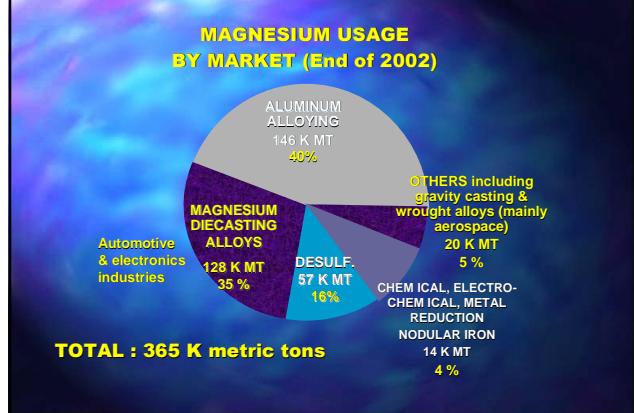


MAGNESIUM ALLOY DEVELOPMENT FOR HIGH-TEMPERATURE AUTOMOTIVE APPLICATIONS

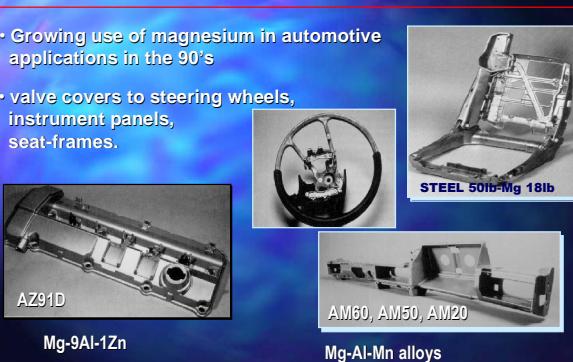
Mihriban Pekguleryuz
McGill University
Metals & Materials Engineering

January 2004



AUTOMOTIVE USE OF MAGNESIUM

- Growing use of magnesium in automotive applications in the 90's
 - valve covers to steering wheels, instrument panels, seat-frames.



AUTOMOTIVE USES OF MAGNESIUM

CURRENT USE: INTERIOR COMPONENTS

- e.g. Instrument Panel, steering wheel
- Stiffness, high ductility
- Energy absorption
- AM alloys

BODY

- e.g. Inner door panel, pillar structures
- Wrought products (formability)
- Structural-casting alloys (ductility)
- Requires new alloys and processes

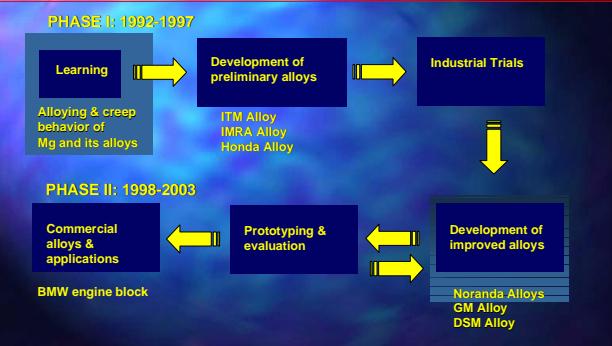
CHASSIS

- e.g. Wheel, suspension arm
- Strength
- High ductility, fatigue
- Corrosion resistance
- Requires new alloys

SHORT TERM : POWERTRAIN

- e.g. Transmission case, engine parts
- Creep resistance (150-200°C)
- Yield strength
- Corrosion resistance
- Mg-Al-RE & Mg-Al-Si
- Requires new alloys

