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Anelasticity of precursor derived Si–B–C–N ceramics

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Abstract

Partially crystalline precursor derived Si–B–C–N ceramics were investigated at elevated temperatures by compression creep experiments. Load change and constant load experiments at various temperatures in the range of 1300–1500 °C yield viscosity data as high as 10^{15}–10^{16} Pa s and the values were determined assuming Newtonian flow. The anelastic behavior was analyzed with the help of Kohlrausch–Williams–Watts equation (KWW) and the fitting parameters are used to describe the relaxation behavior of this family of materials.

Keywords: Precursors-organic; Porosity; Creep; Anelasticity

1. Introduction

Solid state thermolysis of organometallic polymers offers a promising route for the fabrication of quaternary Si–(B)–C–N ceramics for high temperature use, as they possess excellent thermal, chemical and mechanical stability at very high temperatures.[1–6] The absence of a low melting point grain boundary phase in them leads to an entirely different behavior from that of conventionally sintered materials. It was shown that the total deformation rate of as-thermolyzed, i.e. amorphous materials consists of an irreversible stress dependent component, attributed to viscous flow; a stress independent component ascribed to shrinkage (in the case of amorphous materials) or expansion (in the case of crystalline ceramics) and a time dependent reversible anelastic component.[4,6] The anelastic behavior of precursor derived Si–(B)–C–N in the amorphous state was analyzed previously.[4,7] It was shown that the anelastic strain rate decreases (inverse proportional) with time after stress changes. It was further shown that, at a fixed stress difference, the anelastic strain rate is independent of the previous testing time.[7] This paper reports on the anelastic behavior of Si–B–C–N ceramics which have been partially crystallized by heat treatments at 1800 °C after thermolysis.

2. Experimental

Two types of materials obtained from boron modified polyvinylsilazanes with the chemical composition $(B[C_2H_4–Si(H)NH]_3)_n$ and $(B[C_2H_4–Si(CH_3)NH]_3)_n$, hereafter referred to as MW-33 and T2-1, respectively, were investigated. The polymer precursors were synthesized in-house. The details of the polymer synthesis of MW-33 and T2-1 are described elsewhere.[1,8] The brittle unmeltable polymers were ground using a tungsten carbide ball mill and the polymer particles were sieved in to various size fractions. Polymer particles were then compacted in a graphite die at a uniaxial pressure of ∼48 MPa in the polymer softening temperature range of 280–330 °C. The optimum warm pressing temperature is however dependent on the size of the polymer particle distribution used for compaction. The polymer green bodies were then converted to amorphous ceramics by solid state thermolysis in argon atmosphere by heating them up to 1300 °C for 2 h. For the present study, as-thermolyzed MW-33 derived ceramics were heat treated for crystallization at 1800 °C under the following conditions: (i) 1 h, 1 MPa N_2, (ii) 3 h, 1 MPa N_2, (iii) 1 h, 10 MPa N_2 and (iv) 3 h, 10 MPa N_2. The as-thermolyzed T2-1 derived materials were heat treated at 1800 °C for 3 h, and at 1 MPa N_2. The heat treatments were done in a high temperature furnace (FCT, Germany).

Load change experiments on MW-33 derived materials and constant load experiments on T2-1 derived materials by compression creep were conducted in atmospheric ambience in the temperature regime of 1300–1500 °C. Load change experiments were carried out by loading the specimens at 100 MPa for the

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time period of 2×10^5 s, followed by loading at 150 MPa for 3×10^5 s and finally at 200 MPa for 5×10^5 s. The specimens were then unloaded to 5 MPa, which is just sufficient enough to hold the specimen in position. Subsequently, the displacement was recorded until it reached a constant value. Constant load experiments were carried out at four different compressive loads (25, 50, 75 and 100 MPa) at 1500 °C for 200 h. The universal testing machines from Amsler and Zwick were used for the creep measurements of MW-33 and T2-1 derived materials, respectively. The load is applied via a spiral spring preloaded by a spindle and with a linear potentiometer the compression of the spiral spring is measured. The uniaxial deformation of the samples was measured using three scanning pins. Two scanning pins are connected to the upper SiC load pad, while the third touches the lower SiC load pad. The distance between the upper and lower load pads is measured via an inductive strain gauge, which is located in the cold part of the testing machine.[9]

