J Mater Sci (2010) 45:589–592
DOI 10.1007/s10853-009-3931-8

# Sc-strengthened commercial purity aluminum under high pressure

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Received: 2 October 2008 / Accepted: 26 September 2009 / Published online: 15 October 2009

**Abstract** Aluminum alloyed with approximately 1,000 at. ppm Sc was studied by high-pressure energy dispersive X-ray diffraction in two different states, homogenized and aged to peak microhardness. The microhardness of the aged sample is about three times higher than the microhardness of the homogenized sample (as a result of the formation of nanosize $Al_3Sc$ precipitates in the aged sample). The results, which were refined using the Rietveld analysis technique, indicate a single cubic phase with no phase transition up to a pressure of 32 GPa. The Vinet equation was used to fit the volume–pressure curve to the equation-of-state. The bulk modulus ($B_0$) is found to be 73 ± 5 GPa, and is equal to the value measured for an unalloyed aluminum sample. The fact that the bulk modulus does not change, despite a large difference in microhardness between the samples, is the result of the different origins of the two quantities.

## Introduction

Al(Sc)-based alloys are promising candidates for use in the aerospace and terrestrial vehicle industries. They have excellent creep properties [1–4]. Their strain is increased from the formation of nanosize $Al_3Sc$ precipitates with the $L1_2$ structure, which forms homogeneously during aging from a single-phase, supersaturated solid solution [5, 6]. The misfit between the $Al_3Sc$ precipitates and the α-Al matrix is about 1.10% at 300 °C [7], which allows the precipitates to remain coherent up to diameters of about 40 nm [8, 9]. Because of the formation of these nanometer scale precipitates during aging, the hardness of the aged alloy can be up to few times higher than the hardness of homogenized alloy. However, the behavior of homogenized and aged samples under high pressure has not been compared.

In this research, we focus on commercial purity (CP) aluminum, where Si and Fe are the major impurities (about 500 wppm each), alloyed with about 1,600 wppm Sc. This alloy was characterized [10] by optical microscopy, by SEM including energy dispersive spectrometry (EDS), and by local-electrode atom-probe (LEAP) tomography. It was found [10] that no extra phase exists in the bulk sample, but different precipitates do exist. The as homogenized sample and the aged sample contain micrometer scale $Al_{\sim 3}$(Fe,MM) precipitates. In the homogenized sample, the Sc is fully dissolved in the Al matrix while in the aged sample, the Sc is precipitated to form nanometer scale $Al_3Sc$ precipitates ($L1_2$ structure). Based on the LEAP measurements [10], the average radius of the $Al_3Sc$ precipitates is found to be about 2 nm, their number density is about $6 \times 10^{22}$ $m^{-3}$, and the average distance between two adjacent precipitates is about 25 nm.

The alloy reached peak microhardness (MH) after about 8 h of aging at 300 °C [10], and stayed at peak for about 1 week before over-aging began. The as homogenized Vickers microhardness value is 23 (226 MPa), and the peak value is 65 (635 MPa). The higher MH of the aged alloy is the result of the formation of the nanometer scale $Al_3Sc$ precipitates, and the strengthening mechanism is the Orowan dislocation looping [10], where dislocations

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bypass coherent precipitates due to the linear elastic stress fields associated with them.

Here, this alloy was examined under high pressure in two conditions: homogenized and aged at 300 °C for 48 h to its maximum microhardness. In the second condition, the alloy has a MH about three times higher than in the first condition. A reference sample of the CP aluminum, without Sc alloying, was also examined.

## Sample preparation

All alloys were cast using master alloys and pure aluminum. The Al-MM (MM = mischmetal) master alloy is created by arc melting commercial purity Al (Chemical analyses is given in Table 1) and 99.99% pure MM under an Ar atmosphere. The composition of MM is 23 at.% La, 55 at.% Ce, 5 at.% Pr, 17 at.% Nd. A commercial alloy is used for the Al-2 wt% Sc master alloy.

The proper weights of master alloy and commercial purity (CP) aluminum are melted at 775 °C in a resistance furnace under air atmosphere using an alumina crucible coated with a zirconia wash. To minimize oxidation of the alloying elements, the aluminum is melted before adding the master alloy, which is wrapped in 99.99% pure aluminum foil. The melt is then stirred with an alumina rod to ensure homogeneity, and cast into a graphite mold in the shape of four rods, each of which is about 12 mm in diameter and 100 mm in length.

