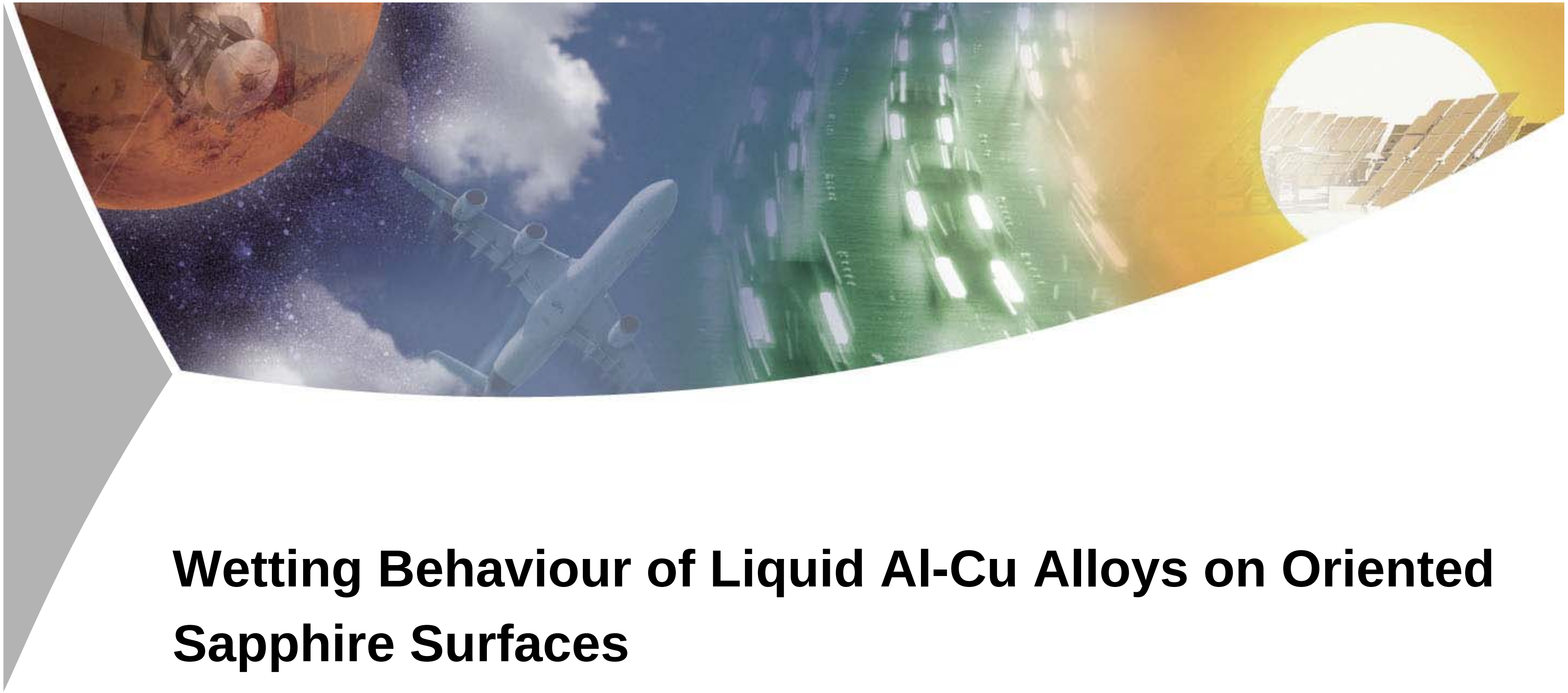


Wetting Behaviour of Liquid Al-Cu Alloys on Oriented Sapphire Surfaces

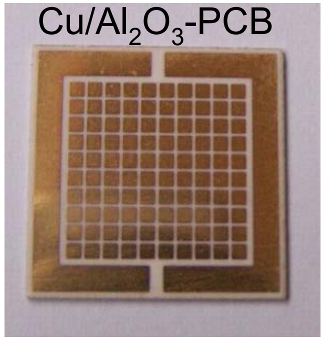
Julianna Schmitz, Jürgen Brillo, Ivan Egry

Sitzung des AKT, Berlin, 24.03.2011

Deutsches Zentrum
DLR für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

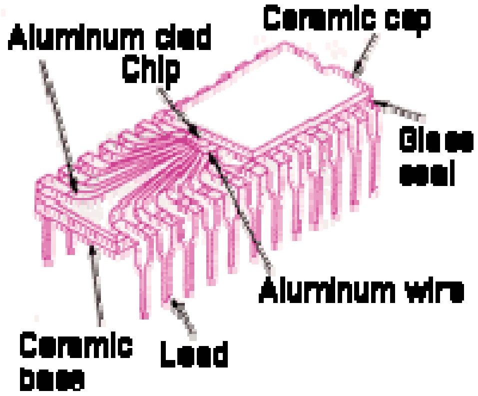
Motivation

- Adhesion at M/MO-interface important for technical applications:
    - Composite materials, Microelectronics
    - Miniaturisation: System dimensions reach the order of crystallite size