3. Results and discussion

Although the polymers used are quite differently structured, the composition of both ceramic materials is quite similar.[8,10] However, due to the different processing conditions their microstructures differ substantially. The MW-33 derived materials have low porosity with small pores (<10 μm) contrary to T2-1 derived materials, which exhibited substantial porosity and pores in the size range of ~200 μm with associated open pore channels. Fig. 1 shows representative micrographs corresponding to MW-33 derived and T2-1 derived materials exhibiting the pore size, morphology and distribution. The differences in the microstructures were due to the fact that T2-1 derived materials were produced using coarse powder fraction (80–160 μm) for compaction into a green body unlike the MW-33 derived materials where a wide range of polymer particle sizes were used. Around 40% of polymer particles in the size range of 32–80 μm, and 18% in the size range <32 μm which were used for compaction along with coarser fractions resulted in denser compacts. The studies have indicated a pronounced influence of the size of polymer particles on the resulting microstructure and henceforth on the oxidation behavior and the high temperature mechanical properties.[11]

The structural characterization of the crystallized materials under investigation has indicated that the kinetics of crystallization strongly depends on the annealing conditions. X-ray diffraction, TEM and solid-state NMR data of MW-33 derived material clearly demonstrate that, within the selected annealing conditions at 1800 °C the material heat-treated for 3 h and at 1 MPa N_2 revealed the highest crystallinity, whereas that annealed for 1 h at 10 MPa is still amorphous. This means that a high nitrogen pressure stabilizes the amorphous state, i.e. retards the crystallization of SiC and suppresses the formation of Si_3N_4 nanocrystals.[12] Therefore, for crystallization of the T2-1 derived material, it was also annealed at 1800 °C for 3 h at 1 MPa N_2. Compression creep studies on MW-33 derived materials indicated that the deformation rates of the crystallized materials are about one order of magnitude smaller than their amorphous counterpart. The observed decreased strain rates in the crystallized materials as compared to the as-thermolyzed materials was mainly due to the densification as a result of annealing and structural changes in the matrix phase.[12] Contrarily, due to the porous microstructure of the T2-1 derived material, the creep behavior was strongly influenced by the excessive internal oxidation of the material. However, in the present study it will be shown that the anelastic behavior of both the materials can be analyzed free of ambiguities irrespective of their processing conditions.