**Table 1** Chemical analysis of the source aluminum (not including gaseous elements)

| Element | Concentration, at. ppm (wt ppm) |
|---|---|
| B | 3 (1) |
| Mg | 4 (4) |
| Si | 259 (270) |
| Ti | 13 (23) |
| V | 20 (37) |
| Cr | 2 (3) |
| Mn | 3 (6) |
| Fe | 126–256 (260–530)[a] |
| Ni | 11 (23) |
| Cu | 1 (2) |
| Zn | 33 (80) |
| Ga | 33 (84) |
| Zr | 2 (8) |
| Mo | 0.6 (2) |
| Pb | 0.7 (5) |
| Total | 510–640 (808–1078) |

Only elements with a concentration greater than 1 wt ppm are listed

[a] The concentrations in CP-Al are nonuniform. In some cases, the Fe concentration is found to be 256 at. ppm. In other cases it is found to be 126 at. ppm

To verify the composition and ensure uniformity, two samples are chemically analyzed. One sample is analyzed from the top of the rod and the other from the bottom. The alloy contains 980 at. ppm Sc and 58 at. ppm MM.

Discs of 4–5 mm in height are cut from the rods. They are placed in a resistance air furnace at 640 °C for 5–7 days to ensure full homogenization, and then water-quenched to room temperature.

The aging treatment is carried out at 300 °C for 48 h and then terminated by water quenching to room temperature.

## X-ray diffraction at ambient and high-pressure

The X-ray diffraction patterns of the different samples were taken at ambient pressure first. The measurements were carried out using Cu–$K_{\alpha 1}$ radiation with a nickel filter and $SiO_2$ monochromator in the angle range of $2\theta = 20$–150°.

The high pressure energy dispersive X-ray diffraction studies were taken at the X17-C beamline of the National Synchrotron Light Source (NSLS).

A pressure of up to 35 GPa was applied via a Merrill-Bassett type diamond anvil cell (DAC) and a “Tel-Aviv”-type DAC. The experiments were conducted using a polychromatic X-ray beam. The sample dimensions for the high-pressure measurements were about 30 μm in height and 80 μm in diameter.

The energy dispersive data were collected with a high purity germanium detector at a fixed Bragg angle ($2\theta = 12°$). The high-pressure X-ray powder diffraction measurements were taken at discrete pressure steps in the range of 0–35 GPa. The data were collected via EDS, using the white beam of the superconducting wiggler at the X17-C beamline. Angle dispersive measurements were carried out in transmission configuration using the image plate technique. The data were analyzed using a commercial Rietveld analysis software package [11].

## Results and discussion

The X-ray diffraction pattern of the unalloyed Al sample was taken at ambient temperature at a pressure range of 0–27 GPa. In Fig. 1, it can be seen that the unalloyed Al sample (marked as Al_Pure) keeps the same symmetry with a reduction in volume of ~11% at 27 GPa. No hysteresis was detected while the pressure was released.

The X-ray diffraction patterns of the homogenized Al(Sc), marked as Al(Sc) (H), and the aged Al(Sc), marked as Al(Sc) (48 h), were taken at ambient temperature at a pressure range of 0–32 GPa. In Figs. 2 and 3, it can be seen

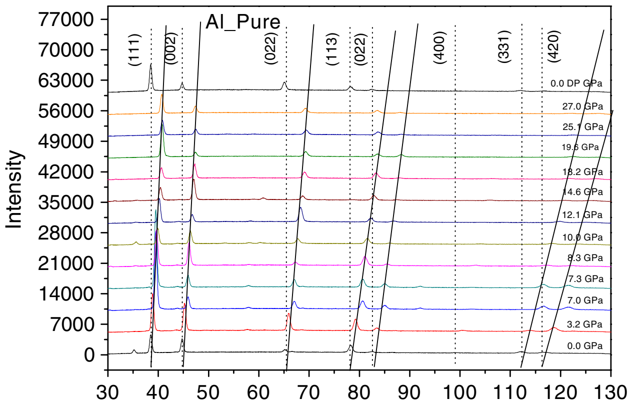

**Fig. 1** X-ray diffraction of pure Al under pressure. The EDS data was converted from energy to angle range. The peaks are indexed for the fcc structure

