

## Power-law creep in near-equiatomic nickel–titanium alloys

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The compressive creep behavior of nickel-rich B2–NiTi (with 50–140  $\mu\text{m}$  grain size) was studied over the stress range 3–11 MPa and the temperature range 950–1100 °C. The stress exponent ( $n = 2.7$ ) and activation energy ( $Q = 155 \text{ kJ mol}^{-1}$ ) are compared with a literature review of NiTi creep studies performed over lower temperature and/or higher stresses. Possible explanations for discrepancies between studies are discussed.

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As the medical and engineering applications for shape-memory or superelastic NiTi devices grow, so does the importance of repeatable thermomechanical processing procedures (e.g. extrusion, forging, hot-rolling) to shape as-cast ingots into semi-finished and finished products (e.g. wires, tubes, foils or bars) [1,2]. NiTi products have also been produced by high-temperature densification of pre-alloyed powders [3,4], and NiTi foams have been created by expansion of entrapped argon bubbles at elevated temperature [5,6]. Accurate modeling of the above deformation, densification or foaming processes necessitates knowledge of the high-temperature mechanical constitutive law for NiTi. However, only a few studies exist on the creep properties of NiTi, as reviewed below and summarized in Tables 1 and 2.

In 1968, Mukherjee [7] was the first to study the creep properties of NiTi. The tensile flow stress was measured over six temperatures spanning 700–1000 °C (corresponding to homologous temperatures of 0.61–0.80, using the melting point of 1310 °C for equiatomic NiTi) at three constant strain rates spanning two orders of magnitude. The stress exponent and activation energy for creep were discussed in the light of the then-recent theories of viscous creep. Three decades later, Kato et al. [8] published an extensive study of tensile creep in NiTi wires between 628 and 888 °C. Both constant creep rate and constant load experiments were performed. The creep exponent was determined using two

different methods: first by performing strain rate jumps and measuring flow stress, and second by using the reduction in gauge area occurring during deformation to access many different stresses in a single constant load experiment. The former, more standard method gave a stress exponent more than twice that of the latter method. Eggeler and co-workers [9,10] published two studies where tensile creep was measured at lower temperatures (470–560 °C), at which  $\text{Ti}_3\text{Ni}_4$  precipitates formed during heating to the test temperature and coarsened during creep testing. The evolving microstructure resulted in two sets of results: an initial minimum creep rate which was up to two orders of magnitude slower than the subsequent plateau (steady-state) creep rates. The respective stress exponents and activation energies were also different. These authors studied the dislocation structure developed after creep deformation, and the effect of prior creep upon the phase-transformation of NiTi near ambient temperature. Finally, in a recent study, Lexcelent et al. [11] measured the creep rate of NiTi between 600 and 900 °C and obtained an activation energy higher than the tracer diffusivity activation energy of Ni in NiTi.

In the present study, we measure the creep rate of near-equiatomic NiTi for a so-far-unexplored combination of high temperatures (950–1100 °C) and low stresses (3–11 MPa). Our study is also the first to use compression and to report grain size before and after creep deformation. The results are compared with those of the previous NiTi creep studies reviewed above.

A nickel-rich, superelastic NiTi rod (50.8 at.% Ni, 12.7 mm diameter, produced by Nitinol Devices and

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**Table 1.** Summary of prior and present studies

Investigation	Year	Sample diameter (mm)	Ni content (at.%)	Processing
Mukherjee [7]	1968	6.35	50.6	Hot-swaged rod, annealed at 1000 °C
Kato et al. [8]	1999	0.9	49.5, 50, 50.5	Drawn wires, annealed at 900 °C
Eggeler et al. [10]	2002	13	50.7	Rods, solutionized at 850 °C, precipitation and coarsening during creep
Kobus et al. [9]	2002	–	50.7	Annealed at 500–560 °C
Lexcellent et al. [11]	2005	18.5	50.0	Hot drawn bars
Present study	2007	12.7	50.8	Bars, annealed at 950–1100 °C

