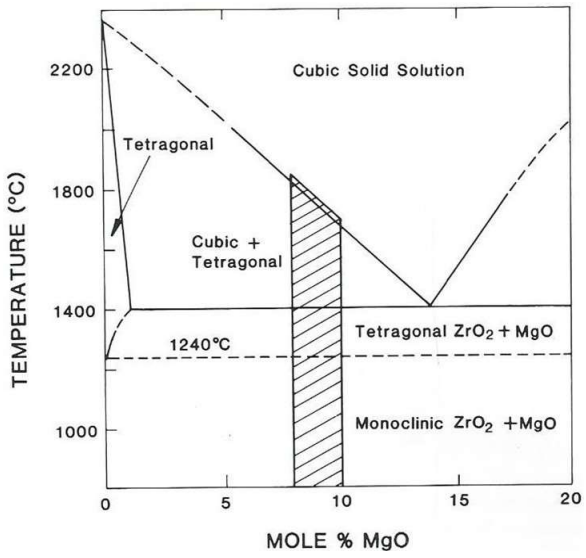


Fig. 1 Phase diagram for Mg-PSZ (after Green et al. [1]).

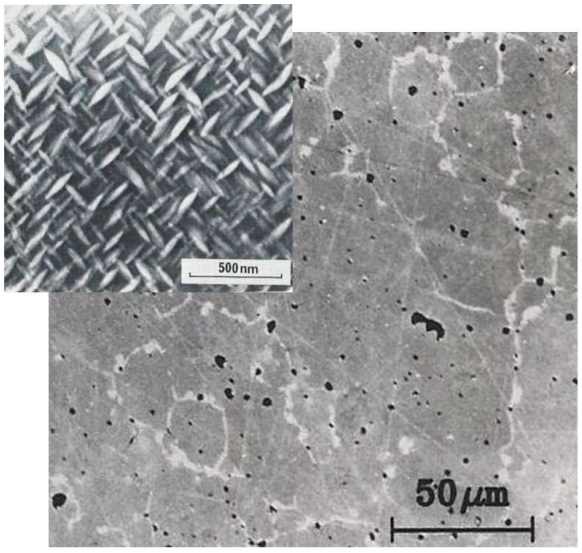


Fig. 2 Optical micrograph of Mg-PSZ showing c-ZrO_2 grains and an electron micrograph showing t-ZrO_2 particles within the grains (after Gross [8]).

In the light of this background, we have studied Mg-PSZ in compression and simultaneously measured sample deformations (using strain gauges) and the accompanying phase and microstructural changes using neutron diffraction at the ENGIN-X beamline on the ISIS, pulsed-neutron source at the Rutherford-Appleton Laboratory, Didcot, Oxfordshire, England.

The results reported here were for one sample for which, following initial neutron diffraction measurements at a very small load, measurements were taken at a series of loads and intervening periods of recovery, as summarised in Section 3. Throughout the total time, mechanical strains were continuously recorded.

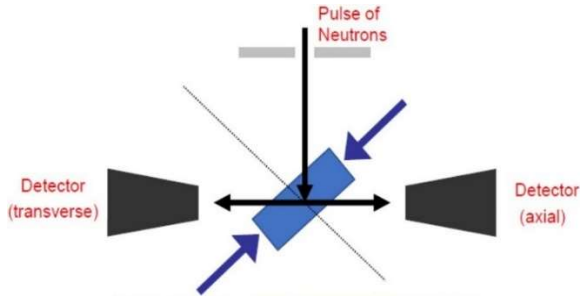
2. Experimental Methods

2.1 Specimen Material

The material used for this experiment was a TS-grade Mg-PSZ, originally supplied by Nilcra Ceramics, a small company which is now owned by Morgan Technical Ceramics Pty., Ltd. [9]. Indeed, the machining of the sample for this current research was done by Morgan Technical Ceramics.

A "dogbone" sample design, based on ASTM C1424-15 (2015) "Test method for monotonic, compressive strength of advanced ceramics at ambient temperature", was used. The design eliminates friction end effects from the platens but introduces a small stress concentration at the shoulder. The stress concentration factor is 1.02. Sample machining to this design was completed by the Technical Department at Morgan Technical Ceramics by diamond machining. The gauge section for the sample was 9 mm in diameter and 21 mm long.