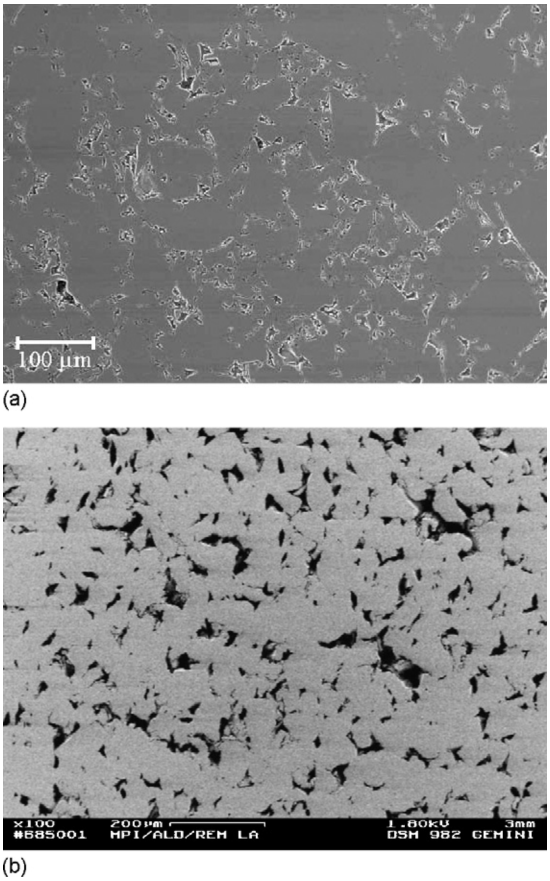

Fig. 1. (a) Optical micrograph of a representative MW-33 derived material annealed at 1800 °C, 3 h, 10 MPa N_2. (b) Scanning electron micrograph of a T2-1 derived material annealed at 1800 °C, 3 h, 1 MPa N_2.

If during a load change experiment the load on the specimen is released or due to the application of a load during a constant load experiment, then a finite time is required to establish equilibrium between stress and strain in the unloading or loading direction, respectively. This time-dependent reversible deformation, which also depends on the applied initial stress, is termed anelastic. In fact, such an anelastic deformation was observed earlier for amorphous precursor-derived Si–C–N and Si–B–C–N ceramics.[4,7] Fig. 2 shows a general trend of the anelastic deformation at loading (a) and at unloading (b) in compression creep experiments. Typical load displacement curves of MW-33 derived materials are shown in Fig. 3. The anelastic strain obtained from the load release experiments was then differentiated to obtain anelastic strain rates for all the materials. In Fig. 4, the time dependence of the anelastic strain rates for the MW-33 derived Si–B–C–N ceramics after different heat

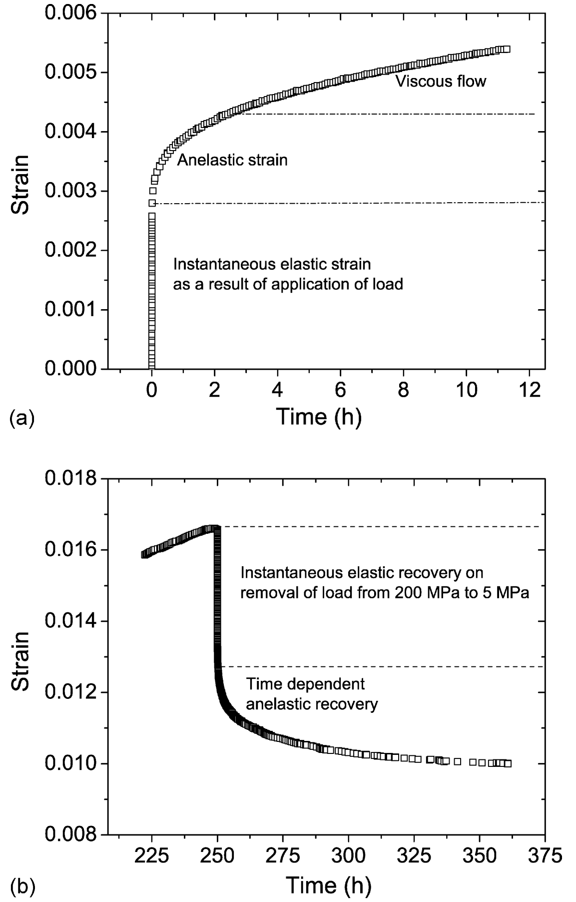

Fig. 2. Evidence for anelastic deformation during (a) constant load experiment and (b) unloading experiment in compression creep studies.

treatments and at a creep temperature of 1400 °C is shown in a double logarithmic representation. Although heat treated under different conditions and structurally being very much different, MW-33 derived ceramics show similar time dependence of anelastic strain rates. Fig. 5 shows equivalent curves derived from T2-1, crystallized at 1800 °C and tested at different loads at a creep temperature of 1500 °C. Similar time dependence of anelastic strain rates was established for T2-1 derived materials obtained from constant load experiments, which was very much analogous to the time dependence observed for MW-33 derived materials. This essentially translates to an unequivocal analysis of the anelastic deformation behavior in both the materials tested by different methods.

