

Short Research Article

Tensile properties of high-purity Ca metal

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ABSTRACT

Recent interest in using calcium (Ca) as a reinforcement metal in Al/Ca metal-metal composites prompted this study of the mechanical properties of high-purity Ca metal. Previously reported measurements of Ca's mechanical properties were performed on Ca of relatively low purity (~95 at%). Ca used in this study was purified by sublimation to reduce O, N, and C concentrations, yielding 99.95% purity metal for fabrication of tensile test specimens. Yield strength, ultimate tensile strength, ductility, and strain rate sensitivity of high-purity Ca were measured at both 77K and 295K for annealed and cold-worked Ca. Annealed samples were found to be more strain-rate sensitive than as-swaged samples. Both as-annealed and as-swaged Ca samples were stronger and more ductile at 77K than at 295K, behavior that seems to be supported by molecular dynamics simulations of perfect Ca single crystals.

Keywords: Calcium metal; mechanical properties; strain-rate sensitivity

INTRODUCTION

Calcium is the fifth most abundant element in Earth's crust. Ca is an inexpensive, low-density, high-conductivity, ductile FCC metal, but it is not used for structural

25 applications because it reacts with water and has an unusually low elastic modulus (21 GPa).
26 Commercial applications of Ca metal are limited to deoxidizing/desulfurizing iron and steel
27 and as an alloying additive to Al, Be, Cu, Mg, and Pb alloys. Recently, Ca has been the object
28 of several studies focused on its rich spectrum of crystal structures at high pressure and its
29 high Curie temperature (29K) for superconductivity at 220 GPa [1].

30 In 1948, Everts et al. [2] reported Ca to have an ultimate tensile strength of 55 MPa
31 with 55% tensile elongation. However, the purity of Everts' Ca was not reported. In 1963,
32 Hampel reported that cold-rolled Ca had a yield strength of 84.8 MPa and an ultimate
33 strength of 115 MPa [3]. The elongation of distilled Ca was found to be 53 percent, whereas
34 extruded wire gave an elongation of 61 percent. Elongation was also found to decrease with
35 lower purity to the point that no elongation was observed for 94-96% pure Ca [3]. These
36 studies were limited to room-temperature testing, and they did not measure strain-rate
37 sensitivity. The mechanical properties of pure alkaline metals are now of renewed interest,
38 due to recent work on Al-Ca and Al-Sr metal-metal nanocomposites for high-voltage electric
39 power transmission [4-10]. In these nanocomposites, pure alkaline metal filaments are
40 embedded within an Al matrix to strengthen the conductor while maintaining high electrical
41 and thermal conductivity.

42 After the reports from Everts and Hampel were published, the mechanical properties
43 of pure Ca metal received little additional study. The need for better data to use in modeling
44 microstructure-property relations in Al/Ca nanocomposites motivated this study of Ca's
45 mechanical properties. A similar study of Sr metal mechanical properties was reported
46 elsewhere [5].

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49 **PROCEDURE**

50 For this study commercially available Ca (Minteq International, Inc. 99.5%, H-Grade)
51 was sublimated [11] by the Materials Preparation Center at the U.S. Department of Energy's
52 Ames Laboratory [12]; glow discharge mass spectroscopy of the sublimed material
53 demonstrated the purity to be 99.95% pure by weight. The Ca metal was sealed into a
54 12.7mm-diameter Ta tube and welded shut *in vacuo*. The sealed Ta tube was then held in a
55 vacuum furnace at 1000°C for one hour. After cooling, the tube was swaged at 22°C from
56 12.7mm diameter to 4.4mm diameter, thereby imparting 88% cold work to the Ca. The tube
57 was then machined on a lathe to a 3.25mm diameter rod while being brushed with mineral
58 oil to prevent oxidation of the Ca once the Ta was removed. The pure Ca rod was then cut
59 into 32mm lengths that were machined on a lathe to form cylindrical tensile test specimens
60 with 2.75mm gauge diameters. Half of the samples were then cleaned, resealed under
61 vacuum in a Ta tube, and annealed *in vacuo* at 380°C for one hour. The tensile specimens
62 were stored in mineral oil prior to tensile testing.

