The International Program to Identify Alternatives to SF6 for Magnesium Melt Protection

International Conference on SF6 and the Environment: Emission Reduction Strategies

November 21-22, 2002
San Diego, CA

James Hillis, Noranda Magnesium Inc.
Chairman. - SF6 Alternatives Committee
International Magnesium Association

IMA/INTERNATIONAL MAGNESIUM ASSOCIATION www.intlmag.org

Why – Melt Protection?

- Magnesium is a reactive metal, like aluminum
- Like aluminum, magnesium melts above 600 ºC (651 vs 660). Typically, melt temp. must be 50 to 100 deg higher to cast.
- Unlike aluminum, magnesium possesses much higher vapor pressures – 3mm Hg at melt point. (bp - 1107 ºC/Mg vs 2467 ºC/Al)

➢ **Mg reactivity plus vapor pressure leads to oxidation and burning of molten metal in air.**

With Poor Protection

Ladling to Mg to Molds

With Poor Protection

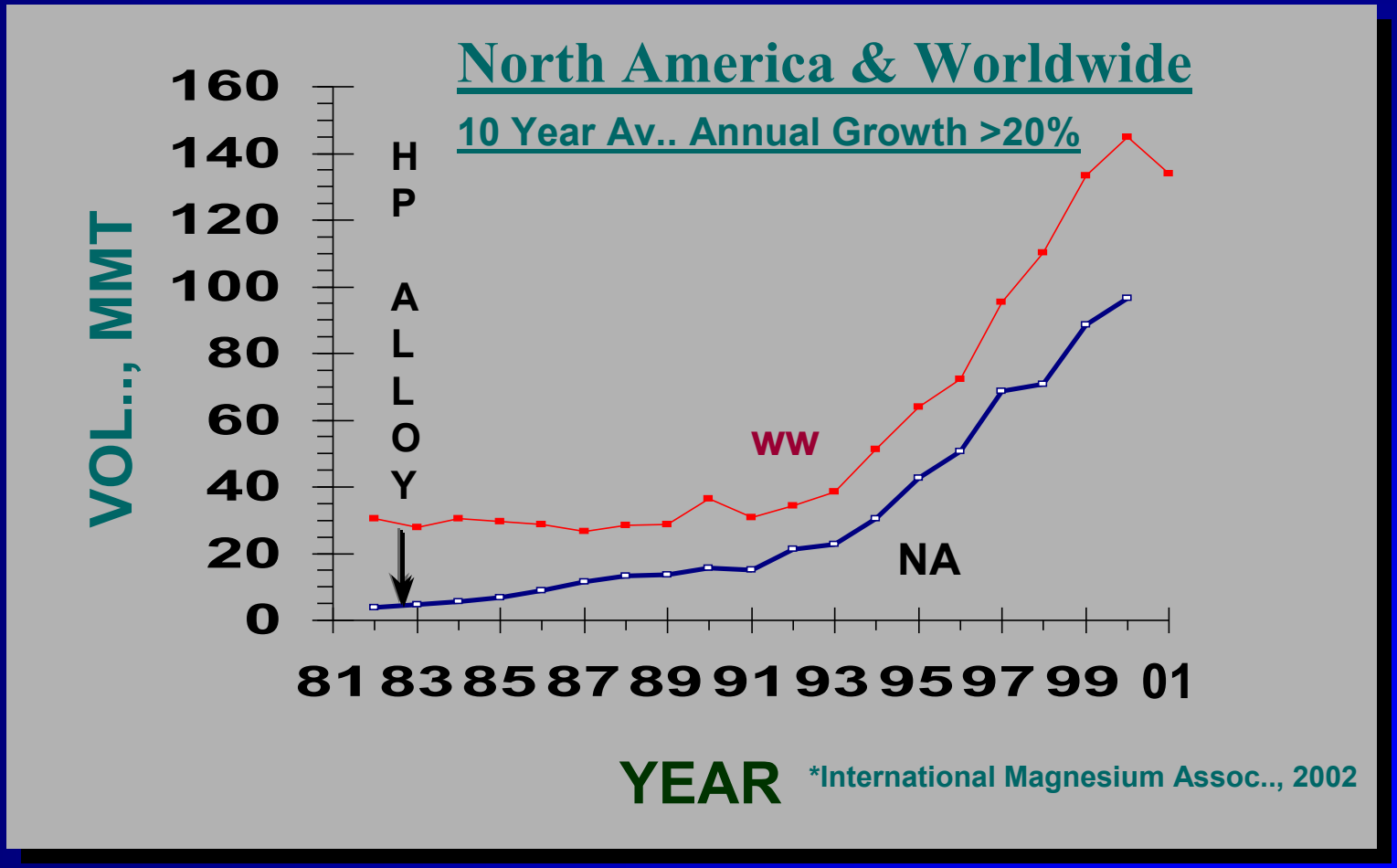
Ladling to Mg to Molds

With Good Protection*

Ladling to Mg to Molds

* D. Milbrath, J. Owen, TMS 2002, Feb. 17, 2002.