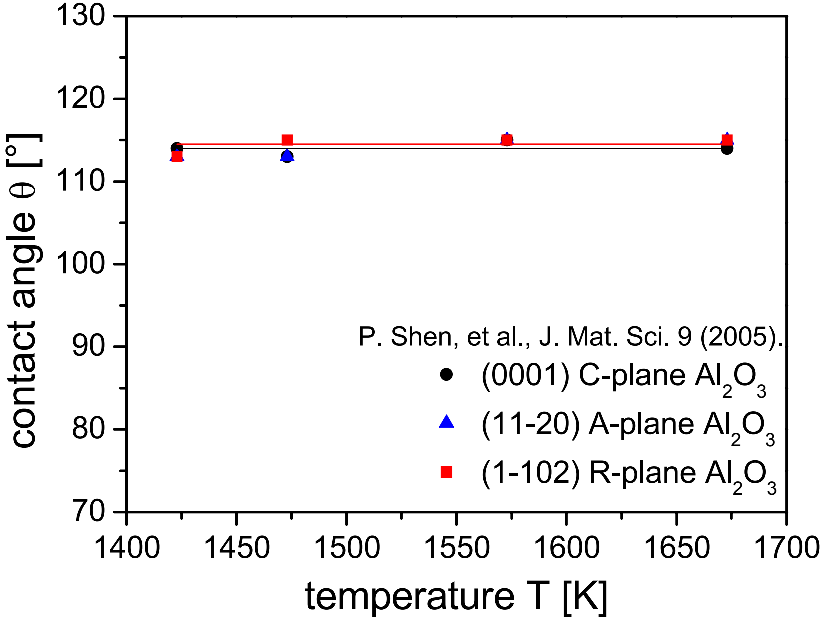
- α-Al_2O_3 commonly used oxide crystal
    - Different kinds of Al_2O_3- surfaces (anisotropy)
    - Some experiments with pure metals show anisotropy in wetting

- Al-Cu/Al_2O_3 composites with promising properties
    - Al-Cu basis for solder materials
    - Anisotropic or isotropic wetting in the system