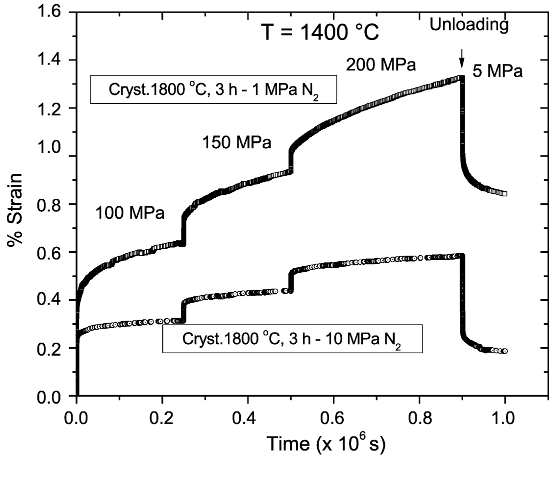

Fig. 3. Representative deformation curves during load change experiments of MW-33 derived partially crystalline Si–B–C–N ceramics at 1400 °C, crystallized at 1800 °C at different nitrogen gas pressure.

The anelastic deformation is analyzed using the well known Kohlrausch–Williams–Watts equation.[13] The phenomenon of the decay of a residual charge in Leyden jars was studied by Kohlrausch, who formulated the relaxation equation for the residual charge, $Q(t)$, as:

$$\frac{\mathrm{d}\,Q(t)}{\mathrm{d}\,t} = -\gamma(t)Q(t), \tag{1}$$

where $\gamma(t)$ decreases with time according to an inverse power law given by the expression:

$$\gamma(t) \approx t^{-(1-\beta)}, \quad 0 < \beta < 1. \tag{2}$$

The integration of the above equation leads to the stretched exponential relaxation and is given by:

$$Q(t) = Q(0)\exp\left[-\left(\frac{t}{t_0}\right)^{\beta}\right]. \tag{3}$$

Kohlrausch relaxation has been found empirically to describe relaxation processes in many materials systems and the values of the stretched exponent β lies in the interval [0, 1]. The anelastic strain is then given by using a similar analogy as given in Eq. (3):

$$\varepsilon_{\mathrm{an}}(t, T) = \varepsilon_0 \exp\left[-\left(\frac{t}{\tau_{\mathrm{rel}}(T)}\right)^{\beta}\right], \tag{4}$$

where, ε_0 is the pre-exponential constant and τ_{rel} is the total relaxation time, which is a function of temperature and time owing to the nature of the materials under investigation which undergo continuous structural evolution with time. However, if the time dependence of viscosity is utilized as a measure for the structural relaxation, then the time dependence of the anelastic relaxation time can be neglected. That means, the anelastic process is much faster (completed after 10^4 s) compared to the continuous time-dependent rise of the viscosity and hence the dependence of τ_{rel} for the anelastic process on time is neglected in Eq. (4).

The differentiation of Eq. (4) leads to the anelastic strain rate which is used to fit the experimental data obtained so far in the present study, which is given by:

$$\dot{\varepsilon}_{\mathrm{an}}(t, T) = -\frac{\varepsilon_0\beta}{t}\left(\frac{t}{\tau_{\mathrm{rel}}(T)}\right)^{\beta} \exp\left[-\left(\frac{t}{\tau_{\mathrm{rel}}(T)}\right)^{\beta}\right]. \tag{5}$$

The above equation was used to fit the data obtained during load release experiments from 200 to 5 MPa at 1400 °C, for differently heat treated MW-33 derived Si–B–C–N ceramics. The fitting parameters are given in Table 1. In Fig. 4, the curve based on these data and measured data are shown. They are in good accordance. Under identical testing conditions, the stretched