ALLOY DEVELOPMENT FOR MAGNESIUM HIGH-TEMPERATURE APPLICATIONS

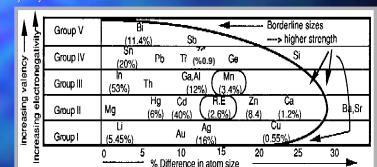


ALLOYING BEHAVIOR OF MAGNESIUM

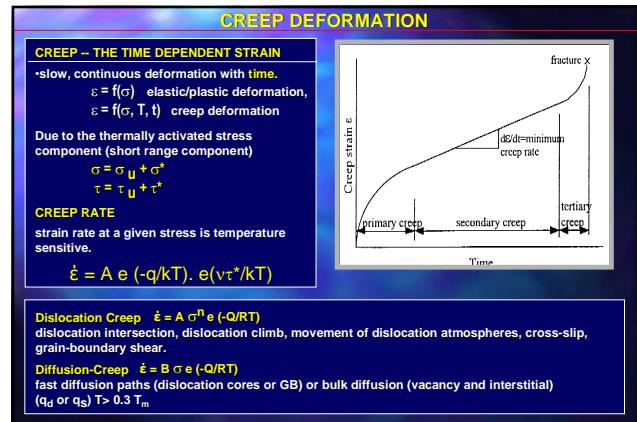
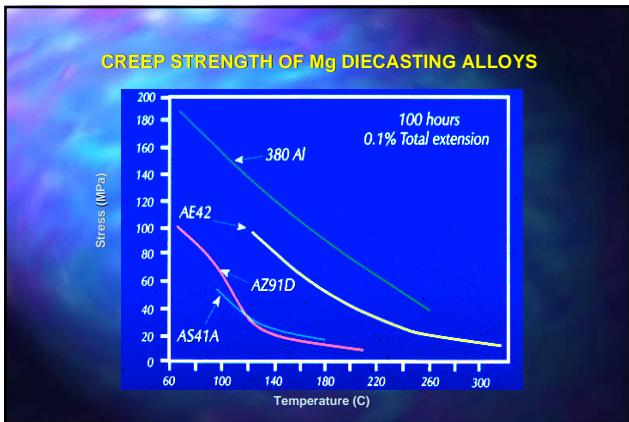
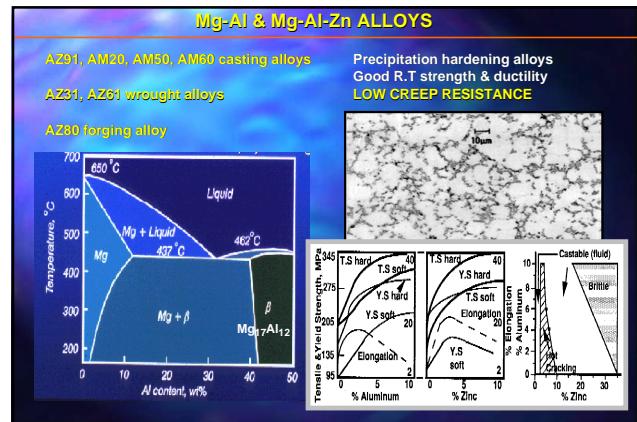
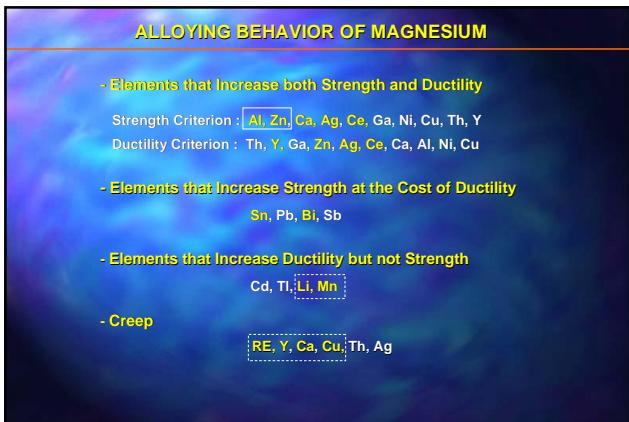
Strength – solid solution hardening & second phase hardening.

HUME-ROTHERY RULES

- **Atomic size ratio (15%)**
Li, Al, Ti, Cr, Zn, Ge, Y, Ce, Zr, Nb, Mo
Pd, Ag, Cd, In, Sn, Pb, Te, Nd, Hf, W,
Re, Os, Pt, Au, Hg, Tl, Pb, Bi,
 - **Similar Crystal Structure**
Zn, Cd
 - **Relative Valency Effect**
Group II - Group VII
 - **Electro-negativity**
Compound formation

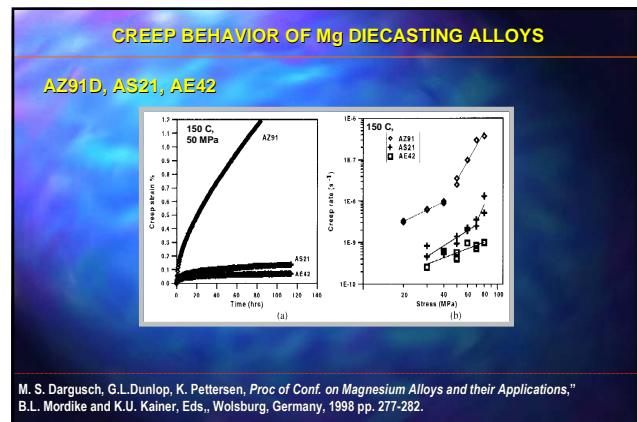


* M. Pekgulyuz, M. Avedesian "Magnesium Alloying-Some Metallurgical Aspects," *Magnesium Alloys and Their Applications*, DGM, 1992, pp. 213-220



CREEP MECHANISMS - What can be Thermally Aided ?