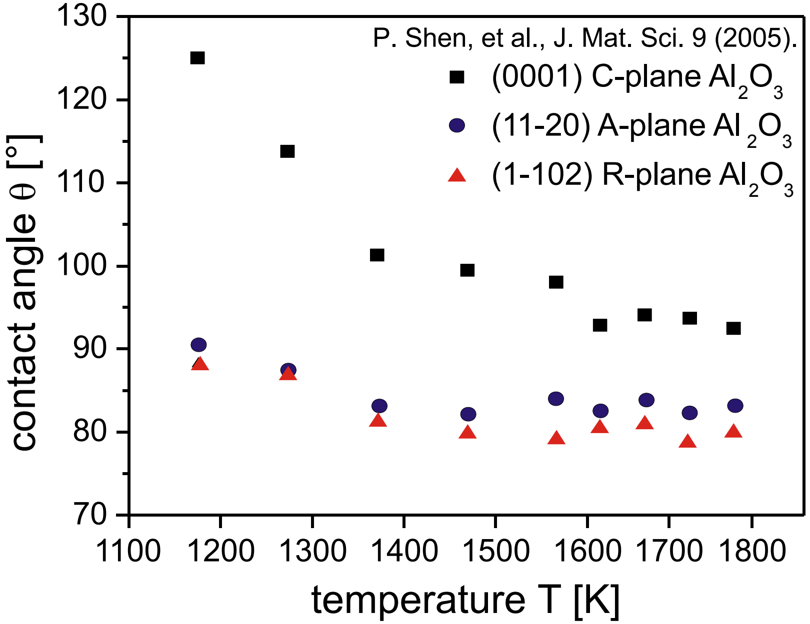
Motivation

Isotropic wetting of Cu on α-Al_2O_3



P. Shen, et al., J. Mat. Sci. 9 (2005).

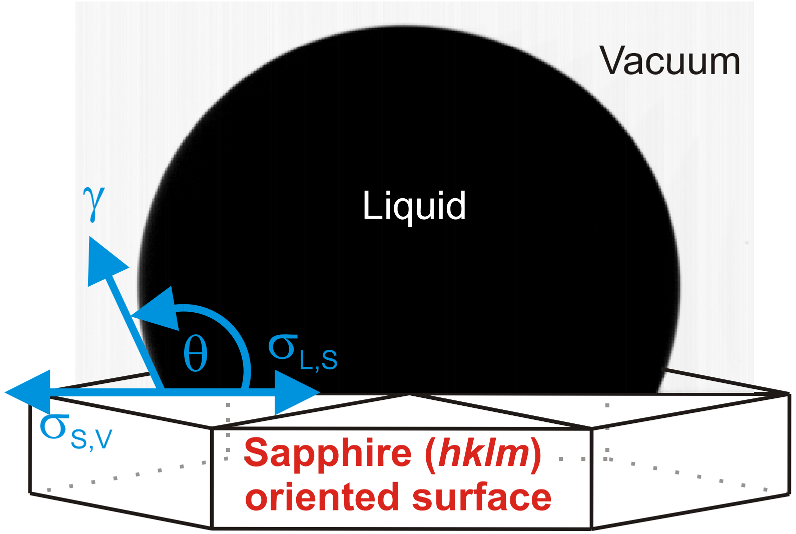
Anisotropic wetting of Al on α-Al_2O_3



P. Shen, et al., J. Mat. Sci. 9 (2005).

- Wetting behaviour mostly unknown for alloys
- Al-Cu/α-Al_2O_3: isotropic or anisotropic?

Fundamentals of wetting – Work of adhesion



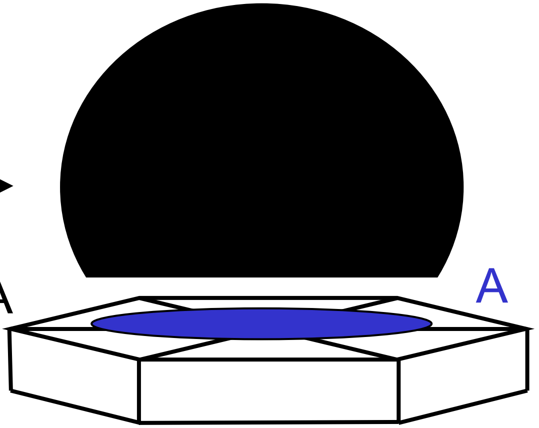
wetting:

$$E_1 = \sigma_{L,S} A$$

$$\xrightarrow{\hspace{3cm}}$$

desorption:

$$E_2 = \sigma_{S,V} A + \gamma A$$



$$(E_2 - E_1)/A = W_{adh} = \sigma_{S,V} + \gamma - \sigma_{L,S}$$

$$\cos\theta = \frac{\sigma_{S,V} - \sigma_{L,S}}{\gamma}$$

Young equation

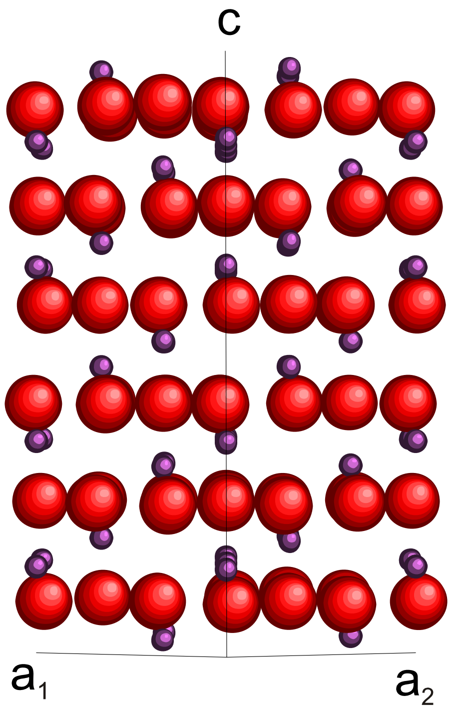
$$W_{adh} = \gamma(1 + \cos\theta)$$

Electromagnetic levitation

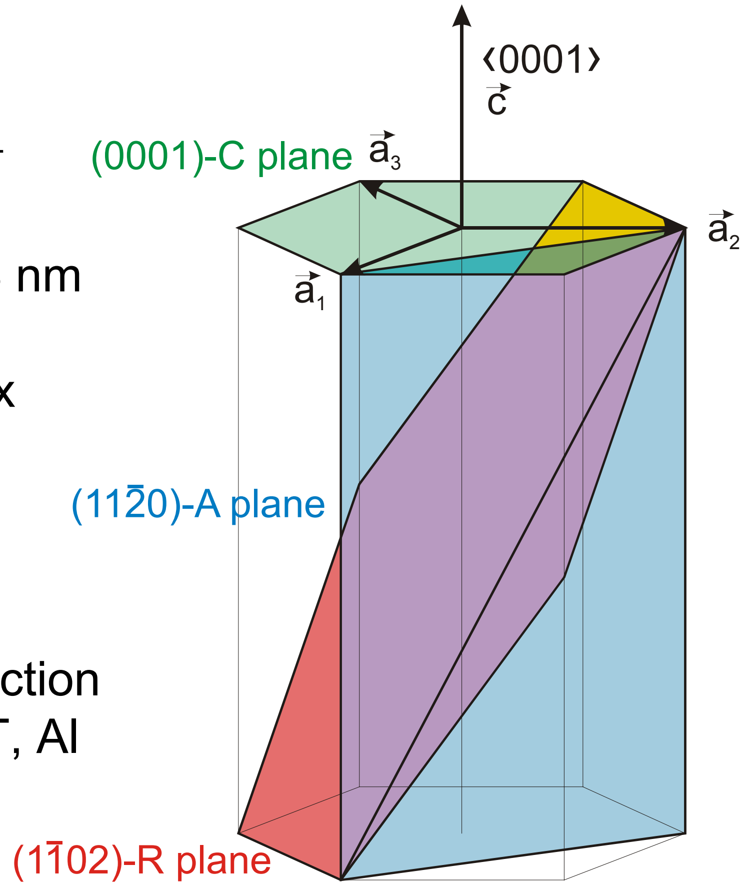
Sessile drop

Crystal structure of α-Al_2O_3 (sapphire)

- hcp stacking of O^{2-}
- 2/3 of octahedron sites occupied by Al^{3+}



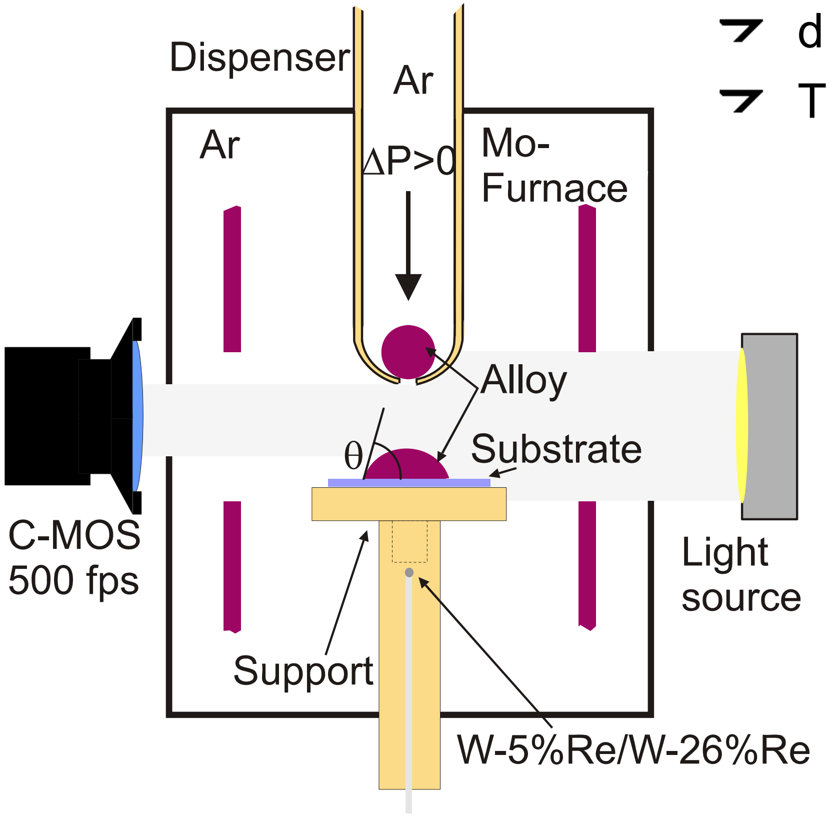
- c=1,3 nm, a=0,48 nm
- different low index crystallographic planes
  → anisotropy
- surface reconstruction of C-plane (high T, Al vapour)

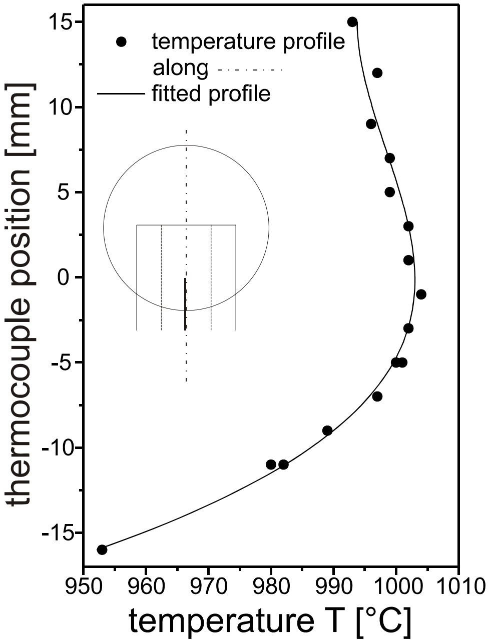


Sessile drop apparatus

well-defined wetting conditions:

- low p_{O2} ($<10^{-6}$ bar)
- drop dispenser
- $T > T_L$(Cu), dT/dx(sample)= -0,03 K/mm





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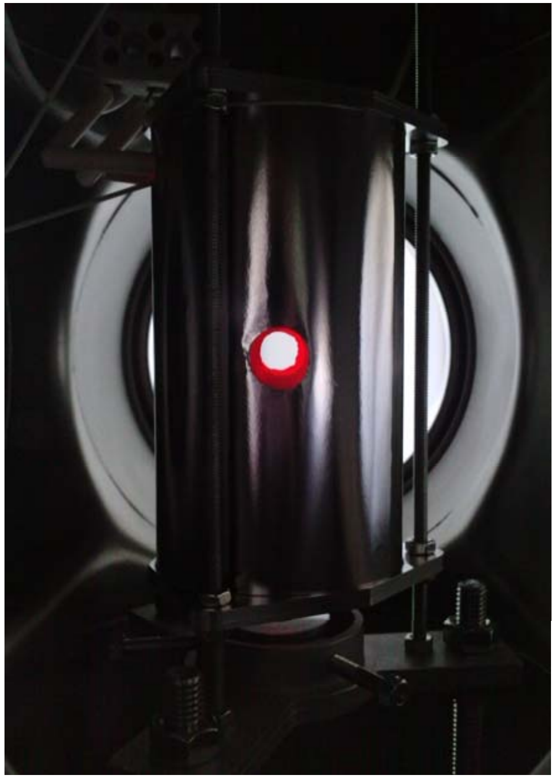
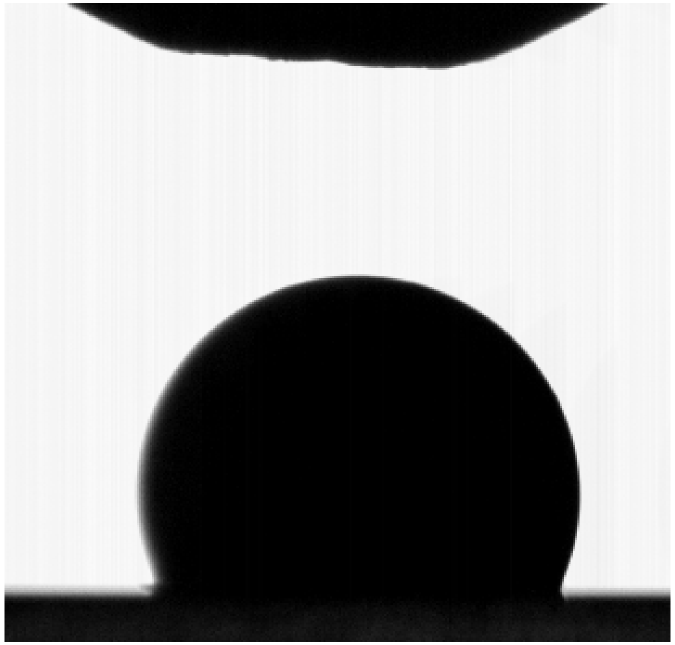
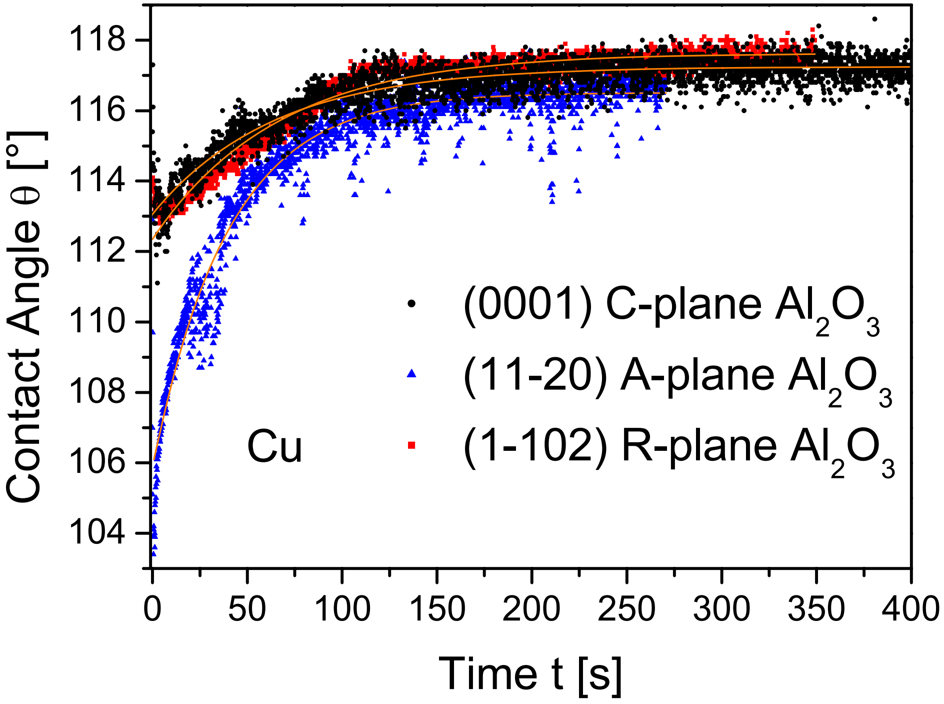