Three strain gauges were placed around the circumference at each of two positions along the gauge length (six gauges) to check for alignment/bending in setting up a compression experiment. But for the final data collection, only the data from the central set of strain gauges were recorded for the subsequent test.



(a)

(b)

Fig. 3 (a) schematic diagram for the time-of-flight diffractometer on the ENGIN-X beamline at the ISIS facility. (b) Picture of the compression sample loaded on the Instron mechanical testing machine.

The compression sample prepared for testing is pictured in Fig. 3.

2.2 In-Situ Mechanical Testing

The specimen was loaded in compression, using the 100 kN Instron at the ENGIN-X beamline on the pulsed-neutron facility, ISIS, of the Rutherford-Appleton Laboratory, Didcot, England, through Experiment RB 1810284.

2.2.1 Initial Sample Loading

The sample was systematically loaded to a low stress (typically ~-300 MPa) in order to check the sample for bending and to record both the Young's modulus, E, and the Poisson's ratio, ν. Values for E and ν of 205.5 GPa and 0.299, respectively, were consistent with the published data for Mg-PSZ [9], and demonstrated that the sample strain gauges were well calibrated.

It must be admitted that while every attempt was made, using the alignment screw adjustments on the Instron, it proved impossible to remove any bending completely, as recorded via the readings of the three strain gauges around the circumference of the gauge length, as these adjustment screws were at their limits. So, at best, the bending was minimised to ~300 με at a load of -200 MPa.

2.2.2 Sample Creep Tests

For the loading sequence given in Section 3, the accompanying mechanical strain-gauge readings were recorded every 0.5 s while the sample phase content was recorded via neutron diffraction patterns every 30 min. Typically, the time to reach the applied load, when the neutron diffraction data collection was commenced, was a few minutes.

While every 0.5 s datum could be used in analysing just the creep strains as functions of time, for comparison of the mechanical strain data with the microstructural changes, the average strains during the time required for statistically acceptable diffraction patterns, could easily be determined.

2.3 Neutron Diffraction

The neutron diffraction measurements were carried out on the ENGIN-X beamline at the ISIS facility of the Rutherford-Appleton Laboratory, Didcot, England. The schematic arrangement for the time-of-flight diffractometer is shown in Fig. 3. For a specimen under compressive load, the detectors (Bank 1 and Bank 2) measure time-resolved diffraction patterns corresponding to scattering vectors aligned at ±45° to the incident beam and for scattering from grains having crystal lattice plane normals aligned axially (Bank 1) and transversely (Bank 2), within the scattering volume. For the data reported here, the timing window was set to $8{,}400 \leq T \leq 60{,}000$ μs, thereby detecting all Bragg reflections from the phases within the scattering volume for $0.459 \leq d_{hkl} \leq 3.281$ Å. The scattering volume as set by the beam collimation, was a section 4 × 4 mm^2 horizontally and 3 mm high. In a preliminary run using this scattering volume in an Mg-PSZ sample blank from the same batch of TS-grade material, it was resolved that a counting time of 30 min gave a diffraction pattern with sufficient peak intensity for reliable data analysis.

Before commencing the Mg-PSZ experiment, the detectors were calibrated following the standard procedure in use at the ENGIN-X beamline, using a NIST standard CeO_2 powder sample. Despite this CeO_2

calibration, a further measurement of a powder sample of NiO, gave values of a_0 for NiO from the Bank 1 and Bank 2 detectors which differed by ~0.63%, which is difficult to explain and which is of concern for the current experiment where anisotropy within the multiphase Mg-PSZ sample may be of concern for the data analysis.

2.4 Neutron Data Analysis

The diffraction data were analysed using the GSAS II software [10] for which, in the case of the pulsed-neutron data from ENGIN-X, an instrument parameter file had been created for each detector bank (Banks 1 and 2) making use of the CeO_2 detector calibration data.

GSAS II also requires a "Blank Phases" file containing the crystallographic data (i.e., space groups and lattice parameters) for all phases in the sample. For Mg-PSZ there are several different possible data sets in the literature, but for our data analysis the "Blank Phases" file from which the analysis of diffraction patterns was commenced, is summarised in Table 1.