63 The tensile tests were performed with an Instron 3367 machine using a 30kN load
64 cell. Collet grips were utilized to grasp the tensile specimen ends. The tensile specimens
65 were cleaned of mineral oil just prior to testing to minimize exposure to air. Crosshead
66 displacement control was used to control the deformation of the samples. Tensile testing
67 was performed at 295K and at 77K. Cryogenic testing was performed with the tensile
68 specimen immersed in liquid N₂ throughout the test. A strain rate of $3.33(10^{-3})\text{ s}^{-1}$ was used
69 on half of the samples. The other half of the samples were pulled at a strain rate of
70 $3.33(10^{-3})\text{ s}^{-1}$ until a strain of 0.0366 was reached; at that point the strain rate was abruptly
71 increased to $8.33(10^{-1})\text{ s}^{-1}$, and that higher strain rate was used from 0.0366 strain to
72 fracture.

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74 **RESULTS**

75 Figures 1 and 2 display the engineering stress-strain plots generated by tensile
76 testing. Values for yield strength ($\sigma_{y,0.2\%}$), ultimate tensile strength (σ_{UTS}), elongation at
77 fracture, and strain rate sensitivity are shown in Tables 1 and 2. In these tables, tensile
78 testing measurements for annealed and heavily cold-worked 99.999% purity Al from Dvorak
79 [13] are included for comparison; in each case the mechanical properties of the two metallic
80 elements are roughly similar to one another. As would be expected, the Ca samples tested
81 at 77K had higher ultimate tensile strengths and higher yield strengths than the samples
82 tested at 295K. Higher strengths at cryogenic temperatures are commonly seen in metals
83 since less thermal energy is available to facilitate dislocation mobility at low temperature.
84 The as-swaged Ca tested at 77K had more than 25% higher ultimate tensile stress and more
85 than 20% higher yield strength than the as-swaged specimens tested at 295K. The annealed
86 Ca tested at 77K had more than 40% higher ultimate tensile stress and more than 25%
87 higher yield strength than the annealed specimens tested at 295K. The as-swaged Ca
88 specimens had five times the yield strength and almost twice the ultimate tensile strength
89 of the annealed Ca specimens at both 295K and 77K as would be expected from the cold
90 work imparted by the swaging. The cold-working of as-swaged samples also reduced their
91 ductility by more than 70% compared with as-annealed samples at both 295K and 77K.

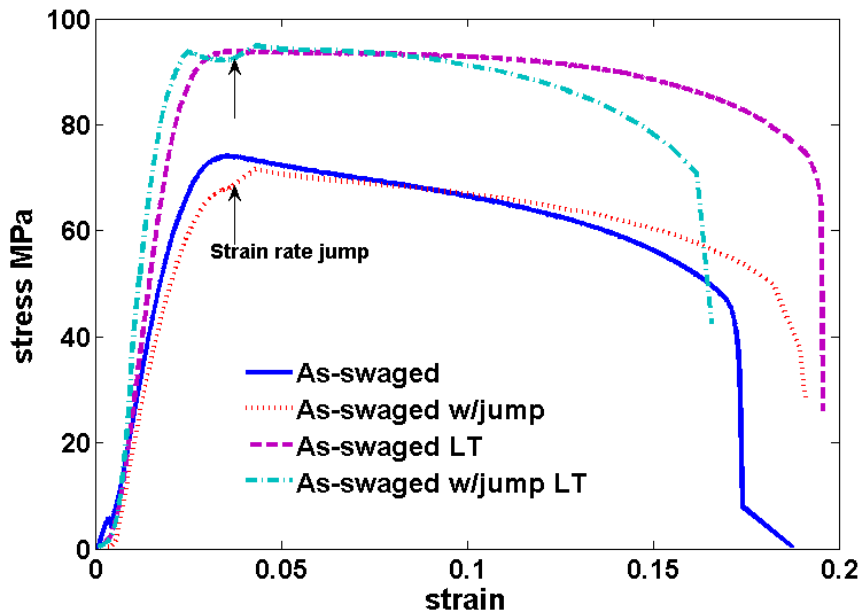


Figure 1. Stress-strain curves for as-swaged Ca samples (88% cold work by swaging). The designation "w/jump" indicates the specimens with a strain rate jump; "LT" indicates testing performed at low temperature (77 K).