Contact angle of Cu on α-Al_2O_3 at T = 1100°C



$$\cos\theta = \frac{\sigma_{S,V} - \sigma_{L,S}}{\gamma}$$

- Exponential increase of θ

$$\theta = \theta_\infty - (\theta_\infty - \theta_0)e^{-\frac{t}{\tau}}$$

$\theta_\infty \approx 116°$, $\theta_0 \approx 110°$ (non-wetting)
$22s < \tau < 275s$

- θ_∞ in agreement with literature data[1,2,3,4] at 10^{-12} bar < p_{O2} < 10^{-6} bar

- $\theta(t)$ due to deoxidation

- Increase of $\sigma_{L,S}$, γ $\quad \frac{d\sigma}{dt} > \frac{d\gamma}{dt}$

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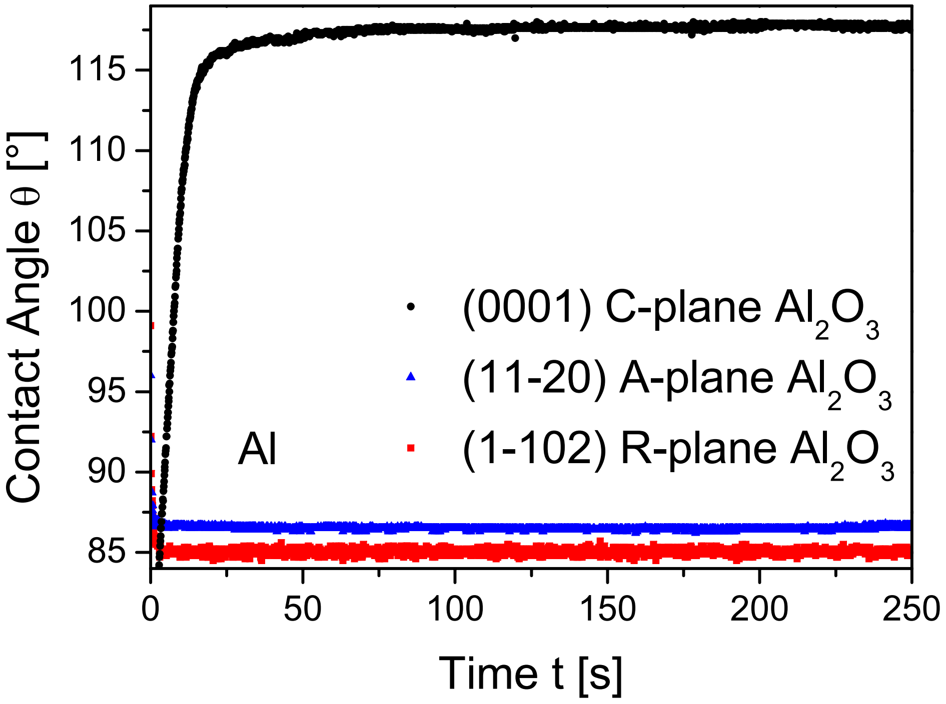
[1] P.D. Ownby, J. Liu., J. Adhes. Sci. Technol. 2 (1988)
[2] M. Diemer et al., J. Am. Ceram. Soc. 82 (1999)
[3] V. Ghetta, et al., Acta Mater. 44 (1996)
[4] T.E. O'Brien, A.C.D. Chaklader, J. Am. Ceram. Soc. 57 (1974)