To achieve a satisfactory fit to most diffraction data sets required systematic refinement of phase fraction, size (in μm) which can be either isotropic or uniaxial (with both equatorial and axial parameters), microstrain (also either isotropic or uniaxial with equatorial and axial parameters), preferred orientation (via spherical harmonics and typically for the t-ZrO_2 and m-ZrO_2 phases), lattice parameters and thermal parameters (typically for t-ZrO_2). While the standard GSAS II software also outputs the weight fraction, W_p, for phase, p, is calculated as follows for a total of N phases in a sample:

$$W_p = \frac{S_{pF} m_p}{\sum_1^N S_{pF} m_p} \quad (1)$$

where S_{pF} is the phase fraction of phase, p, and m_p is the mass per unit cell of phase, p, the volume fraction of the phase, V_p, can then be calculated as follows:

$$V_p = \frac{S_{pF} \upsilon_p}{\sum_1^N S_{pF} \upsilon_p} \quad (2)$$

where υ_p is the volume per unit cell of phase, p, which is the volume output in GSAS II analysis as determined from the refined lattice parameters.

Table 1 Space groups and lattice parameters for the "Blank Phases" file (after Kisi [11]).

Phase	Space Group	Lattice Parameter(s)
c-ZrO_2	$Fm\bar{3}m$	a_0 = 5.07693 Å
t-ZrO_2	$P4_2/nmc$	a_0 = 3.58964 Å, c_0 = 5.18255 Å
m-ZrO_2	$P2_1/c$	a_0 = 5.1477 Å, b_0 = 5.16664 Å, c_0 = 5.32152 Å, β = 98.957°
o-ZrO_2	$Pbc2_1$	a_0 = 5.068 Å, b_0 = 5.26 Å, c_0 = 5.077 Å
δ-$Mg_2Zr_5O_{12}$	$R\bar{3}$	a_0 = 9.43243 Å, c_0 = 8.78925 Å

The quality of GSAS II analysis is determined in part by the data residual, wR, but it is also informative in arriving at a "best fit", to examine three specific peaks, which, traditionally, was known as the "polymorph method" and which includes two distinct peaks, the $(111)_m$ and $(11\bar{1})_m$, from the m-ZrO_2 phase, on either side of a complex peak arising from the $(211)_\delta$, $(3\bar{1}1)_\delta$, $(003)_\delta$ and $(202)_\delta$ peaks from δ-$Mg_2Zr_5O_{12}$, and the $(111)_c$, $(111)_t$ and $(111)_o$ peaks, from c-ZrO_2, t-ZrO_2 and o-ZrO_2, respectively [12].

3. Results

As had been reported previously for Mg-PSZ in compression [7], appreciable change in the phase content for a sample did not occur until a stress of -1,200 MPa was applied to the sample. Something similar was found in the current experiment. The sample was loaded in a sequence of creep tests as follows: loaded to -50 MPa for 322 min; then to -600 MPa for 77 min; to -800 MPa for 86 min; and to -1,000 MPa for 801 min; before being unloaded to -50 MPa, and diffraction patterns recorded.

Mechanical strains were continuously recorded for the next 599 min before neutron diffraction patterns were again recorded with the sample held in the Instron at a load of -21 MPa. A second period of recovery occurred for 1,775 min before further diffraction patterns were recorded with the sample in the Instron at -18 MPa.

The sample was then loaded to -1,200 MPa and diffraction patterns collected for the subsequent 660 min, followed by unloading to -50 MPa and the

collection of further diffraction patterns. A final diffraction pattern was collected at ENGIN-X following a further nine days of recovery.

3.1 Mechanical Strains

The creep strains for a sample under load are determined as follows:

$$\varepsilon_{axial}^{creep} = \varepsilon_{axial}^{meas} - \frac{\sigma_{appl}}{E} \quad (3)$$

$$\varepsilon_{trans}^{creep} = \varepsilon_{trans}^{meas} - \frac{\nu\sigma_{appl}}{E} \quad (4)$$

and

$$\varepsilon_{volume}^{creep} = \varepsilon_{axial}^{creep} + 2\varepsilon_{trans}^{creep} \quad (5)$$

where E is the Young's modulus and ν is the Poisson's ratio for the sample. When the sample has been unloaded or is on the Instron under minimal loading and is in recovery, the measured strains are just the creep strains so that:

$$\varepsilon_{volume}^{creep} = \varepsilon_{axial}^{meas} + 2\varepsilon_{trans}^{meas} \quad (6)$$

In either case, Chen and Reyes-Morel [13] have shown that the shear component of the creep volume strain is given by:

$$\varepsilon_{shear}^{creep} = \frac{5}{6}\varepsilon_{volume}^{creep} \quad (7)$$

The volume creep strains as recorded via the axial and transverse mechanical strains, are plotted in Fig. 4, for each of the loads applied. The times in this figure correspond to those which will be used later for the microstructural analysis.