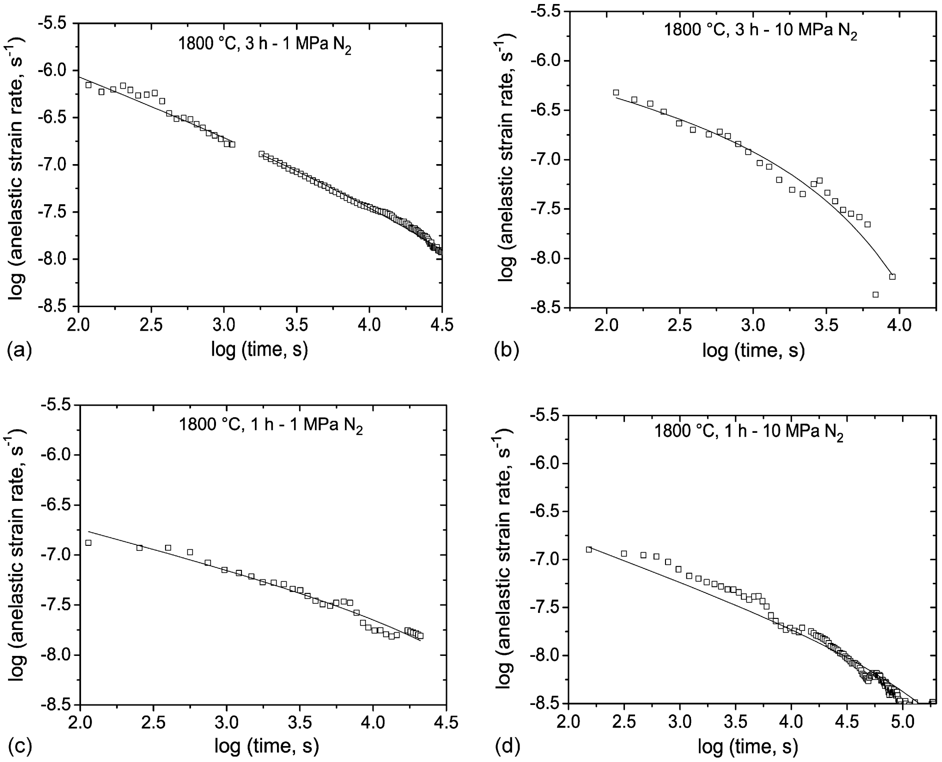

Fig. 4. Time dependence of anelastic strain rates at $T = 1400\,^{\circ}\mathrm{C}$ of MW-33 derived crystalline Si–B–C–N ceramics annealed at 1800 °C: (a) 3 h–1 MPa N_2, (b) 3 h–10 MPa N_2, (c)1 h–1 MPa N_2, (d) 1 h–10 MPa N_2.