Contact angle of Al on α-Al_2O_3 at T = 1100°C

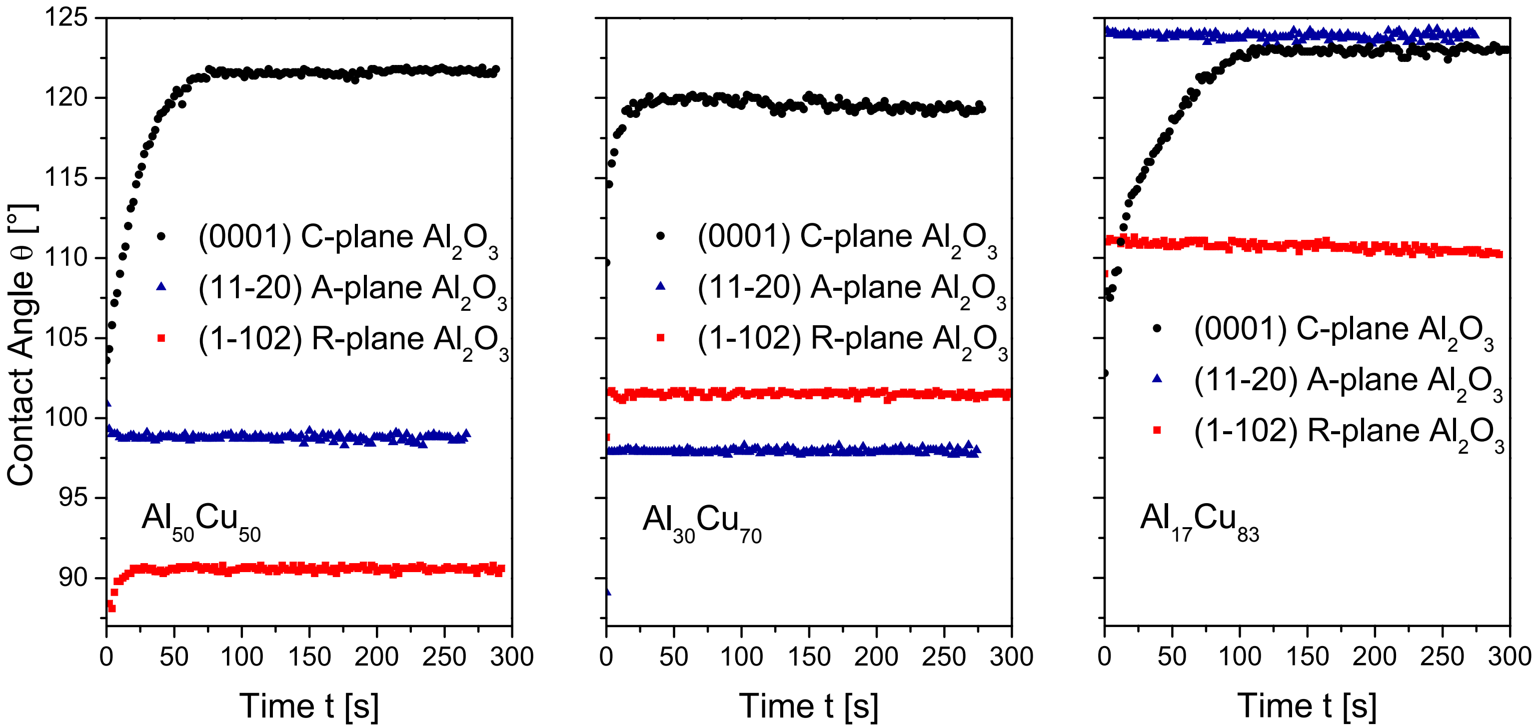


$$\cos\theta = \frac{\sigma_{S,V} - \sigma_{L,S}}{\gamma}$$

- increase of θ only on C-plane
  $\theta_\infty \approx 114°$, $\theta_0 \approx 90°$, $\tau \approx 10$ s
- others: $\theta_0 \approx \theta_\infty \lesssim 90°$ (wetting)
- different θ(t): due to surface specific processes
- θ > 90°: increase due to
  $$\frac{d\sigma_{S,V}}{dt} < 0, \quad \frac{d\sigma_{S,L}}{dt} > 0$$
- θ_∞: surface reconstruction of C-plane[5]
  θ_0: unreconstructed surfaces

