HGI

Sulfuryl Fluoride (SO_2F_2): An Alternative to SF_6 for Blanketing in the Mg Industry

J. Peter Hobbs

Halide Group, Inc.

hobbsjp@halidegroup.com

Outline

- What makes an Ideal Substitute?
- Why SO_2F_2?
- Evaluation of SO_2F_2 in Mg blanketing applications
  - Mg Sand caster trial
  - Mg die caster trial
  - Primary Mg producer trials
- Issues to address in the use of SO_2F_2
- Properties and Handling

What makes an Ideal Substitute?

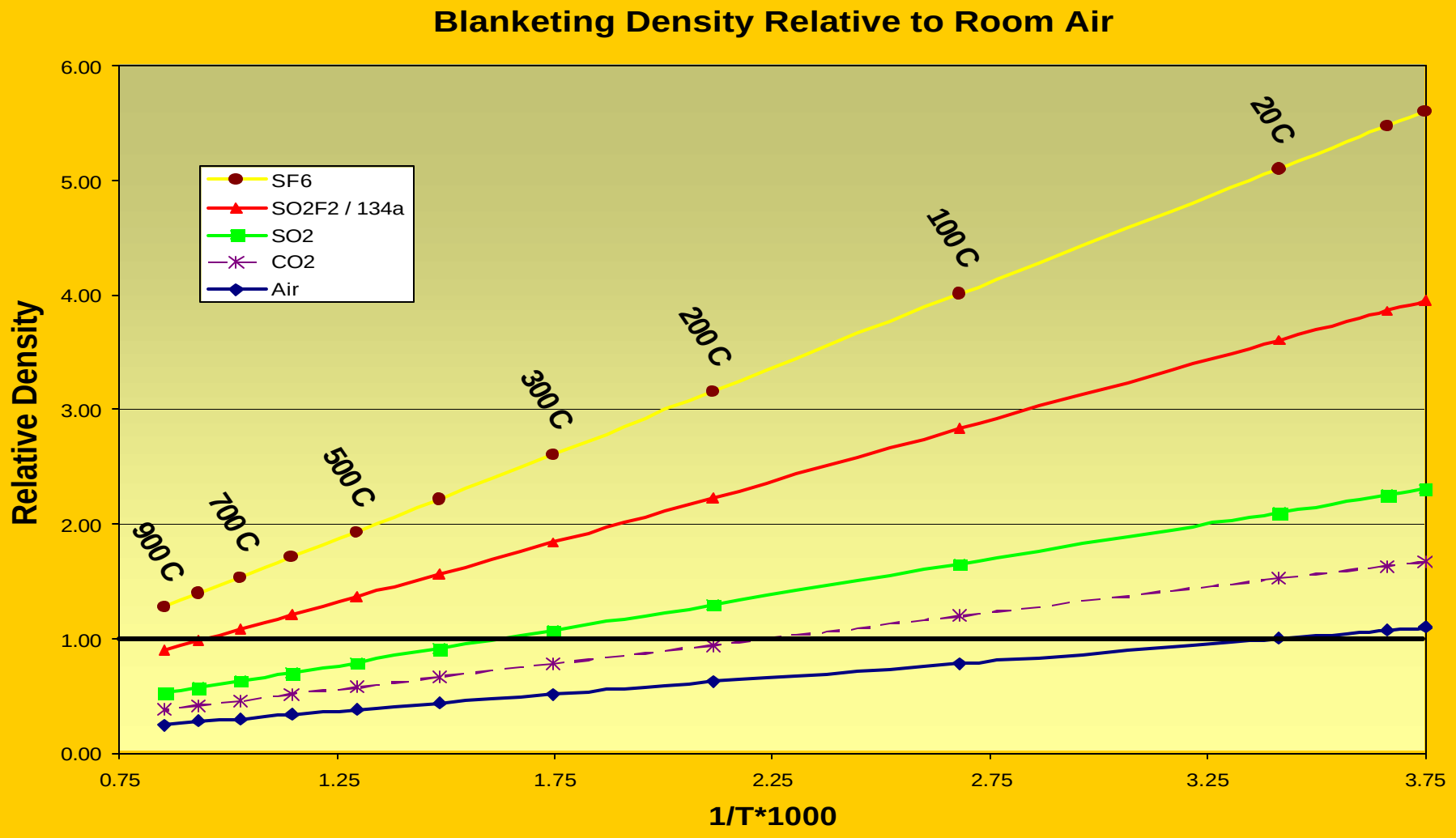
- Environment – both Substitute and By-products
  - No Ozone Layer depletion, No/Low GWP
  - Short life, No/Low toxicity, No Biological Uptake
- On the plant floor
  - Ease of use; "*what we know*"
  - Stable, but Reactive on & over Melt
  - Dense – "*hangs*" in pot well
  - Forgiving
  - Nontoxic
- In Front Office
  - Cost of ownership

Why SO_2F_2?

	GWP_{100}	life	BP °C	SG	PEL ppm	By-product
SF_6	23,900	3,200 yr	-64 sub	5.1	1000	SO_2
SO_2F_2	~0	18 min - 3 day	-55.2	3.6	5	SO_2
134a	1,300	14.6 yr	-26.5	3.5	1000*	HF, PFC
SO_2	~0	~0	-10	2.1	3	SO_2
Novec 612	~0	<10 day	49	?	150†	PFIB,COF_2, PFC
HFE-7100	320	4.1 yr	60	8.6	750*	HF, PFIB, COF_2, PFC

* ACGIH TLV, † 3M

Impact of Temperature on Relative Density



Why SO_2F_2?