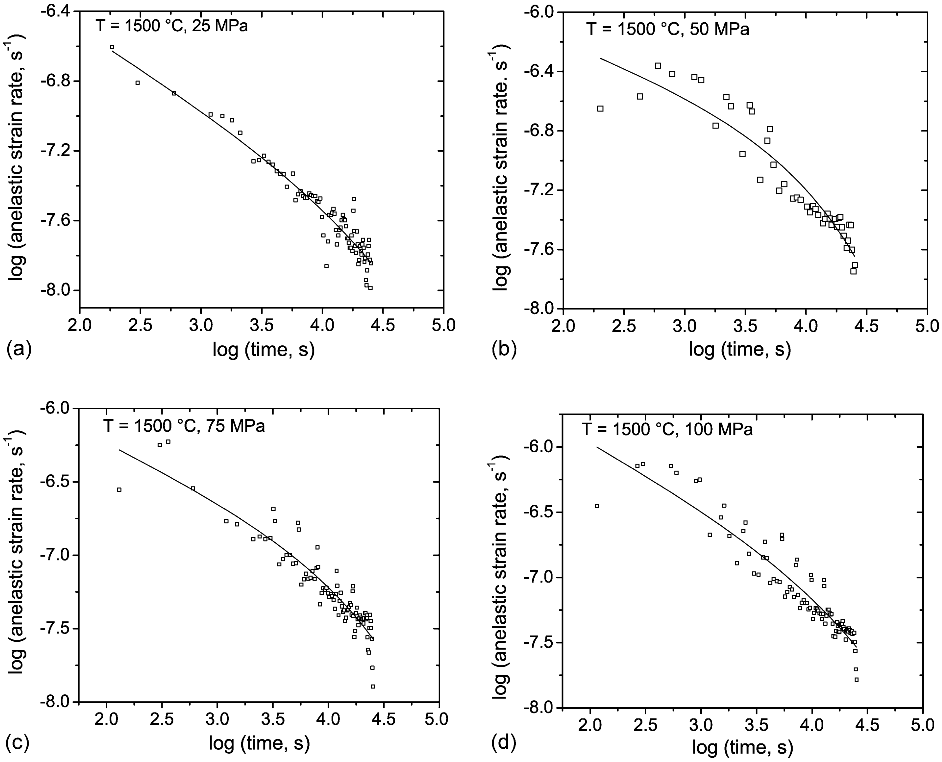

Fig. 5. Anelastic deformation rates of T2-1 derived partially crystalline Si–B–C–N ceramics crystallized at 1800 °C at a creep temperature of 1500 °C and at different stresses: (a) 25 MPa, (b) 50 MPa, (c) 75 MPa, and (d) 100 MPa.

Table 1
KWW fitting parameters ε_0, β and τ determined for differently annealed Si–B–C–N ceramics in the MW-33 system during a load release experiment at 1400 °C

Material	ε_0	β	τ (s)
1800 °C, 3 h–1 MPa N_2	0.0026	0.41	36466
1800 °C, 3 h–10 MPa N_2	0.00054	0.64	1862
1800 °C, 1 h–1 MPa N_2	0.0015	0.61	60000
1800 °C, 1 h–10 MPa N_2	0.0021	0.48	176808

Table 2
KWW fitting parameters ε_0, β and τ at various temperatures determined for partially crystalline Si–B–C–N ceramics in the MW-33 system produced at low and high nitrogen pressure (MW/1 and MW/10, respectively)

	ε_0		β		τ (s)	
	MW/1	MW/10	MW/1	MW/10	MW/1	MW/10
1300 °C	0.0028	0.0011	0.42	0.50	26943	8093
1350 °C	0.0036	0.0010	0.41	0.66	50997	10898
1400 °C	0.0026	0.0005	0.41	0.64	36466	1862

exponent β for the four crystalline materials heat treated differently varies from 0.41 to 0.64 (Table 1) indicating that the relaxation is dominated by multiple relaxations and the relaxation spectrum broadens to a number of activation times and energies. The pre-exponential constant (ε_0) varied from 0.001 to 0.002, except for the material annealed at 1800 °C, for 3 h and 10 MPa N_2 pressure, which exhibited unusual low values of ε_0 and τ_{rel} in contrast to the other materials. The differences in the relaxation behavior of the partially crystalline materials produced at low and high nitrogen pressures (for example: 1800 °C, 3 h and 1 MPa N_2—denoted as MW/1, and 3 h and 10 MPa N_2 pressures—denoted as MW/10) which are structurally very much different,[12] are depicted in Table 2. The values of ε_0 and τ_{rel} at all temperatures investigated are lesser for the material produced at high nitrogen pressure as observed in Table 2. But the stretched exponent β is much higher in the order of 0.5–0.6, which is more close to their amorphous counterparts[12] in contrast to a value of around 0.4 observed for the more crystallized material (MW/1).

The parameters ε_0, β and τ_{rel} used for fitting Eq. (5) to the experimental data of the T2-1 derived material shown in Fig. 5 are given in Table 3. The parameters β and τ_{rel} seem to be independent of the stress; however the parameter ε_0 exhibits stress dependence. Hence the KWW pre-exponential parameter ε_0 is plotted as a function of the applied stress as shown in Fig. 6.