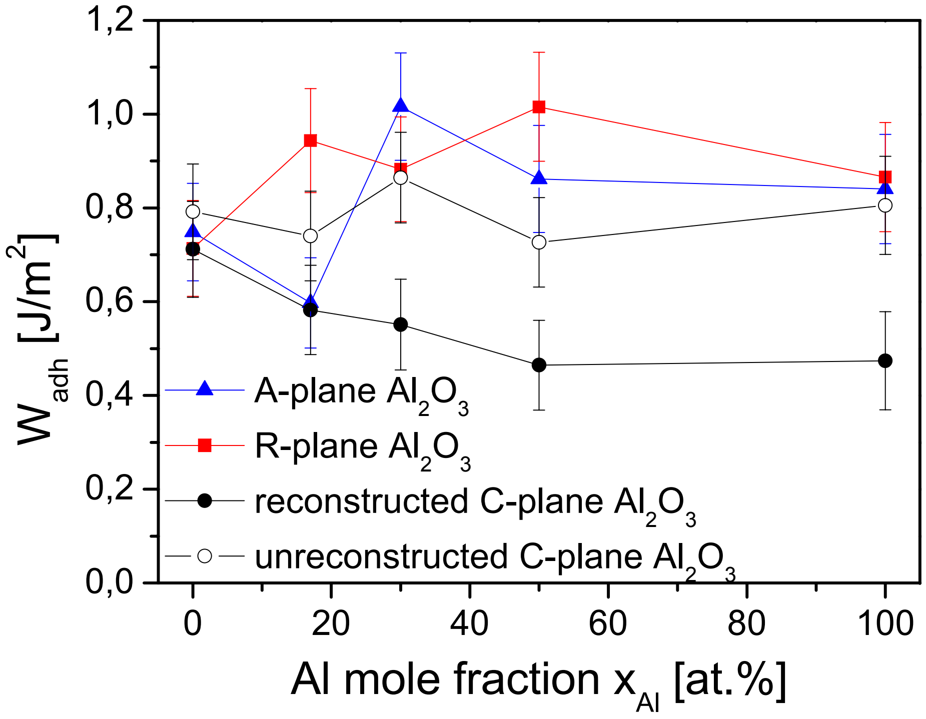
[5] P. Shen, H. Fujii, T. Matsumoto, K. Nogi, Acta Mater. 51 (2003)

Contact angle of Al-Cu on α-Al_2O_3 at T = 1100°C



- qualitative behaviour like wetting of Al on the substrates
  - No significant change in θ for C-surfaces
  - Increase of θ for R- and A-surfaces with x_{Cu}

Work of adhesion of Al-Cu/α-Al_2O_3 at T = 1100°C



$$W_{adh} = \gamma \cdot (1 + \cos \theta)$$

- reconstructed C-plane: decrease of W_{adh} with x_{Cu}
- others: small increase with x_{Al}
- pronounced anisotropy for $x_{Al} \leq 50\%$
- thermodynamic model[6] explains behaviour for dilute solutions
  - adsoption of Al at each interface

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[6] JG Li, L. Coudurier, and N. Eustathopoulos. J. Mat. Sci., 24 (1989)

Atomic interactions at the Al-Cu/α-Al_2O_3 interface

	ε [kJ/mol][7]
Al-Al	133
Al-Cu	217
Cu-O	269
Al-O	511

- Cu/α-Al_2O_3: $\varepsilon_{Cu\text{-}O} \approx \varepsilon_{Cu\text{-}Al}$
  wetting independent of surface termination
- Al/α-Al_2O_3: $\varepsilon_{Al\text{-}O} \approx 4\varepsilon_{Al\text{-}Al}$
  stonger interaction with O-rich surfaces
  reduced wetting by reconstruction (C-plane)
- Al-Cu/α-Al_2O_3: adsorption of Al
  $x_{Al}^{Interface} > x_{Al}^{Bulk}$
  mainly Al-Al, Al-O interactions, surface termination affects wetting for $x_{Al}^{Bulk} \geq 17\%$

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[7] P. Shen, H.Fujii, T.Matsumoto, and K.Nogi. J. Mat. Sci., 40 (2005)

Summary

- no anisotropy in wetting of Cu of different α-Al_2O_3 surfaces (non-wetting)
- anisotropy in wetting of pure Al and Al-Cu of different α-Al_2O_3 surfaces:
  - Al or Al-Cu/ C-plane Al_2O_3: $\theta_\infty \approx 120°$, decrease of θ_0 with x_{cu}
  - Al or Al-Cu/ A- and R-plane Al_2O_3: $\theta_\infty = \theta_0 = \theta_0$(C-plane) (wetting)

  - enhanced wetting of Al-rich Al-Cu alloys on A-,R- and unreconstructed C-plane α-Al_2O_3
- no transition isotropic-anisotropic wetting observed for low x_{Al} (17 at.%)
- behaviour of $W_{adh}(x_{Al})$ suggests Al adsorption at surface and interface