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Tensile Properties of High-purity Ca Metal

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Authors' contributions

This work was carried out in collaboration between all authors. Author AR designed the study. Author AS performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed the literature search. Author LT performed the molecular dynamics simulations. All authors read and approved the final manuscript.

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Short Research Article

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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.

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

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

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

2. PROCEDURE

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

The tensile tests were performed with an Instron 3367 machine using a 30kN load cell. Collet grips were utilized to grasp the tensile specimen ends. The tensile specimens were cleaned of mineral oil just prior to testing to minimize exposure to air. Crosshead displacement control was used to control the deformation of the samples. Tensile testing was performed at 295K and at 77K. Cryogenic testing was performed with the tensile specimen immersed in liquid N_2 throughout the test. A strain rate of $3.33(10^{-3})\ s^{-1}$ was used on half of the samples. The other half of the samples were pulled at a strain rate of $3.33(10^{-3})s^{-1}$ until a strain of 0.0366 was reached; at that point the strain rate was abruptly increased to $8.33(10^{-1})\ s^{-1}$, and that higher strain rate was used from 0.0366 strain to fracture.

3. RESULTS AND DISCUSSION

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

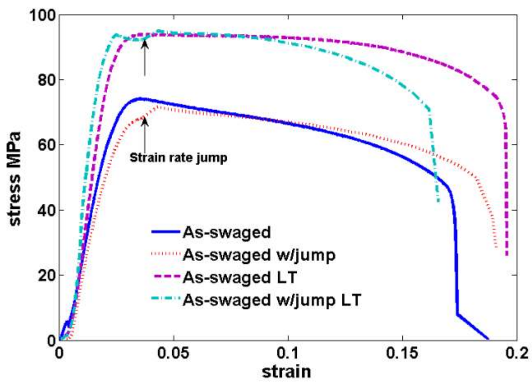

Fig. 1. Stress-strain curves for as-swaged Ca samples (88% cold work by swaging). The designation "w/jump" indicates the specimens with a strain rate jump; "LT" indicates testing performed at low temperature (77 K)

All as-annealed samples showed higher ductility at low temperature (77 K) than their counterpart at 295 K. This is mildly surprising since the {111}<110> slip system in fcc Ca is harder to operate at 77 K 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 77 K 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.

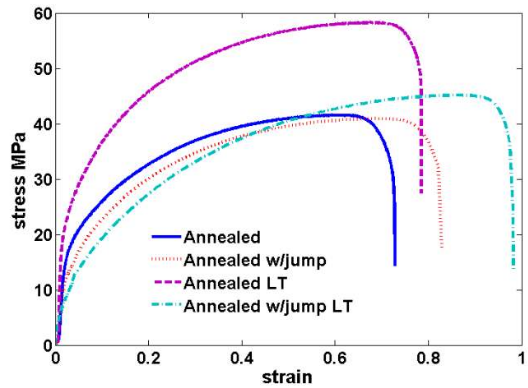

Fig. 2. Stress-strain curves for annealed Ca samples. The designation "w/jump" indicates the specimens with a strain rate jump; "LT" indicates testing performed at 77 K

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 75 K. It is clear that the Ca single crystal has both higher strength and higher ductility at 75 K compared with 300 K. 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 77 K in Fig. 3 seems to support the twinning mechanism explanation for the high ductility in these Ca specimens at 77 K. Twinning would be the only reasonable mechanism at low temperature because other deformation mechanisms are thermally activated. The higher strength at 75 K may result from either of two factors: (1) less thermal energy is available at 75 K to overcome the energy barrier associated

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 295 K with strain rate jump	48.7	71.6	19.1	0.0089
As-Swaged Ca tested at 295 K	65.0	74.1	17.4	
*Heavily work-hardened, high-purity Al tested at 295 K**	*38.4*	*75.4*	*31.4*	
As-Swaged Ca tested at 77 K with strain rate jump	81.2	94.8	16.6	0.0050
As-Swaged Ca tested at 77 K	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 $8.3(10^{-3})\ s^{-1}$*

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 295 K with strain rate jump	11.1	40.9	82.8	0.015
Annealed Ca tested at 295 K	14.0	41.6	72.9	
*Annealed high-purity Al tested at 295K**	*13.3*	*36.8*	*49.6*	
Annealed Ca tested at 77 K with strain rate jump	5.4	45.1	98.1	0.027
Annealed Ca tested at 77 K	16.1	58.3	78.4	

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

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

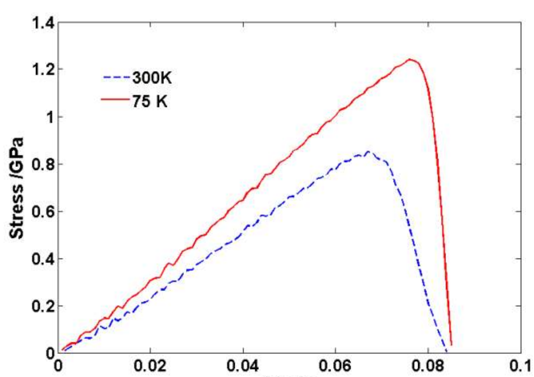

Fig. 3. The tensile stress-strain curves of bulk perfect Ca single crystal samples with the tensile axis parallel to the <100> direction as calculated by LAMMPS molecular dynamics at 300 K and 75 K

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 $1(10^{10})\ s^{-1}$. 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.

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

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

where σ_1 is the stress value at a strain rate of $\dot{\varepsilon}_1$ and σ_2 is the stress value immediately after the strain rate was abruptly increased ("jumped") to a higher value, $\dot{\varepsilon}_2$.

All the strain rate sensitivity (m) values tabulated in Tables 1 and 2 are small, which is typical of high-purity FCC metals. At both testing temperatures, m values for the annealed specimens were higher than the values for the cold-worked specimens. One might expect especially low strain-rate sensitivity in Ca because its large atomic radius provides larger interstices for interstitial impurity atoms, whose pinning effects on dislocations are major contributors to strain-rate sensitivity.

4. CONCLUSION

The tensile properties of swaged and annealed high-purity Ca metal were measured using both constant strain rate tests and strain-rate jump tests. Tensile testing was performed at 295 K and at 77 K. The samples tested at 77 K had higher yield strength, higher ultimate tensile strength, and in some cases higher ductility than the samples tested at 295 K. Deformation twinning could be responsible for the higher ductility of polycrystalline Ca at 77 K than 295 K, as implied by the molecular dynamics simulation of the tensile test of a perfect Ca single crystal. The strain rate sensitivity of the Ca was small for all specimens. Annealed samples tend to be more strain-rate sensitive than as-swaged samples.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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