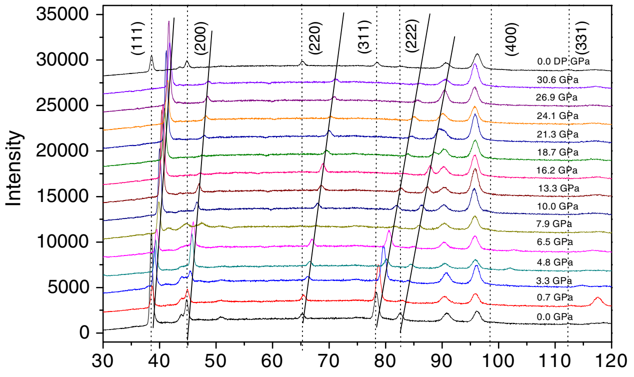

**Fig. 2** X-ray diffraction of Al(Sc) (H) under high pressure. The peaks are indexed for the fcc structure. The two peaks at $2\theta = 91°$, 97° originate from fluorescence (Ta and W belong to collimation due to a small sample) and were excluded in the Rietveld analysis

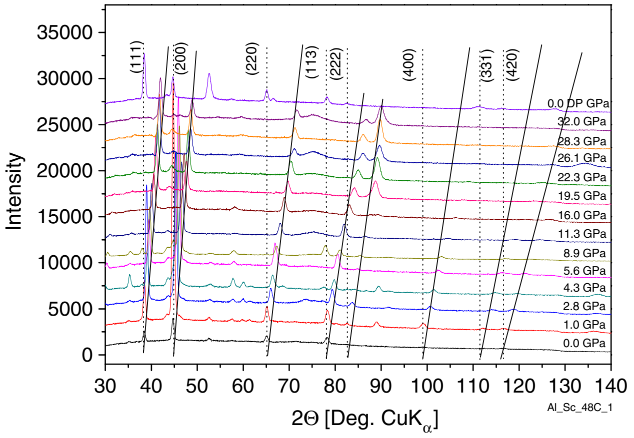

**Fig. 3** X-ray diffraction of Al(Sc) (48 h) under high pressure. The peaks are indexed for the fcc structure (The few unmarked peaks belong to the gasket and show mostly in the diffractions at 1.0 and 8.9 GPa. They are used as extra calibrators of the pressure)

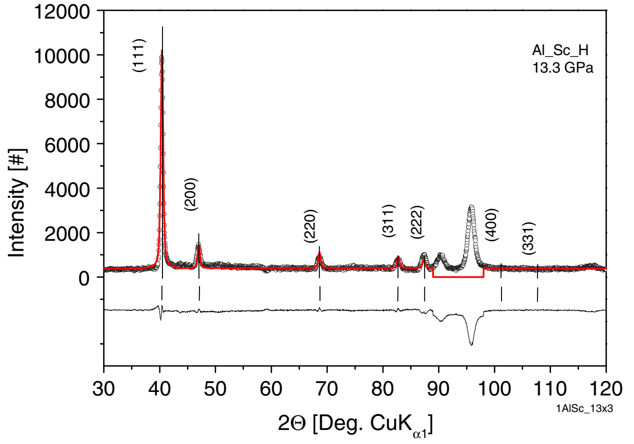

**Fig. 4** Rietveld refinement of an XRD pattern of Al(Sc) (H) at 13.3 GPa. The peaks are indexed for the fcc structure. The two peaks at $2\theta = 91°$, 97° originate from fluorescence (Ta and W belongs to the collimation due to a small sample) and were excluded in the Rietveld analysis

that the Al(Sc) (H) and Al(Sc) (48 h) samples keep the same symmetry, respectively. No hysteresis was detected while the pressure was released. The two peaks at $2\theta = 91°$, 97° originate from fluorescence (Ta and W that belongs to the collimation) and are excluded in the Rietveld analysis.

An example of a Rietveld analysis of X-ray diffraction data for a pressure of 13.3 GPa is given in Fig. 4 for the Al(Sc) (H) pattern sample. As pressure increases, the unit cell parameter shrinks monotonically with no phase change.

The EDS X-ray spectra were mathematically converted to an angle dispersive system due to fitting convenience. The data from the energy dimension were converted to $2\theta$, for Cu K$_{\alpha1}$ radiation, $\lambda = 1.54056$ Å.

The acquisition data each contain three sets of peaks from different origins. The fluorescence lines originate from the elements, the diffraction peaks originate from the crystallography, and the escape peak, which is a very weak peak (~4%), originates from the Ge detector, adding −9.8 keV to each original peak.