DIE CAST ALLOY VOLUME



Why the Growth?

- Automotive wt. reduction – 25-33% less than Al
- Improved fuel efficiency (CAFE) & reduced CO2 emissions over vehicle life (GHG)
- High Die Castablility – thinner walls, greater complexity, more part integration, tighter tolerances, low tool wear
- Highly recyclable - < 5% metal loss
- Ductile alloys – Crash energy management
- Improved quality castings – due to fluxless SF_6 melt protection & hi-purity alloys - 70's & 80's.

SF_6 - A Potent GHG

BUT After 1990

- Climate Change and the Global Warming Issue.
- The initial focus was CO2, Nitrogen oxides, and methane.
- In their 1994 report IPCC introduced fully fluorinated chemicals (FFC's) as a critical issue.
- SF6 – Most potent GHG ever evaluated!
  - Lifetime – 3,200 years
  - GWP (100 yr) - 24,900

Why the Growth?

- Light weight – 25-33% less than Al
- ~~Improved fuel efficiency (CAFE) & reduced CO2 emissions over vehicle life (GHG)~~
- High Die Castability – thin walls, greater complexity, more rapid solidification, tighter tolerances, low tool wear
- Ductile alloys – Crash energy management
- Improved corrosion resistance – due to **fluxless melt protection** & hi-purity alloys - 70's & 80's.

New Reality

Quest for SF_6 Alternatives

- 1995 – Industry leaders begin evaluation of SF6 emissions and alternatives.
- 1997/98 – IMA develops and publishes guidelines for SF6 Conservation in melt protection
- 1998 – IMA appoints committee on SF6 Alternatives
- 1999 – Board approves Committee recommendation for IMA funded research program; … members join EPA Partnership for SF6 Reduction in the industry.
- 2000 – Research Program funded and begun at SINTEF at NTNU in Trondheim, Norway.

GWP's of Leading Alternatives

	Compound	Lifetime (yr)	GWP -100
Benchmarks	CO_2	100 – 150	1
	N_2O	120	360
	CH_4	12	24
	SO_2 *(-- other enviro. & health issues)*	--	---
	SF_6	3,200	23,900
Current Alts	CF_3CH_2F -F134A (CSIRO)	13.6	1,600
	$C_4F_9OCH_3$ -HFE7100 (3M)	4.1	320
	$C_4F_9OC_2H_5$ -HFE7200 (3M)	0.8	55
	$C_3F_7COC_2F_5$ -FK(3M)	0.014	~ 1
	SO_2F_2 - *fumigant* (Air Prod Inc.)	---	~ 1

Novec 612-3M

Ladling to Mg to Molds *

* D. Milbrath, J. Owen, TMS 2002, Feb. 17, 2002.

F134A, HFE7100, & Novec 612 Alternatives

- Competitive performance with SF6
- Non-toxic
- Non-flammable
- Non-ozone depleting
- Short atmospheric lifetime
- Much Reduced GWP's
- As SF6 replacement - the potential to reduce total GW impact by 95 - 99.9+% for Mg-melt protection

Commercial Scale Trial –

Hydro Magnesium, Porsgrunn, Norway
September 2 - 13

- ***Gases*** – HFC134a; HFE 7100; Novec 612 @ 500ppm in dry air or CO2 +5% air
- ***Gas Flows*** - varied 2.5, 5, 10, & 20 l/min
- ***Furnace*** – 500 kg "bath tub", 0.5 m^2 surface area
- ***Melts*** – AM50 and ZE41/RZ5 @ 680 & 710 ^oC
- Gas Analysis – Inlet by IR; Outlet by FTIR
- Performance Monitored by Video & Digital Image

Furnace & Gas Inlets

SF_6 -
CO2 + 5% Air AM50 @ 680 °C

AM50 - SF_6 / CO_2 + Air - 10 l/min - 680 °C

AM50 - SF_6 / CO_2 + Air - 5 l/min - 680 °C

Acceptable!

