SAND2012-9895C

Reactive Al/Pt Multilayers: Investigating the Stoichiometric Limits of Self-Sustained Reactions

Poster ID: OO5.11

Abstract:

Point ignition tests of sputter-deposited Al/Pt multilayers demonstrate that foils of different net composition (from $Al_{0.25}Pt_{0.75}$ to $Al_{0.75}Pt_{0.25}$) exhibit self-propagating, high temperature reactions. Equiatomic Al/Pt multilayers exhibit the maximum reaction rate consistent with the largest measured heat of formation ($|\Delta H_o|$) for the Al-Pt system. The reaction propagation speeds vary with bilayer thickness for all tested film compositions; peak speeds for $Al_{0.5}Pt_{0.5}$ are approximately 80 m/s. X-ray diffraction shows that phase formation is mostly consistent with published Al-Pt phase diagrams. However, a recently-discovered metastable, complex metal alloy phase having 39 formula units per rhombohedral unit cell forms over a range of composition from $Al_{.56}Pt_{.44}$ – $Al_{.47}Pt_{.53}$.

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Materials Research Society

Fall Meeting, 2012 Session OO

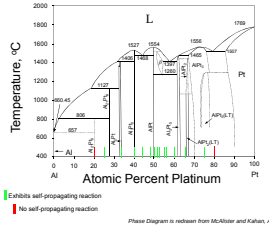
Boston, MA

Goals of this study include:

- Evaluate whether nanoscaled Al/Pt multilayers made of different composition exhibit self-sustained, high temperature formation reactions.
- Determine the propagation speeds for different compositions and bilayer thicknesses; compare with the stored chemical energy in each multilayer.
- Determine the phases that form as a result of self-propagating reactions (for all tested compositions).
- Determine the range of solubility for a recently-discovered metastable, complex metal alloy (R-3 AlPt).

Background: Al/Pt System

Al - Pt phase diagram (indicating tested compositions)



Phase Diagram is redrawn from McAlister and Kahan, ASM 1986

Summary of reported equilibrium phases (indicated in phase diagram)

Phase	Range at.% Pt	Space Group	ΔH_o (kJ/mol-at)*	K_{eff} (W/mK)#
$Al_{25}Pt_5$	19.2	-	-57	205.5
$Al_{21}Pt_5$	27	$I4_1a$	-72	
Al_2Pt	31.5 - 33.5	$Fm3m$	-84	181.8
Al_3Pt_2	40	$P3m1$	-95	
AlPt	50	$P2_13$	-100	154.3
β AlPt (HT)	~52 – 56	$Pm3m$	unknown	
Al_3Pt_5	~61.5 – 63	$Pbam$	-88	134.5
$AlPt_2$	~66 – 67	$Pnma$	unknown	
$AlPt_2$ (LT)	~66 – 67	$Pmma$	-88	126.7
$AlPt_3$	67 – 78	$Pm3m$	unknown	
$AlPt_3$ (LT)	73-100	$P4/mbm$	-70	112.9

* Data is taken from the Boer et al. Cohesion in Metals : Transition metal Alloys 1988 and Pretorius et al. J. Appl. Phys. 2991.

Estimates based on a rule of mixtures

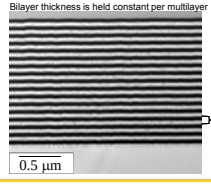
Sputter Deposition

Parameters

Sputter gas: 99.995% Ar
Gas pressure: 10 mTorr
Deposition rate (average): 2 Å/s
Method: DC magnetron

Design

Alternating Al / Pt layers
Multilayer thickness (fixed) = 1.6 μm
Bilayer thickness is held constant per multilayer



XS TEM

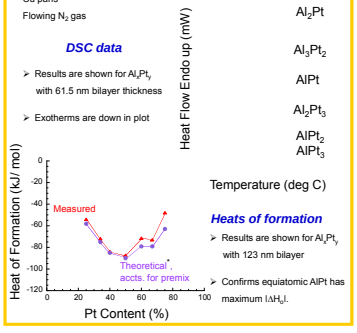
Calorimetry

Equipment and procedure

Perkin Elmer 8500 Differential Scanning Calorimeter (DSC)
Heating rates from 40 K/min
Two bilayer thicknesses (61.5 nm, 123 nm)
Multilayers with different composition
Cu pans
Flowing N_2 gas