**Table 2.** Summary of creep conditions and creep parameters measured in prior and present studies

Investigation	Temperature (°C)	Strain rate (s <sup>-1</sup> )	Stress (MPa)	<i>n</i>	<i>Q</i> (kJ mol <sup>-1</sup> )	Grain size (μm)
Mukherjee [7]	700–1000	6 × 10 <sup>-5</sup> –6 × 10 <sup>-3</sup>	6–178	3 ± 0.2	251 ± 13	–
Kato et al. [8]	628–888	1 × 10 <sup>-5</sup> –2 × 10 <sup>-2</sup>	11–81	1 and 5.9 (2.5 ± 0.2 <sup>a</sup> )	230–253	15
Eggeler et al. [10]	470–530	2 × 10 <sup>-9</sup> –8 × 10 <sup>-6</sup>	90–150	2	334	35
Kobus et al. [9]	500–560	2 × 10 <sup>-7</sup> –3 × 10 <sup>-5</sup>	120–180	5	421	–
Lexcellent et al. [11]	597–897	3 × 10 <sup>-3</sup> –4 × 10 <sup>-2</sup>	10–35	3	222 ± 30	–
Present study	950–1100	1 × 10 <sup>-6</sup> –1 × 10 <sup>-5</sup>	4.7–11	2.7 ± 0.2	155 ± 14	48–140

<sup>a</sup> Single sample method.

Components) was cut into 25.4 mm high cylindrical specimens whose ends were ground flat and parallel. Compressive creep experiments were performed under constant load in vacuum (0.5 mTorr residual pressure) in a hydraulic testing machine. The samples were placed in a WC–Co creep cage, consisting of a sleeve and two pistons, with Mo foils as spacers. Each sample was heated to a particular temperature (950, 1000, 1050 or 1100 °C) at a rate of 10 °C min<sup>-1</sup> and annealed for 1 h. The sample was then subjected to a constant stress until a constant strain rate was achieved. This procedure was repeated in a series of increasing stress values spanning 3–11 MPa until a total strain of 12% had been accumulated.

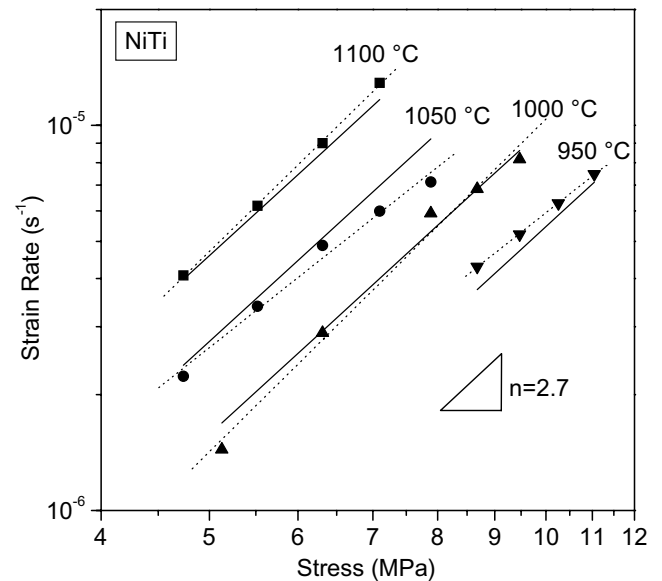
The secondary strain rates  $\dot{\epsilon}_s$ , which were achieved after a short primary creep period, are plotted as a function of stress  $\sigma$  in Figure 1 for the four temperatures *T* studied here. The power-law creep equation

$$\dot{\epsilon}_s = A\sigma^n \exp\left(-\frac{Q}{RT}\right), \quad (1)$$

where *R* is the gas constant, was used to fit the creep data simultaneously for the Dorn constant *A*, stress exponent *n* and activation energy *Q*. The overall best-fit lines (with  $A = 0.05 \pm 0.04 \text{ MPa}^{-n} \text{ s}^{-1}$ ,  $n = 2.66 \pm 0.23$  and  $Q = 155 \pm 14 \text{ kJ mol}^{-1}$ ) are shown in Figure 1, together with best-fit lines for each temperature, with *n* varying between 2.3 and 2.9.

Metallography was performed on diamond-polished cross-sections which were etched with a modified Kroll's reagent (5% HNO<sub>3</sub>, 10% HF, balance water). Grain boundaries were imaged with an optical microscope and line analysis [12] was used to determine the average grain size, which was found to be  $48 \pm 5 \mu\text{m}$  for as-received NiTi and  $140 \pm 13 \mu\text{m}$  for a sample which had been crept for 12 h at 1050 °C.