• Dislocation Intersection - work required to force a dislocation through the stress field of another can be thermally aided. Mg single crystals	$\dot{\varepsilon} = A e^{[-(q_i - \tau^* b^2)/kT]}$
• Activated Cross Slip - Thermally activation to unite partial dislocations and to breakdown into partials on different slip systems.	$q = 100 \text{ kJ/mol}$ for high stacking fault metals
• Movements of Dislocations with jogs - formation (q_j) and movement (q_{mj}) of vacancies. Self diffusion ($q_d = q_f + q_m$).	$\dot{\varepsilon} = A e^{[-(q_j - \tau^* b^2)/kT]}$ $q_f \text{ Mg } 135 \text{ kJ/mol, } q_m \text{ Mg } 125 \text{ kJ/mol.}$
• Dislocation Climb - Climb of dislocations over sessile dislocations or precipitates. Vacancy diffusion to and from edge dislocations (q_e) and formation of jogs (q_j). Activation energy, $Q = Q_d + Q_j$	$\dot{\varepsilon} = A \sigma^n e^{(-q_e)/kT}$ $\dot{\varepsilon} = B \sigma^{1/2} e^{(-q_j)/kT}$ $Q \text{ in the range of } q_d (135 \text{ kJ/mol})$
• Movement of Dislocation Atmospheres - Diffusion of solute atoms and the viscous behavior of the solute atmosphere	$\dot{\varepsilon} = A \sigma e^{(-q_s)/kT}$ $q_s \text{ in Mg } 143 \text{ kJ/mol}$
• Grain Boundary Shear - relative movement of grains, deformation in very narrow region adjacent to the GB, the shear direction lies in the boundary with the max resolved shear stress. Affective at high temperatures, usually when the recovery temperature is achieved. Discontinuous. GBs recover before the grains, softening. Accounts for 30% of the deformation.	Grain boundary diffusion: 80 kJ/mol



CREEP BEHAVIOR OF Mg-Al ALLOYS (AZ, AM)

AZ91D -- Activation energy in $\dot{\epsilon} = A\sigma^n \exp(-Q/RT)$, 125-175°C, 50 MPa was 30-45 kJ/mol¹, n=2

self-diffusion of Mg (135 kJ/mol¹) or diffusion of Al in Mg (143 kJ/mol¹) or grain boundary diffusion (80 kJ/mol¹)

Q for discontinuous precipitation of $Mg_{17}Al_{12}$ = 30 kJ/mol
Creep induced $Mg_{17}Al_{12}$ aids easy grain boundary sliding and migration.

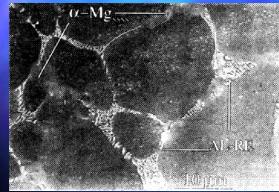
At higher stresses: 95 kJ/mol, n = 5
Activated cross slip
Dislocation intersection ?

M. S. Dargusch, G.L.Dunlop, K. Pettersen, Proc of Conf. on Magnesium Alloys and their Applications," B.L. Mordike and K.U. Kainer, Eds., Wolfsburg, Germany, 1998 pp. 277-282.

CREEP BEHAVIOR OF Mg-Al-RE ALLOYS (AE)

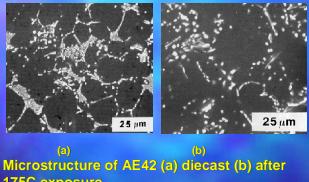
Mg-Al-RE

- Activation energy 35-40 kJ/mol¹
- Higher creep resistance
- Stable Al-RE containing phases
- No $Mg_{17}Al_{12}$ phase but some Al coring



M. S. Dargusch, G.L.Dunlop, K. Pettersen, Proc of Conf. on Magnesium Alloys and their Applications," B.L. Mordike and K.U. Kainer, Eds., Wolfsburg, Germany, 1998 pp. 277-282.

Metallurgical Stability in Mg-Al-RE ALLOYS (AE)



(a) Microstructure of AE42 (a) diecast (b) after 175C exposure

T (C)	Mg	Al ₁ RE ₃	Al ₂ RE	Mg ₁₇ Al ₁₂
As-cast	97.5	1.8	0.8	0.0
25C	97.7	1.5	0.8	0.0
150 C	97.0	1.2	1.3	0.6

Ref : B. R. Powell, V. Rezhets, M.P. Balogh, and R.A. Waldo, "Microstructure and Creep Behavior in AE42 Magnesium Die-Casting Alloy", Journal of Metals, TMS, August 2002, pp. 34-38

ALLOY DESIGN FOR CREEP IN Mg DIECASTING ALLOYS

GENERAL PRINCIPLES

AVOID $Mg_{17}Al_{12}$
creep induced precipitation, e.g. $Mg_{17}Al_{12}$ aging, microstructural instability Sr, Ca, RE

STRONG GRAIN BOUNDARIES
High temperature surface active solutes Sr, Ca, RE
Second phases (line compounds, coherent particles) Sr, Ca, RE
Sb, Bi, Sn

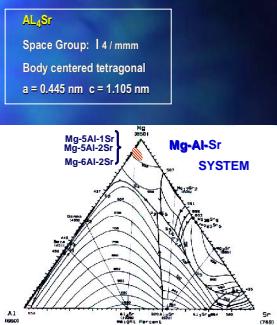
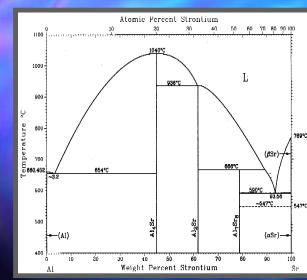
MICROSTRUCTURAL MODIFICATION Sr, Ca, RE
Sb, Bi, Sn

* M. Pekguleryuz, M. Avedesian "Magnesium Alloying-Some Metallurgical Aspects," Magnesium Alloys and Their Applications, DGM, 1992, pp. 213-220