Table 3
KWW fitting parameters ε_0, β and τ at various stresses at a test temperature of 1500 °C determined for partially crystalline Si–B–C–N ceramics (T2-1 derived materials)

Stress (MPa)	ε_0	β	τ (s)
25	0.00184	0.41	26385
50	0.00258	0.40	29315
75	0.00295	0.42	24555
100	0.00378	0.42	25511

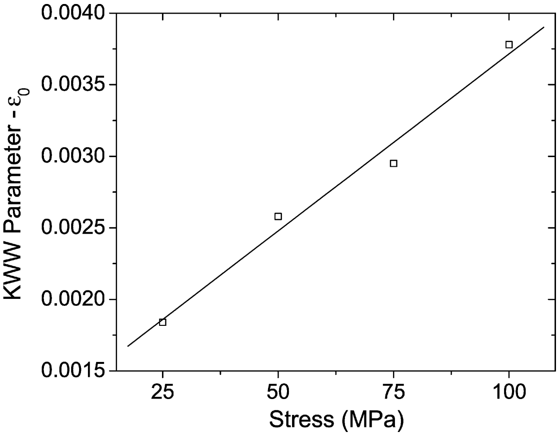

Fig. 6. Stress dependence of the anelastic deformation rate of T2-1 derived material at 1500 °C according to Eq. (5).

A linear dependence of ε_0 with stress is observed, such that an equation of the form $\varepsilon_0 = \varepsilon_c\sigma$ can be formulated, where ε_c is a proportionality constant.

A quantitative microscopic theory was offered by Phillips,[13] which can explain the observed β values for both types of materials, and to understand the microscopic relaxation kinetics. Based on the trap model,[14] the value of β was given by a simple relation which is equal to $d/(d+2)$ where d is the dimensionality of the configuration space in which Brownian motion occurs. According to this model, there exists a static distribution of traps or sinks towards excitations diffuse or disappear in glasses and the stretched exponential reflects the depletion of excitations near traps as time passes. Depending on whether long range Coulomb forces or short range forces dominate the relaxation kinetics, the stretched exponent assumes values equal to 0.43 or 0.62. The nature and effect of these forces on the relaxation behavior of various electronic and molecular glasses, polymers, metallic and oxide glasses are elucidated in literature.[13,15,16]

When long range Coulomb forces dominate the relaxation kinetics, then $d = 3/2$ and $\beta = 3/7$ (0.43) which is in accordance with the experimental values obtained for MW/1 at all temperatures and T2-1 derived materials which exhibited similar values (Table 3) at all stresses. Hence for the more crystallized state of materials, the microscopic relaxation kinetics can be considered to be governed by long range Coulomb forces along with density fluctuations. For a three-dimensional space, where short range forces dominate the microscopic relaxation process, $\beta = 3/5$ (0.62) which is in agreement with the more amorphous state of such materials as in MW/10. However, a β-value of 0.5 for MW/10 at the lowest temperature investigated (Table 2) is close to that obtained for oxidic glasses,[17] which is neither close to 0.43 nor 0.62 and could not be explained using the trap model.

4. Conclusions

Load change and constant load compression creep experiments were used as probes for the investigation of anelasticity of partially crystalline Si–B–C–N ceramics synthesized from two boron modified polyvinylsilazanes (MW-33 and T2-1, respectively). It has been shown that irrespective of the material investigated (MW-33/T2-1) and the testing method, the time dependence of the anelastic strain rate follows Kohlrausch's relaxation. Experimental data obtained from anelastic measurements are in good accordance with the fitted data by the use of the KWW equation. Irrespective of the material and kind of testing, the values of the stretched exponent β range from 0.4 to 0.6 indicating a relaxation spectrum, which cannot be described by a single activation energy.

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