Specifically for the sample loaded at -1,200 MPa for which the observed mechanical creep was most pronounced, the components of mechanical creep strain (axial, ε_l, transverse, ε_t, volume, ε_{vol}, and shear, ε_{shear}, (Eqs. (3) to (7))) are shown in Fig. 5.

3.2 Microstructural Data

Fig. 6 shows an example of a complete neutron diffraction pattern, plotted as Intensity vs. Time-of-Flight. (For a more conventional diffractionist, one might picture this as Intensity vs. Two-Theta, going from right

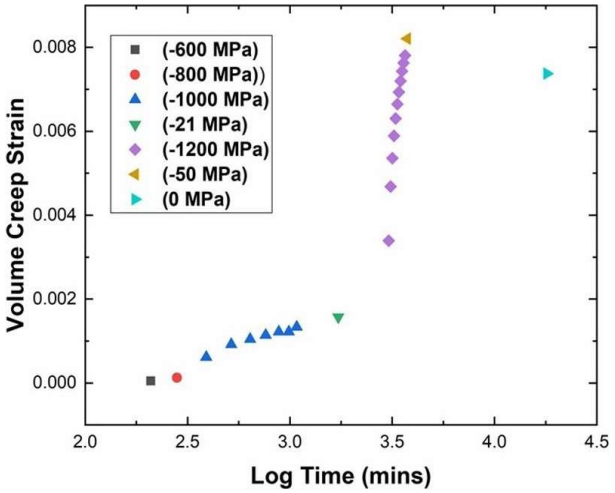


Fig. 4 Volume creep strains for the sample, measured by the mechanical strain gauges, for the various applied loads.

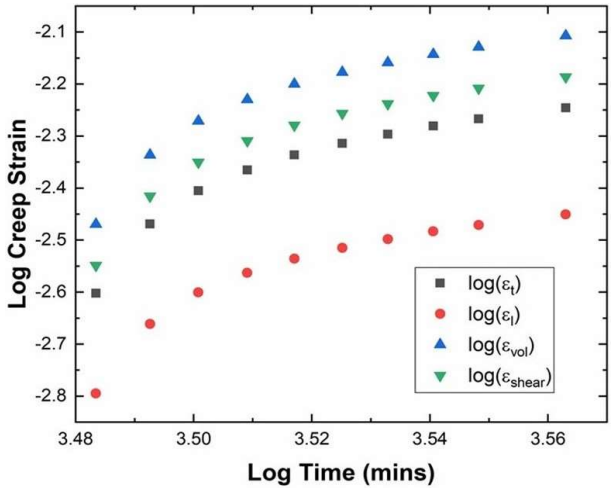


Fig. 5 Components of mechanical creep strain vs. time, for the sample under -1,200 MPa.

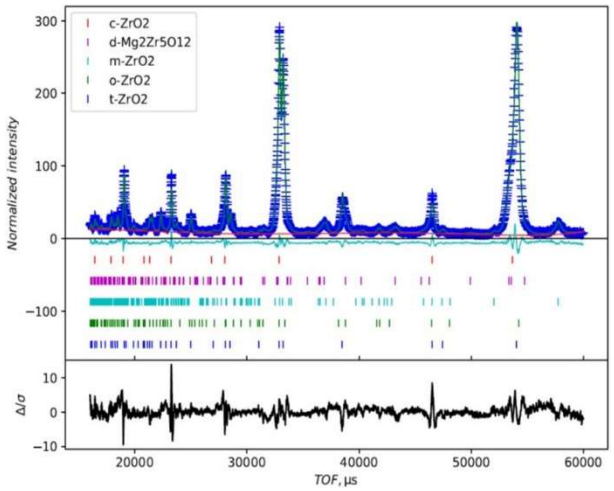


Fig. 6 Typical diffraction pattern from the "as-received" Mg-PSZ showing analysis using GSAS II software [10], for which wR = 8.065%.

to left.) As is mentioned above, achieving a "best fit" to the difraction data analysis is partly based on the the data residual, wR, from the GSAS II program but in addition, the polymorph method [12] was also used on each diffraction pattern refinement. An example of this for the "best fit" to the data in Fig. 6, is shown in Fig. 7.