RATIONALE FOR ALLOY SYSTEM SELECTION

- AVOID COSTLY OR RARE ELEMENTS (Sc, Rare earths, Ag, etc)
- MAINTAIN ALUMINUM FOR GOOD DIE CASTABILITY (5-6%)
- USE ALKALINE EARTH ELEMENTS (Ca, Sr)
 - second phases for grain boundary pinning
 - solute segregation
- AVOID ELEMENTS THAT CAN ADVERSELY EFFECT CORROSION (Cu, Ni)
- CHOOSE TERNARY SYSTEMS FOR SIMPLICITY & COST AND EASE OF MANUFACTURING
- Mg-Al-Sr SELECTED AS THE OPTIMUM ALLOY SYSTEM TO DEVELOP

GRAIN BOUNDARY PINNING



Mg-Al-Sr ALLOY COMPOSITIONS

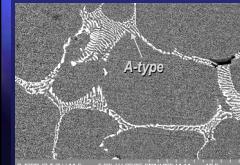
Alloy designation : AJ Alloys where J designates Sr

ALLOY	Al wt. %	Sr wt. %
AJ51x	4.5 - 5.5	1.2- 1.5
AJ52x	4.5 - 5.5	1.6- 2.3
AJ62x	5.5-6.5	2.0- 2.6
AJ62Lx	5.6-6.6	1.5- 1.9

Microstructure of Diecast AJ Alloys

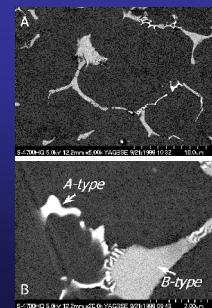
AJ51x
AJ62Lx

α -Mg solid solution and a lamellar intermetallic (Type A)



AJ52x
AJ62x

α -Mg and
Type A
Type B
intermetallics



Sr/Al < 0.3

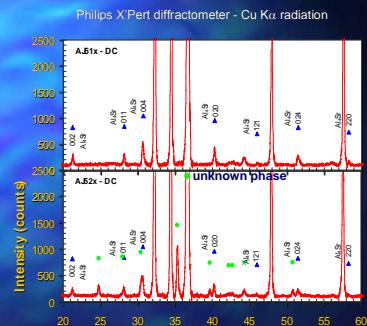
Sr/Al > 0.3

Mg-Al-Sr Alloy Phases

Using XRD coupled with analytical STEM

AJ62x, AJ51x:

Type-A compound is isomorphous to Al_3Sr and Al/Sr ratio is close to Al_3Sr with some Mg in solution.

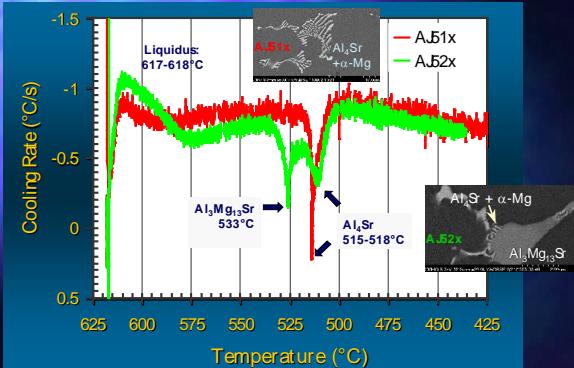


AJ52x:

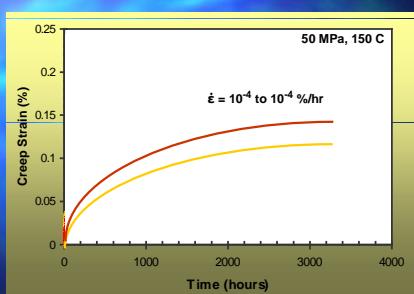
Type-A compound corresponds to Al_3Sr with 15 wt.% Mg.

Type-B compound does not correspond to any known crystal. Tentative : $\text{SrAl}_3\text{Mg}_2\text{Sr}$