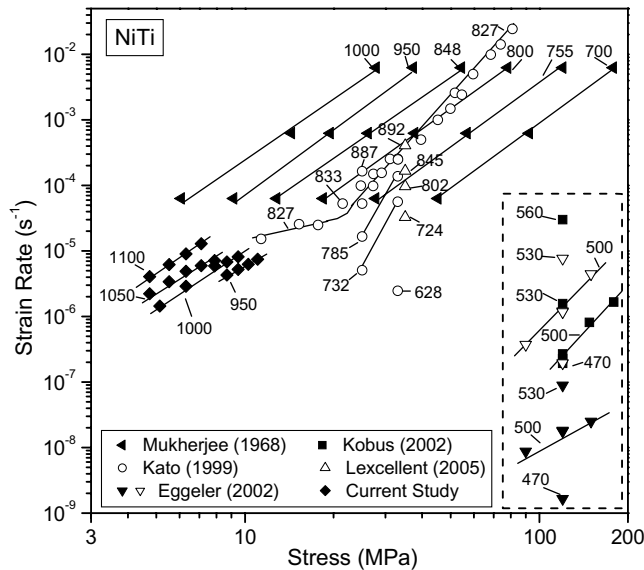
Figure 2 summarizes the creep data from the current study (Fig. 1) and from the five previous creep studies reviewed above. In some cases (e.g. Lexcellent et al. [11]), the individual creep data leading to values of *n* or *Q* were not reported by the authors and are thus



**Figure 1.** Plot of compressive strain rate vs. compressive stress for NiTi measured in the present study, showing best-fit for each temperature (dashed lines) and overall best-fit for all four temperatures (solid lines) with  $n = 2.7$ .

not plotted in Figure 2. The stress in Figure 2 is not normalized by the shear modulus, since a study by Hasiguti and Iwasaki [13] has shown that the shear modulus of NiTi remains near-constant up to 800 °C, reaching a maximum value at ~550 °C (only 20% higher than the room temperature value) and then decreasing slowly (with the shear modulus at 800 °C being nearly identical to the room temperature value).

It is apparent from Figure 2 that discrepancies exist between the six studies, preventing the determination of overall values for *A*, *n* and *Q*. The two studies by Eggeler and co-workers [9,10] examined NiTi containing fine precipitates whose presence affect *A*, as well as *Q* and *n*, if a threshold stress is present [14]. The effect of precipitate growth at low-temperature is visible in the



**Figure 2.** Plot of strain rate vs. stress for NiTi summarizing present study and previous literature data. Data within the dashed box is for NiTi with  $\text{Ti}_3\text{Ni}_4$  precipitates. Steady-state and minimum rates are shown with different symbols for the study by Eggeler et al. [10]. Test temperatures are given in °C.

vast difference observed between the initial minimum creep rates and the subsequent plateau (steady-state) creep rates, as discussed in detail by Eggeler et al. [10]. Thus, these two studies [9,10] cannot be compared with the other four creep studies performed at higher temperatures, for which it can be safely assumed that precipitates are dissolved or coarsened to the point that they do not significantly affect creep rates.

These four high-temperature studies, however, remain inconsistent with each other. In particular, it is apparent that three of the studies (Refs. [7,11] and the present study) report a stress exponent of about 3, while the fourth, by Kato et al. [8], lists values of  $n = 2.5$  or 5.9, depending on the technique used (Table 2). The latter value was obtained at a single temperature (827 °C) for three slightly different compositions. Also, considering the activation energy, the present study finds a value ( $Q = 155 \text{ kJ mol}^{-1}$ ) significantly lower than those of the other three studies [7,8,11] ( $Q \sim 250 \text{ kJ mol}^{-1}$ , as summarized in Table 2). Some possible reasons for these discrepancies in  $n$  and  $Q$  values among the four high-temperature studies are discussed below.