As mentioned above, the GSAS II software outputs the weight fraction for each of the phases (Eq. (1)) and as shown earlier, the volume fraction of each phase in the microstructure, V_p, can be determined using Eq. (2). As observed in Fig. 4, while there was a mechanical creep strain observed for all applied loads, as well as during periods of recovery, the volume creep strain was most marked under the applied load of -1,200 MPa.

In Fig. 8, the corresponding variations in phase content for each of the five phases, are plotted, where the most noticeable changes in phase content are a decrease in the tetragonal phase and increases in the monoclinic and orthorhombic phases, suggesting that "creep", as measured by microstructural changes, can be represented as:

$$\text{Vol. "creep" strain} = 0.0425\times\Delta V_{\text{mono}} + 0.0115\times\Delta V_{\text{ortho}} \quad (8)$$

where ΔV_{mono} and ΔV_{ortho} are the differences between V_{mono} and V_{ortho}, after any time and the respective phase volume fractions measured in the sample in its as-receieved condition. The constants, 0.0425 and 0.0115 are the volume strains accompanying the t-ZrO_2 to m-ZrO_2 and t-ZrO_2 to o-ZrO_2 transformations, respectively [14].

Fig. 9 shows the complete data set for all loads as well as for the sample in recovery following any respective load cycle. Fig. 10 shows the volume creep strains measured from the microstructural changes as a function of those measured mechanically (Fig. 4), where the correlation persists even for data during recovery stages (i.e., -21 MPa, -50 MPa and 0 MPa.)

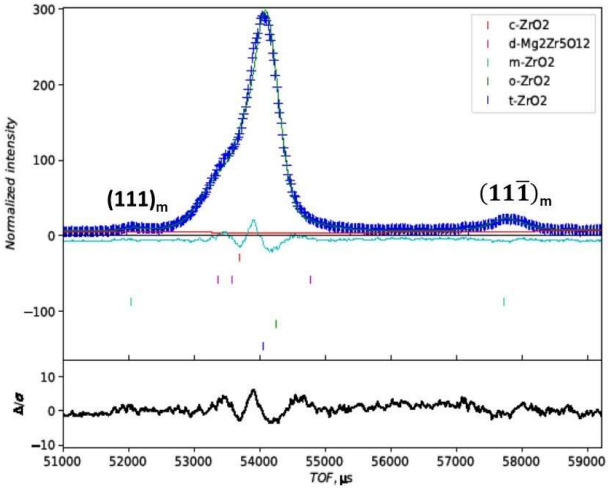


Fig. 7 Example of the polymorph method [12] used to determine the "best fit" to the complete neutron diffraction pattern, as in Fig. 6.

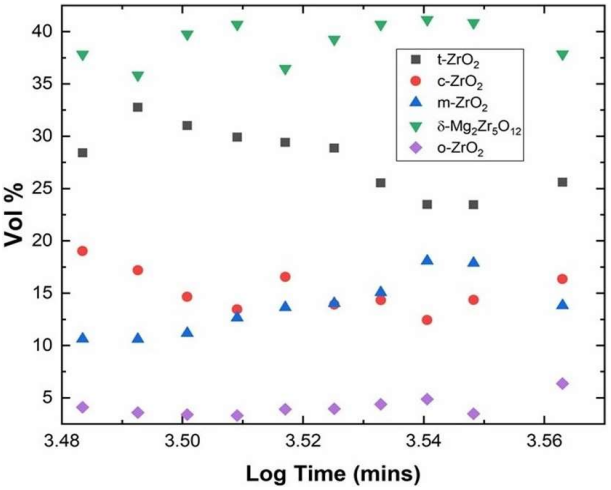


Fig. 8 Variations of the phase contents for the Mg-PSZ sample, under -1,200 MPa.

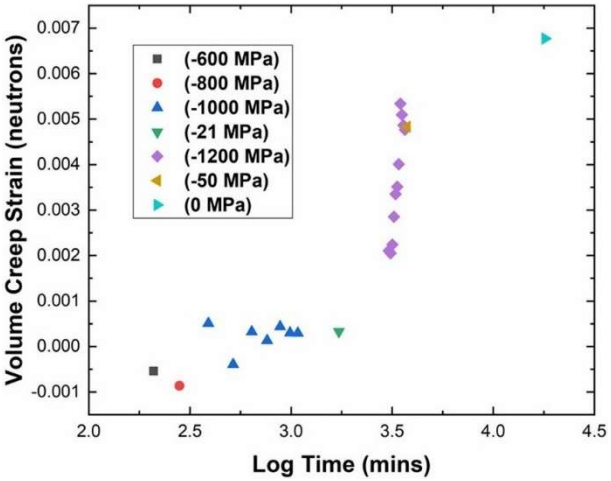


Fig. 9 Volume creep strain as measured from the sample microstructure determined by neutron diffraction.