Solidification Curves of AJ51x and AJ52x

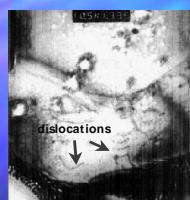


TYPICAL CONSTANT LOAD CREEP CURVES



* E. Landriaut, Ecole Polytechnique, M.Eng. Thesis

CREEP DEFORMATION IN AJ52x



CREEP DEFORMATION

50 MPa, 150 C, 500 hours creep samples shows very little dislocation pile up, and some sub-grain formation

ACTIVATION ENERGY *

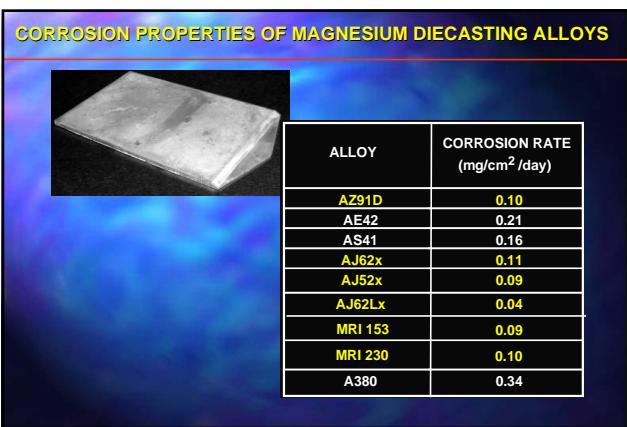
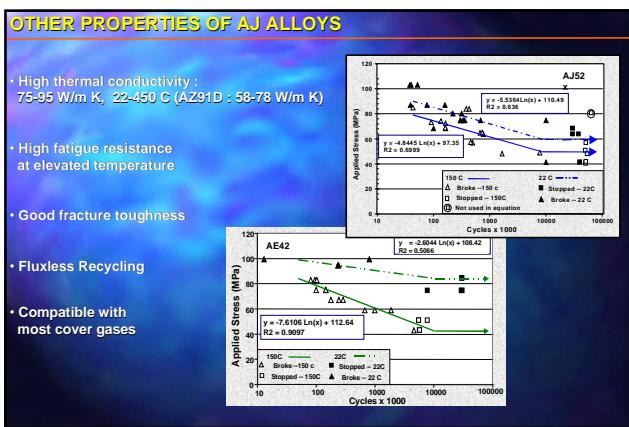
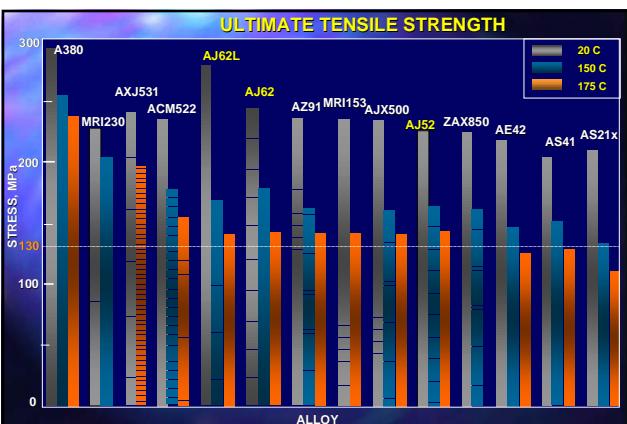
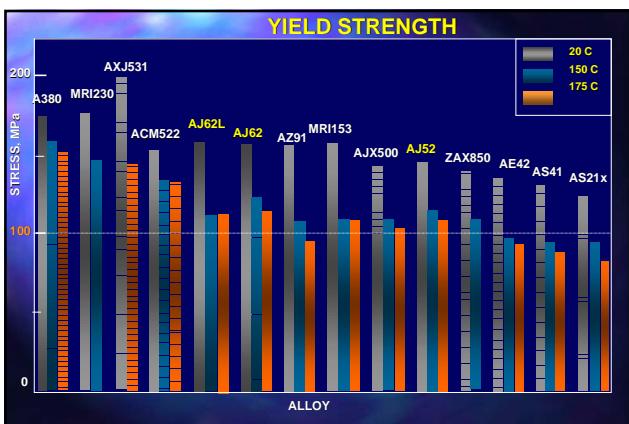
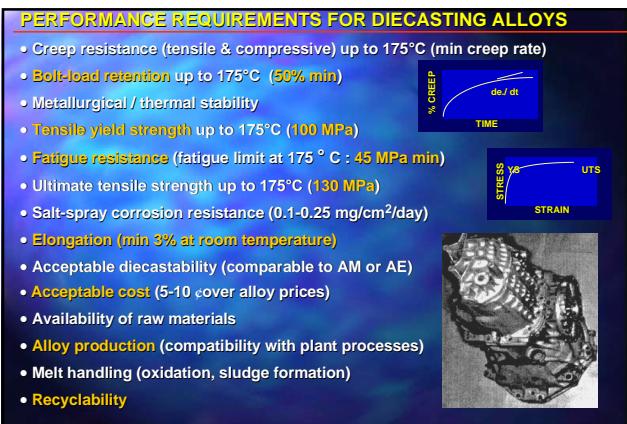
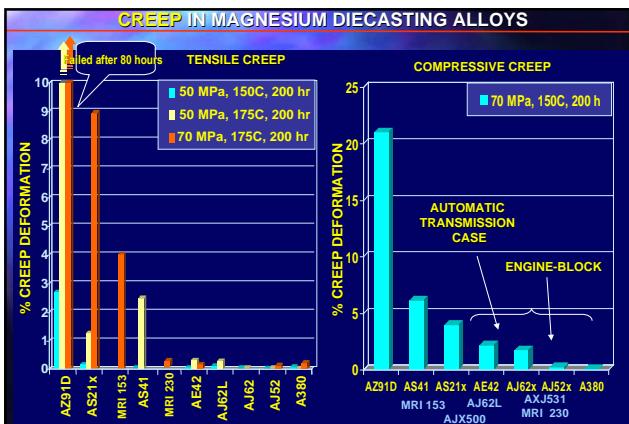
150-175C, 35-100 MPa range
 $Q = 32-25 \text{ kJ/mol}$