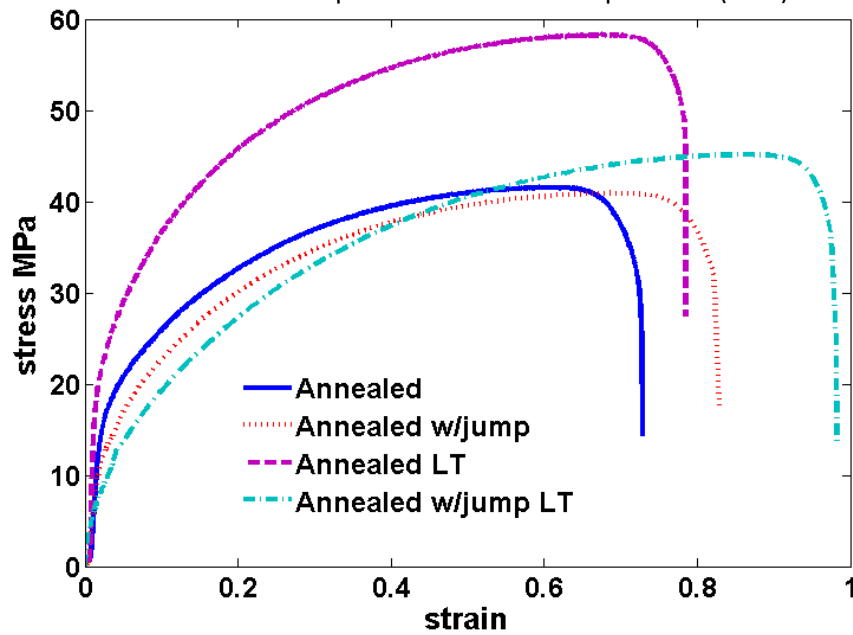


Figure 2. Stress-strain curves for annealed Ca samples. The designation "w/jump" indicates the specimens with a strain rate jump; "LT" indicates testing performed at 77 K.

Table 1: Mechanical properties of work-hardened Ca measured by uniaxial tensile testing with a comparison to work-hardened, polycrystalline high-purity Al [13].

Sample	0.2% offset yield stress (MPa)	Ultimate stress (MPa)	Elongation (%)	Strain rate sensitivity
As-Swaged Ca tested at 295K with strain rate jump	48.7	71.6	19.1	0.0089
As-Swaged Ca tested at 295K	65.0	74.1	17.4	
<i>Heavily work-hardened, high-purity Al tested at 295K*</i>	<i>38.4</i>	<i>75.4</i>	<i>31.4</i>	
As-Swaged Ca tested at 77K with strain rate jump	81.2	94.8	16.6	0.0050
As-Swaged Ca tested at 77K	82.4	93.9	19.6	

* 99.999% purity Al, work-hardened by two passes of equal channel angular pressing at 295K; tensile tested at a strain rate of $8.3(10^{-3}) \text{ s}^{-1}$

Table 2: Mechanical properties measured by uniaxial tensile testing of annealed Ca with comparison to annealed, high-purity, polycrystalline Al [13].

Sample	0.2% offset yield stress (MPa)	Ultimate stress (MPa)	Elongation (%)	Strain rate sensitivity
Annealed Ca tested at 295K with strain rate jump	11.1	40.9	82.8	0.015
Annealed Ca tested at 295K	14.0	41.6	72.9	
<i>Annealed high-purity Al tested at 295K*</i>	<i>13.3</i>	<i>36.8</i>	<i>49.6</i>	
Annealed Ca tested at 77K with strain rate jump	5.4	45.1	98.1	0.027
Annealed Ca tested at 77K	16.1	58.3	78.4	

* 99.999% purity Al, annealed for 4 hrs at 400°C; tensile tested at a strain rate of $8.3(10^{-3}) \text{ s}^{-1}$

All as-annealed samples showed higher ductility at low temperature (77K) than their counterpart at 295K. This is mildly surprising since the $\{111\}\langle 110 \rangle$ slip system in fcc Ca is harder to operate at 77K compared with 295K for dislocation glide. There are several major deformation mechanisms of dislocation-containing metals: dislocation mediated gliding; grain boundary sliding; twinning; and phase transformation [14-16]. The calcium phase diagram suggests no phase transformation during the temperature range from 77K to room

temperature. Grain boundary gliding usually occurs in nanocrystalline metals at elevated temperature since it is a thermally activated process [15]. A possible explanation of the higher ductility at low temperature observed in these experiments may be that dislocation glide was augmented by deformation twinning, which is a common deformation mechanism at low temperature and has been frequently observed in the deformation of hcp metals such as Mg at room temperature and deformation of fcc metals like Cu at cryogenic temperatures [14, 16]. Another important role of twinning in plastic deformation is that it can change the atomic plane orientations so that further dislocation slip can occur.