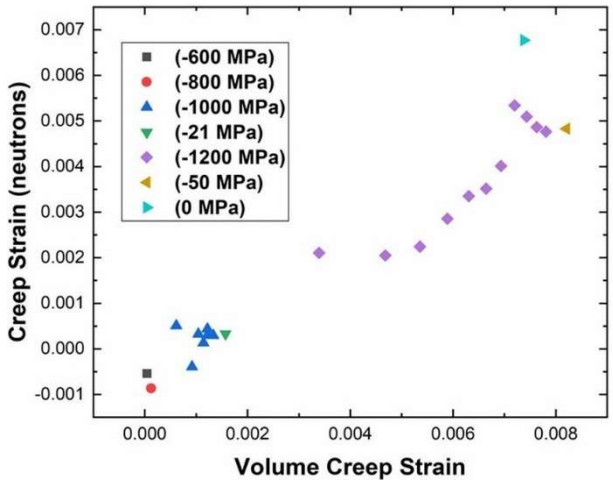


Fig. 10 Correlation of microstructural and mechanical creep strains for all loads, including times for the sample in recovery.

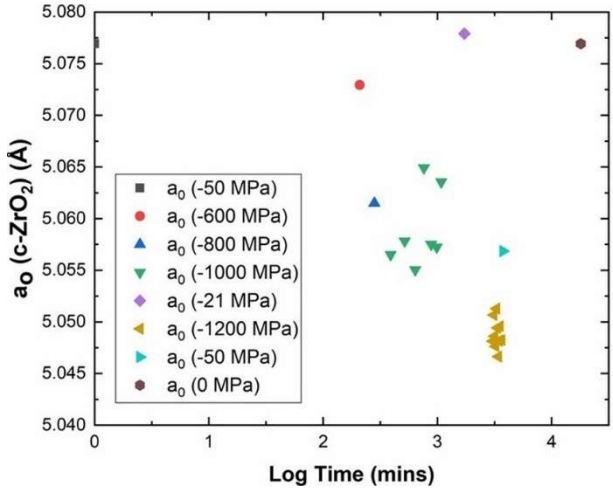


Fig. 11 Lattice parameter for the c-ZrO_2 (matrix) phase for the various applied loads (including minimal loads following periods of recovery) vs. time.

4. Discussion

The question is how the correlation shown in Fig. 10 might be explained. To this end, the lattice parameters for all five phases resulting from the microstructural analysis have been closely examined. With the exception of the lattice parameters for c-ZrO_2, (essentially the matrix phase for the composite sample microstructure (Fig. 2)), the variations are simply those that would be expected with the application of the applied stress. However, for the c-ZrO_2, the lattice parameters as plotted in Fig. 11, show that while the sample was held under load, the lattice parameters are slightly larger than those expected on the basis of the elastic constant for Mg-PSZ [9]. For example, on application of -1,200 MPa, the lattice parameter for the c-ZrO_2 phase was 5.048 Å, compared with 5.047 Å expected from the elastic constant. But on removal of the -1,200 MPa (i.e., the -50 MPa datum), the lattice parameter does not recover to its expected value of 5.076 Å, as expected from the elastic constant, but was 5.057 Å. These differences suggest the development of a matrix stress as the source for further transformation in the recovery stage of the experiment.

5. Conclusions

Time-dependent deformation (creep) has been observed for Mg-PSZ at room temperature under all compressive loads but with most marked deformation occurring for -1,200 MPa. A correlation has been observed between the volume creep deformation recorded mechanically (via strain gauges) and that measured microstructurally using neutron diffraction. The creep strain is caused by the stress-induced transformation of tetragonal phase to monoclinic and orthorhombic phases due to volume strains associated with the phase transformations. Ongoing transformation in the sample, followiing the removal of the applied load, is driven by a stress in the cubic matrix.

Acknowledgements

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