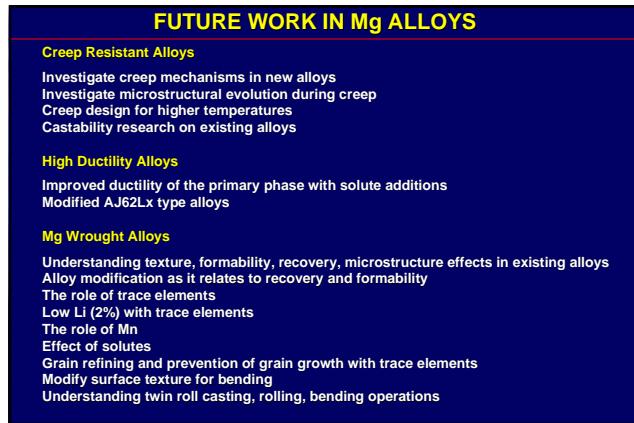
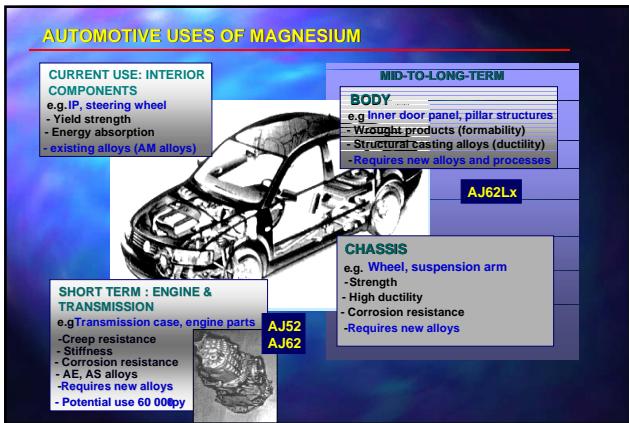
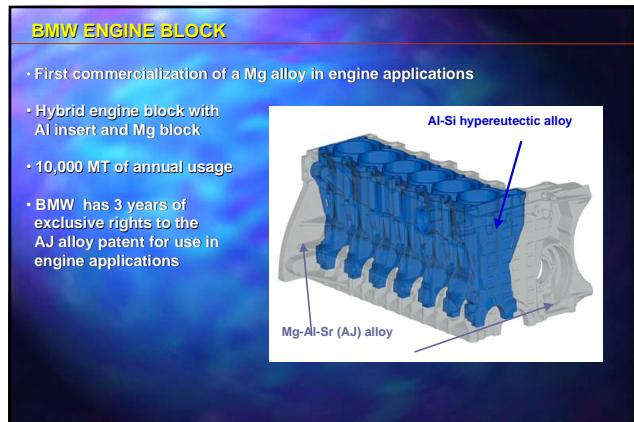
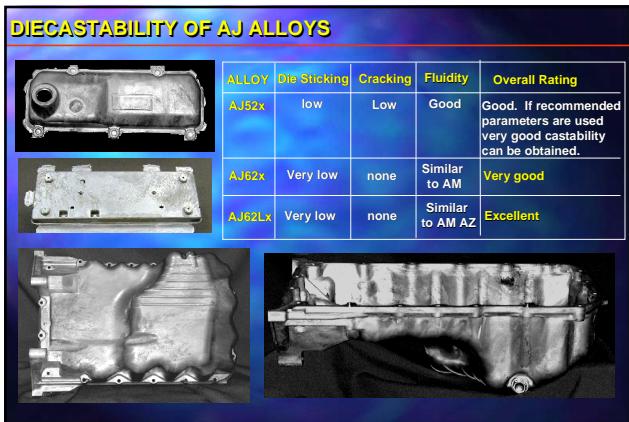
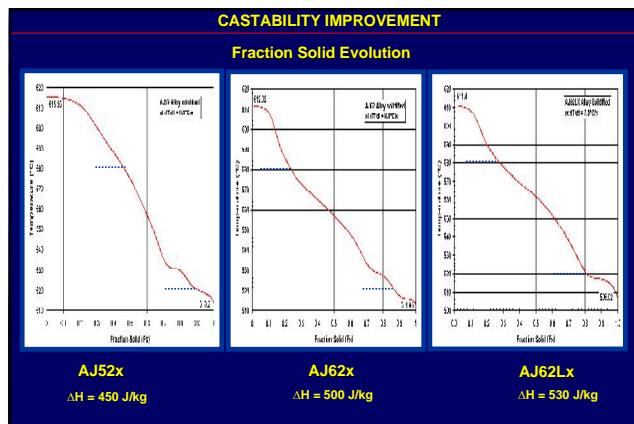
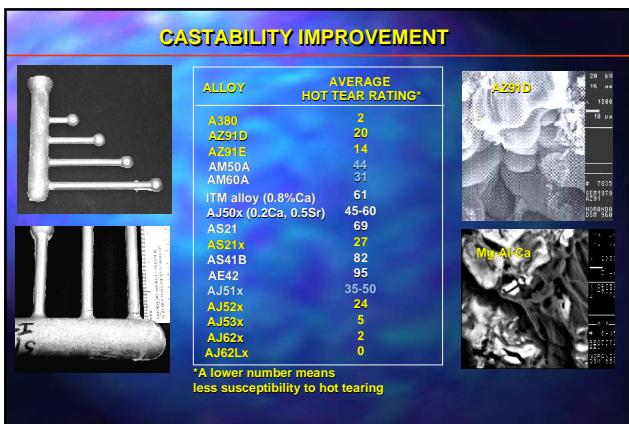