If twinning is indeed the **mechanism responsible** for higher ductility at low temperature in polycrystalline samples, it should also lead to higher ductility at low temperature for a bulk perfect single crystal because twinning is an intra-grain process. This seems to be supported by simple molecular dynamics simulations of bulk, perfect-single-crystal uniaxial tensile tests performed by LAMMPS [17]. Fig. 3 shows the calculated tensile stress-strain curves for bulk perfect Ca single crystals at room temperature and **at 75K**. It is clear that the Ca single crystal has both higher strength and higher ductility at 75K compared with 300K. If grain boundary sliding were responsible for higher ductility at low temperature in polycrystalline samples, it would not cause such an effect in a bulk single crystal sample **(as shown in Fig. 3)**, since it is an inter-grain process. The observed higher ductility at 77K in Fig. 3 seems to support the twinning mechanism explanation for the high ductility in these Ca specimens at 77K. Twinning would be the only reasonable mechanism at low temperature because other deformation mechanisms are thermally activated. The higher strength at 75K **may result from either of two factors: (1) less thermal energy is available at 75K to overcome the energy barrier associated with shearing of atomic planes,**

resulting in larger external stress needed for deformation proceeding, and /or (2) the twin boundaries could act as barriers to the shearing across atomic planes.

The simulation used to generate Fig. 3 involved a total of 1000 atoms inside the simulation box for calculation under periodic boundary condition to minimize system size effect. The strain rate in the tensile test is $1(10^{10}) \text{ s}^{-1}$. In all atomistic simulations, the strain rate is unrealistically high since the intrinsic limit in simulation time is limited to times on the order of nanoseconds. Molecular dynamics calculations need to be performed with femtosecond-scale time steps in order to resolve vibration motion. The available computational power allows calculation up to a million time steps, which still limits the time for strain to occur to the order of nanoseconds, hence the very high strain rate.

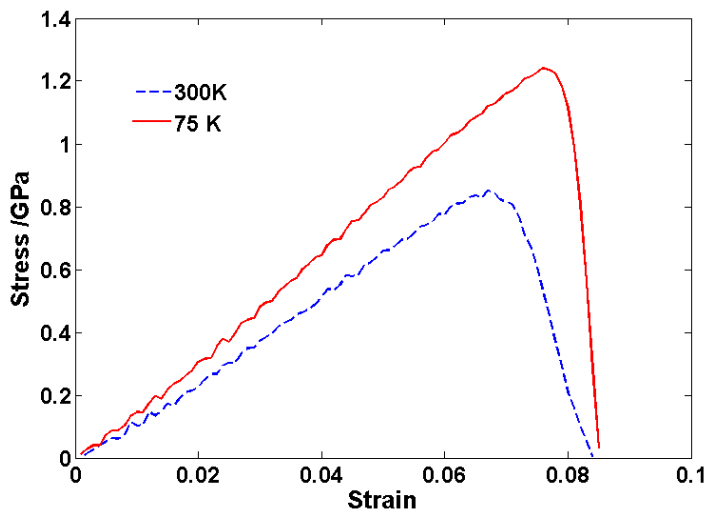


Fig. 3. The tensile stress-strain curves of bulk perfect Ca single crystal samples with the tensile axis parallel to the $\langle 100 \rangle$ direction as calculated by LAMMPS molecular dynamics at 300K and 75K.

The strain rate sensitivity (m) was determined by the equation shown below:

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$$m = \frac{\ln\left(\frac{\sigma_2}{\sigma_1}\right)}{\ln\left(\frac{\dot{\epsilon}_2}{\dot{\epsilon}_1}\right)}$$

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where σ_1 is the stress value at a strain rate of $\dot{\epsilon}_1$ and σ_2 is the stress value immediately after

163

the strain rate was abruptly increased ("jumped") to a higher value, $\dot{\epsilon}_2$.

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165 All the strain rate sensitivity (m) values tabulated in Tables 1 and 2 are small, which is typical

166 of high-purity FCC metals. At both testing temperatures, m values for the annealed

167 specimens were higher than the values for the cold-worked specimens. One might expect

168 especially low strain-rate sensitivity in Ca because its large atomic radius provides larger

169 interstices for interstitial impurity atoms, whose pinning effects on dislocations are major

170 contributors to strain-rate sensitivity.

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172 **CONCLUSION**

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174 The tensile properties of swaged and annealed high-purity Ca metal were measured using

175 both constant strain rate tests and strain-rate jump tests. Tensile testing was performed at

176 295K and at 77K. The samples tested at 77K had higher yield strength, higher ultimate

177 tensile strength, and in some cases higher ductility than the samples tested at 295K.

178 Deformation twinning could be responsible for the higher ductility of polycrystalline Ca at

179 77K than 295K, as implied by the molecular dynamics simulation of the tensile test of a

180 perfect Ca single crystal. The strain rate sensitivity of the Ca was small for all specimens.

181 Annealed samples tend to be more strain-rate sensitive than as-swaged samples.

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