A first possible reason is that all previous studies used tensile stresses, whereas the current tests were performed under compression. Two possible sources for tension/compression asymmetries exist. First, cavitation can occur in tension but usually not in compression, thus lowering the cross-sectional area and producing stress concentrations that lead to higher strain rates and higher sensitivity to both stress and temperature (i.e. higher  $n$  and  $Q$ ) [14]. Second, some intermetallics are known to show an intrinsic tension/compression asymmetry even in the absence of cavitation, as shown by NiAl (with the same B2 crystal structure as NiTi), where both  $n$  and  $Q$  are different in tension and compression [15]. This effect could be examined in NiTi by carrying out tensile

and compressive tests on specimens produced from the same ingot.

A second possible source for discrepancy is variation in grain size between studies. At a given temperature, fine-grained NiTi may exhibit diffusional creep with lower  $n$  and  $Q$  than coarse-grained NiTi creeping by dislocation motion (climb or glide). Among the four high-temperature studies, only Kato et al. [8] and the present study provide initial grain sizes. Kato et al. report an initial grain size of 15  $\mu\text{m}$ , which is quite small for a metal, and may be responsible for the three data points at their lowest stress showing  $n = 1$  (Fig. 2), typical of diffusional creep. Kato et al. however do not report the grain size after creep testing. In our experiments, the grain size increased from 48  $\mu\text{m}$  prior to testing to 140  $\mu\text{m}$  after testing, indicative of moderate grain growth which may have occurred during the 1 h anneal period or during testing. The discrepancy between our results and those of Mukherjee (e.g. extrapolating our data at 1000 °C to higher strain rates produces an overlap with his data at 800 °C) may be due to anomalously fast creep in Mukherjee's experiment due to small grains. This explanation is speculative, since Mukherjee did not report a grain size, but the small grain size in his material is credible, since it had been hot-swaged prior to testing, and was thus very likely recrystallized. A further confounding effect is the value of the stress exponent  $n = 3$ , which may represent viscous glide of dislocations in one case, or transition between diffusional creep ( $n = 1-2$ ) and dislocation creep ( $n = 4-6$ ) in another. A future study on NiTi creep would have to use coarse-grained samples with a grain size that does not evolve during the experiment.

Third, it is possible that deviation in the stoichiometric NiTi composition may affect creep response, even in the absence of precipitates, through concentration-dependence of the diffusion coefficient (as reported in NiAl [16] with the same B2 structure as NiTi) or through decrease of the solidus temperature. Kato et al. [8] showed that creep rates at 827 °C were faster by a (relatively small) factor of two for equiatomic NiTi, as compared with Ni-49.5% Ti and Ni-50.5% Ti. Here, too, a systematic study of NiTi composition on creep behavior would be needed.

Fourth, some intermetallics (e.g. B2-FeAl [17]) show a transition between low- and high-temperature creep behavior, characterized by creep activation energy on the order of the activation energy for bulk diffusion at high temperatures and much higher values at lower temperatures. Our study, performed at the highest temperatures, also exhibited the lowest activation energy (which is equal to that for Ni diffusion in NiTi [11]) and may thus represent high-temperature creep behavior.

Finally, the presence of texture may also have affected the various creep rates of NiTi compiled in Figure 2, as reported in B2-NiAl [18]. All NiTi specimens were subjected to various thermomechanical processes (i.e. swaging and drawing, Table 1) expected to produce texture, which may have been retained partially or fully despite the subsequent heat treatment and creep testing. A future study would have to test texture-free materials with equiaxed grains to ascertain the true creep behavior of NiTi.

In conclusion, nickel-rich, near-equiatomic NiTi with a grain size of 48–140  $\mu\text{m}$  was deformed in compression between 950 and 1100  $^{\circ}\text{C}$  over a stress range of 3–11 MPa, resulting in strain rate spanning  $1.4 \times 10^{-6} - 1.3 \times 10^{-5} \text{ s}^{-1}$ . Best-fit of the creep data to a power-law equation results in a stress exponent  $n = 2.7 \pm 0.2$  and an activation energy  $Q = 155 \pm 14 \text{ kJ mol}^{-1}$ . Only five previous studies on the creep of NiTi exist, and it is impossible to harmonize data among the different studies to achieve a single constitutive power-law equation. This is most probably due to additional variables affecting creep of NiTi, including tension/compression asymmetry, the presence of precipitates, deviation from stoichiometry, the presence of texture and the dominance of different creep mechanisms (i.e. diffusional and dislocation creep) due to different grain size and testing temperatures.

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