The volume–pressure curve, calculated from the data, is depicted in Fig. 5 for all samples. The relationship between pressure and volume change was determined by the Vinet equation of state [12]:

$$P(V) = 3B_0\left(\frac{v}{V_0}\right)^{\frac{-2}{3}}\left(1-\left(\frac{v}{V_0}\right)^{\frac{1}{3}}\right)$$
$$\exp\left(\frac{3}{2}(B_0'-1)\left(1-\left(\frac{v}{V_0}\right)^{\frac{1}{3}}\right)\right)$$

$B_0$ is the isothermal bulk modulus at room temperature and ambient pressure, and $B_0'$ is the partial derivative of the isothermal bulk modulus against pressure under the same

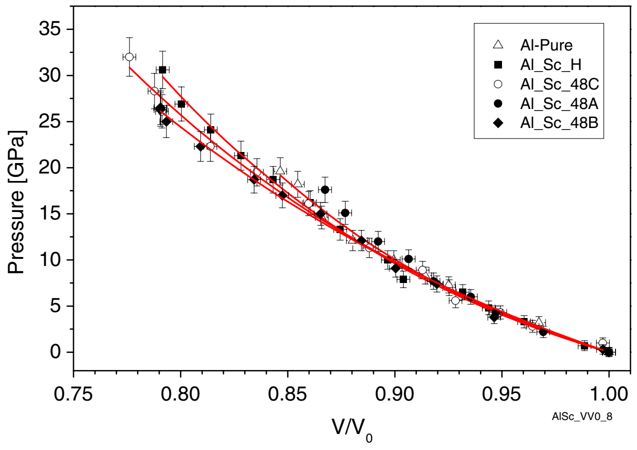

**Fig. 5** The volume–pressure curve derived from the X-ray high-pressure diffraction Rietveld refinement for Al(Sc) samples. The *solid line* is the result of the Vinet equation fit [12]. Al-Pure is the unalloyed aluminum, Al_Sc_H is the homogenized sample, and the rest are different aged samples (48 h at 300 °C)

conditions. This constitutive relationship was shown to be universally valid for all solids under the same conditions. The $B_0'$ varies as the solute atom is changed in the range of 73 ± 5 GPa.

It can be seen that, within measurement accuracy, no distinction can be made between the behavior of the different sample types. The similarity between the unalloyed Al and the homogenized Al(Sc) suggests that the small Sc addition, of about 1,000 at. ppm, does not change the bulk modulus of the Al matrix. Hence, it is also expected that the depletion of Sc from the Al matrix due to the formation of the nanosize $Al_3Sc$ precipitates in the aged sample will not affect the Al bulk modulus.

While the microhardness increased by a factor of ~3, the relative stability of the bulk modulus demonstrates the difference in origin of the two phenomena. The bulk modulus of the Al originates from the shape of the interatomic potential, which is practically unaffected by the small Sc addition. On the other hand, the microhardness increases due to the formation of nanosize $Al_3Sc$ precipitates, which are very effective barriers for dislocation movement.

## Conclusions

CP aluminum alloyed with about 1,000 at. ppm Sc and about 60 at. ppm MM was characterized under high pressure in two different states, homogenized and aged to peak microhardness. The microhardness of the aged sample is about three times higher than the microhardness of the homogenized sample.

It was found that the bulk modulus, calculated using Vinet equation of state, is equal to 73 ± 5 GPa for both samples, which equals the bulk modulus of unalloyed CP aluminum. The fact that the bulk modulus does not change, despite the big difference in the microhardness between the samples, results from the difference in origin of the two quantities.

**Acknowledgement** This research is supported by the US Department of Energy through Grant DE-FG02-98ER45721.

## References

1. van Dalen ME, Dunand DC, Seidman DN (2005) Acta Mater 53:4225
2. Seidman DN, Marquis EA, Dunand DC (2002) Acta Mater 50:4021
3. Fuller CB, Seidman DN, Dunand DC (2003) Acta Mater 51:4803
4. van Dalen ME, Dunand DC, Seidman DN (2006) J Mater Sci 41:7814. doi:10.1007/s10853-006-0664-9
5. Royset J, Ryum N (2005) Int Mater Rev 50:19
6. Hyland RW (1992) Metall Trans A 23A:1947
7. Harada Y, Dunand DC (2002) Mater Sci Eng A 329–331:686
8. Marquis EA, Seidman DN (2001) Acta Mater 49:1909
9. Iwamura S, Miura Y (2004) Acta Mater 52:591
10. Beeri O, Dunand DC, Seidman DN (2010) Mater Sci Eng A (to be published)
11. Rietveld HM (1969) J Appl Crystallogr 2:65
12. Vinet P, Ferrante J, Rose JH, Smith JR (1987) J Geophys Res 92:9319