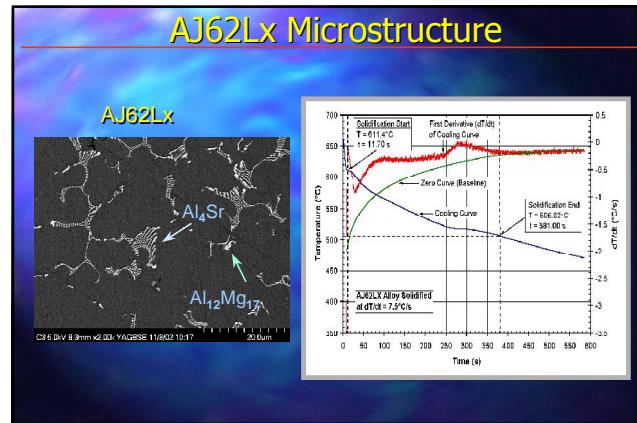
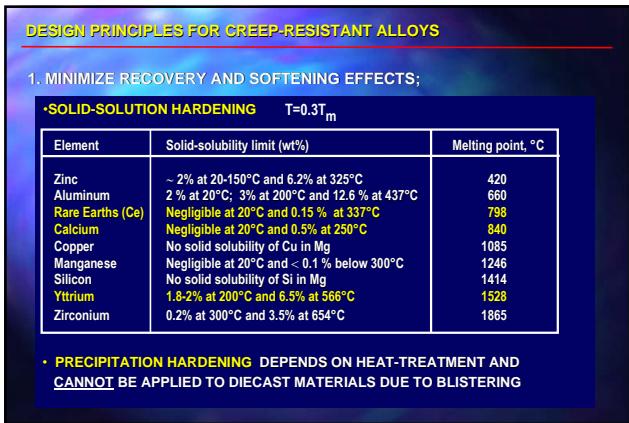
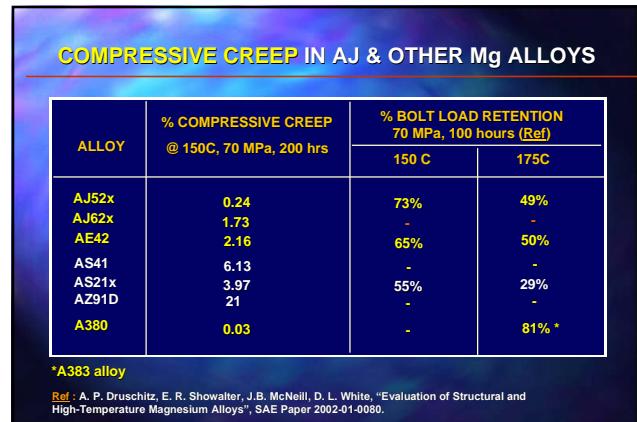
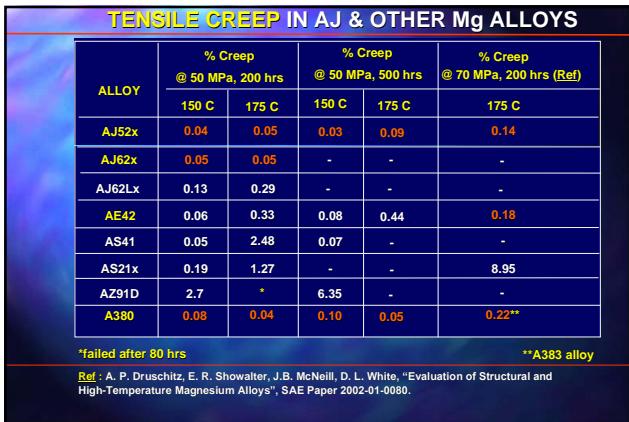
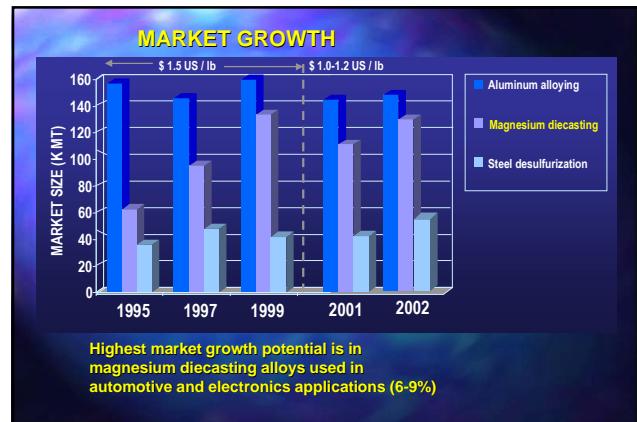
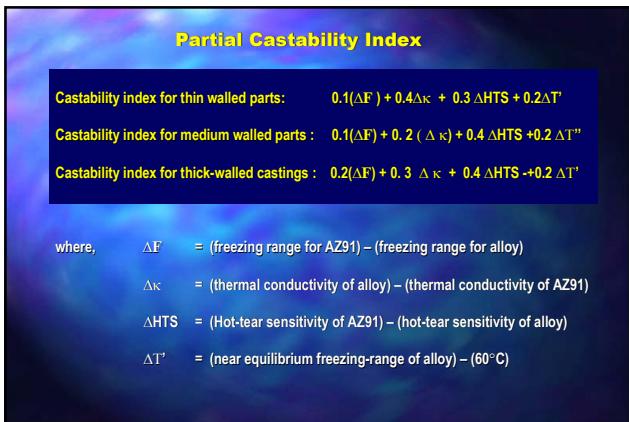
POSSIBLE MECHANISMS