Not Acceptable!

HFC134a –
CO2 + 5% Air AM50 @ 680 °C

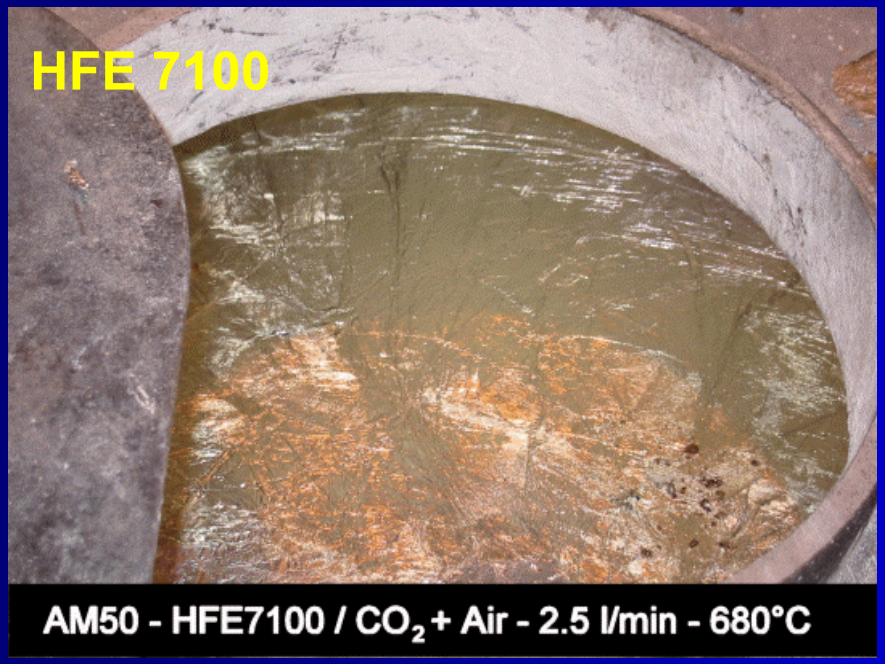
AM50 - HFC 134a / CO_2 + Air - 5 l/min - 680 °C

AM50 - HFC 134a / CO_2 + Air - 2.5 l/min - 680 °C

Acceptable!

Not Acceptable!

HFE7100 & Novec 612 –
CO2 + 5% Air AM50 @ 680 °C



Acceptable!

Acceptable!

HFC134a –
different carriers; AM50 @ 710 °C

AM50 - HFC 134a / Air - 20 l/min - 710 °C

AM50 - HFC 134a / CO_2 + Air - 5 l/min - 710 °C

Not Acceptable!

Acceptable!

Novec 612 –
different carriers; AM50 @ 710 °C

AM50 - Novec 612 / Air - 10 l/min - 710 °C

AM50 - Novec 612 / CO_2 + Air - 5 l/min - 710 °C

Not Acceptable!

Acceptable!

Novec 612 –
dry air; AM50 @ 680 °C

AM50 - Novec 612 / Air - 10 l/min - 680 ºC

Acceptable!

AM50 - Novec 612 / Air - 5 l/min - 680 ºC

Not Acceptable!

Summary

- All three alternative agents provide better melt protection than SF_6 at same flow and level.
- All protective gas mixtures provide better protection in CO_2-air than in Dry Air alone.
- At 710 ^oC melt protection is much greater challenge and CO_2-air is preferred carrier.
- Since new agents are less stable thermally than SF_6, gas distribution will be of greater importance.

Summary

- The governing parameter with these gases appears to be the amount of fluorine delivered per unit time and melt area. Therefore at given concentration and flow the order of efficiency (least to best) would be – HFC134, HFE 7100, Novec 612 - with 4, 9, & 12 F atoms, respectively.
- Use of these gases in magnesium processing should reduce GHG emissions (in CO2 equivalents) by > 95% relative to SF_6 use.

----- Further details pending completion of a full report.
----- Commercial Development trials have begun

Acknowledgements

- International Magnesium Association
- US EPA
- Canada's Action Plan 2000 on Climate Change

SINTEF/MATERIALS TECHNOLOGY

& the NTNU research team

- **Knut Bech,** PhD, Res. Scientist, SINTEF/MT
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