DSC data

- Results are shown for Al_3Pt_2 with 61.5 nm bilayer thickness
- Exotherms are down in plot



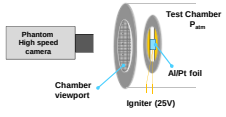
Heats of formation

- Results are shown for Al_3Pt_2 with 123 nm bilayer
- Confirms equiatomic AlPt has maximum $|\Delta H_o|$.

Self-Propagating Reaction Rates

Depiction of test setup

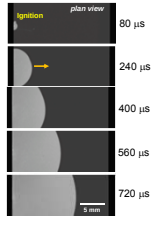
Point ignition
Freestanding multilayer (foil)
No preheating above ambient
Tested in air



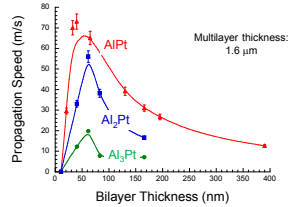
Details of advancing front

Stable reaction front (no instabilities)
Uniform radial velocity
No secondary combustion reactions w/ air

High speed photography



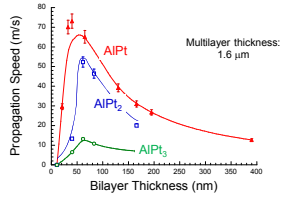
Plot of propagation speeds: Al rich and equiatomic compositions



Lines are guides to the eye

- Bilayer thickness dependence is explained by
  - increased heat release rate with decreased bilayer
  - premixed reactant effects (for small bilayer).
- Propagation speeds are largest for equiatomic composition compared with Al rich multilayers.

Plot of propagation speeds: Pt rich and equiatomic compositions

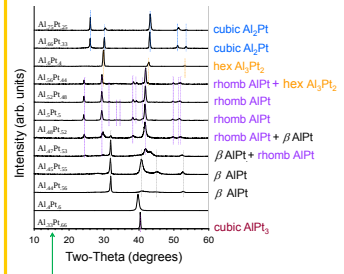


Lines are guides to the eye

- Propagation speeds are largest for equiatomic composition, compared with Pt rich multilayers.
- Multilayers with non-equiatomic compositions appear to be characterized by a reduced range of bilayer thicknesses.

Characterization of Phase (post reaction) using XRD and WDS

X-ray diffraction (all multilayers)

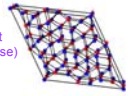


Electron Microprobe (WDS) determines stoichiometry

Depictions of formed phases Al in red, Pt in blue

cubic Al_2Pt

hexagonal Al_3Pt_2

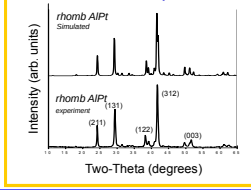


rhombohedral AlPt (new metastable phase) See details below

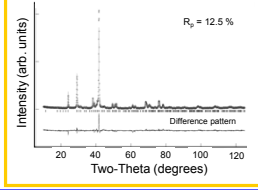
β AlPt

cubic $AlPt_3$

Rhombohedral AlPt simulation vs. experiment



Rietveld refinement of XRD



2θ range: 15-125°
Number of Reflections: 864
Peak shape function: Pseudo- Voigt (3 parameters)

Results:
System: Rhombohedral
Space Group: R-3 (#148)
Formula units, Z: 39
a axis: 15.634 Å
c axis: 5.308 Å
Unit cell volume: 1123 Å^3

Conclusions:

- Sputter-deposited Al/Pt multilayers exhibit high speed, self-propagating formation reactions.
- Equiatomic Al/Pt multilayers exhibit the greatest propagation speed and the largest ΔH_o.
- Equiatomic AlPt forms a complex 78 atom / unit cell, rhombohedral crystal structure.
- High temperature β AlPt is observed for a range of composition from 52 - 56 at % Pt - consistent with published equilibrium phase diagrams (constitutes third report of β phase).

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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