- Sub-grain formation (stress activated recovery)
- Precipitation induced creep ? (change in relative fractions of phases)
- Grain migration ?

* E. Landriaut, Ecole Polytechnique, M.Eng Thesis

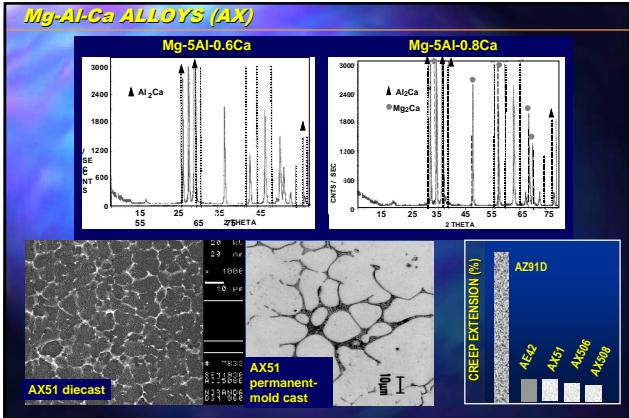






CHARACTERISTICS OF SECOND PHASES IN Mg DIECASTING ALLOYS					
ALLOY	SECOND PHASES		MELTING POINT	CREEP INDUCED PRECIPITATION	CREEP RESISTANCE
	PHASE	TYPE			
Mg-Al (AM)	Mg ₁₇ Al ₁₂	42- 58% Al Incoherent with α -Mg	437°C	Mg ₁₇ Al ₁₂ (eutectoid)	Low
Mg-Al-Si	Mg ₁₇ Al ₁₂ Mg ₂ Si	See above Line compound**	1085°C	Mg ₁₇ Al ₁₂ (eutectoid)	Borderline
Mg-Al-RE (AE42)	Al ₂ RE Al ₁ RE ₃	Line compounds**	1480°C	Mg ₁₇ Al ₁₂ and Al ₂ RE (above 150 °C)	Good
Mg-Al-Ca	Al ₂ Ca	Line compound **	1079°C	-	Good
Mg-Al-RE-Ca-Mn	Al ₂ RE, Al ₁ RE ₃ Al ₂ Ca	Line compounds** Line compound**	1480°C 1079°C	-	Good
Mg-Al-Sr	Al ₂ Sr and Al-Mg-Sr		1040°C	-	Good

**(Laves phase)



ALLOYS DEVELOPED IN 1992-2002

ALLOY	DESIGNATION	INVENTOR	STATUS / COMMENTS
Mg-Al-Si	AS41 (Mg-4Al-1Si) AS21 (Mg-2Al-1Si)	VW	Commercial
Mg-Al-Si (RE)	AS21x	Hydro Mag.	PATENTED
Mg-Al-RE	AE42 (Mg-4Al-2 RE)	Dow	Commercial
Mg-Al-Ca	AX51 (Mg-5Al-(2-8)Ca)	ITM	WO96/25529 (1995), PD*
Mg-Al-RE-Ca	AEX ACM522-(Mg-5Al-2RE-2Ca)	Nissan-UBE Honda	EP 0799901 A1 (1997) NK** EP 0791 662A1 (NK**)
Mg-RE-Ca (Mn)	EX (Mg-(2-5)RE-(0-1)Ca)	MEL	WO96/24701 (NK**)
Mg-Zn-Al-Ca	ZAX850	IMRA	US 6855697 (1999)
Mg-Al-RE-Ca (Sr)	MRI 153, MRI 230D	DSM-VW	US 6139651 (2000)
Mg-Al-Sr	AJ (Mg-(2-9)Al-(5-7)Sr)	Noranda	US 6322644 (2001)
Mg-Al-Ca-Sr	AXJ (Mg-5Al-(2-3)Ca-0.07Sr)	GM	US 6264763 (2001)
Mg-Al-Sr-Ca	AJX (Mg-(2-9)Al-(2-6)Sr-(15-3Ca))	Noranda	US 6342180 (2002)

* PD: public domain ** NK: status not known