- Advantages
  - 0 GWP
  - Gas at room temperature
  - Good gas density (~2x CO_2)
  - Non-hygroscopic, non-corrosive
  - By-products like SF_6
  - No high toxicity or high GWP by-products
    - PFIB, PFC
  - Does not produce HF
  - Gas cost lower in most cases

Why SO_2F_2?

Disadvantages

- Poisonous gas, CAS# 002699-79-8
  - toxicity SF_6, 134a< Novec 612 << SO_2F_2 < SO_2 < HF
- OSHA PEL is 5 ppm
- IDLH is 1000 ppm

- Equipment upgrade - alarms, gas blender

Availability of SO_2F_2

- Commercially available
  - Insecticidal fumigant Vikane® – Dow AgroSciences
  - Solvay Fluor

Evaluating SO_2F_2 in Mg Metal Blanketing Applications

Site	Site SF_6 Standard	SO_2F_2
Sand Caster ZE-41	1.7-1.9% in CO_2/air 26 scfh	2900 ppm in CO_2/air 54 scfh
Die Caster AM-60	3000 ppm in dry air 88 scfh	1500 ppm in CO_2/air 88 scfh

Evaluating SO_2F_2 in Mg Metal Blanketing Applications

Site	Site SF_6 Standard	SO_2F_2
Primary Trial 1 Pure Mg, AZ91, WE54	1.7% in CO_2/air 3 slpm	1500 ppm in CO_2/air 3 slpm
Primary Trial 2 Pure Mg, and other alloys		950 ppm in CO_2/air 3 slpm

SO_2F_2 Commercial Trial Results
4 tests, 3 venues

- Thin, flexible, adherent, silver/grey skin formed
- Bottom dross levels similar to SF_6
- Yttrium loss levels similar to SF_6
- Higher temperatures appear to be tolerated
- Off-gas analysis (FT-IR) from melt:
  - Similar to SF_6 - SO_2, CO, no HF, no CF_x

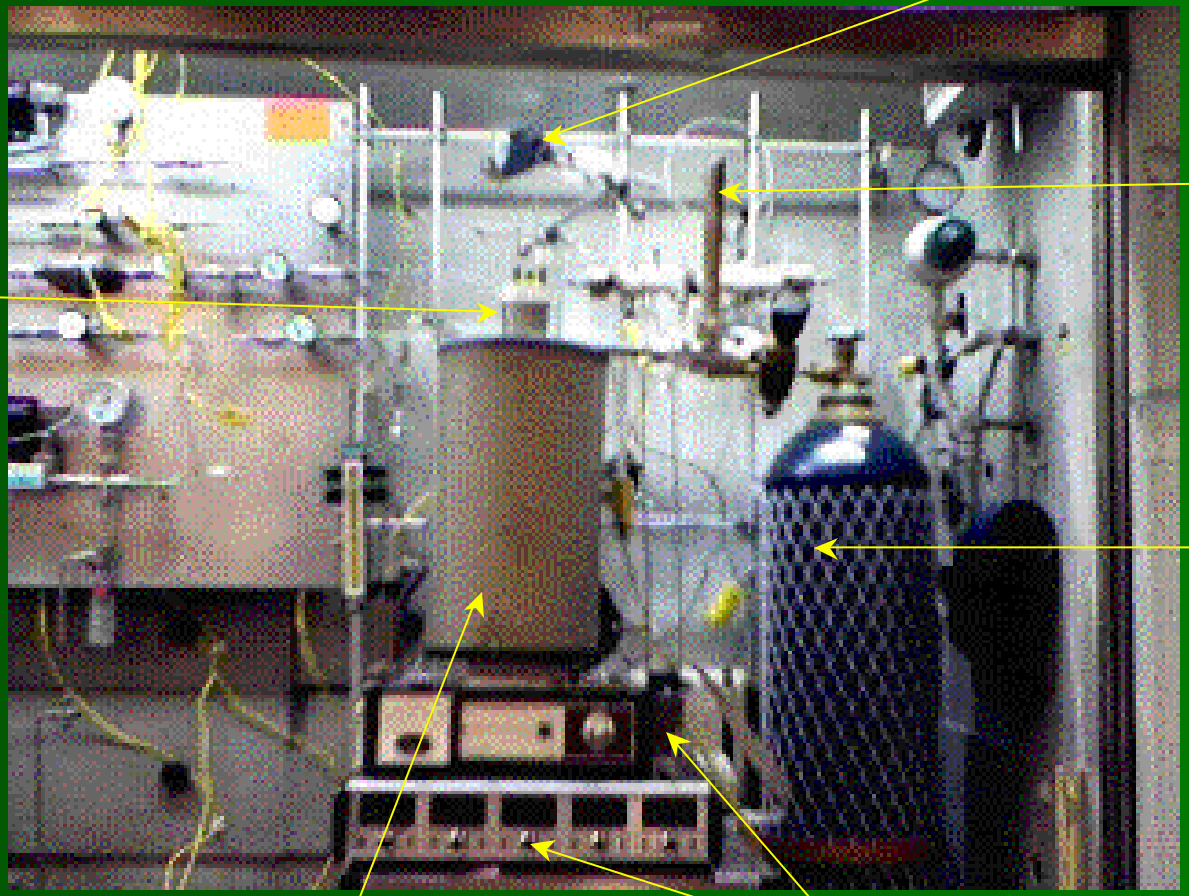
Commercial Trial Results

- SO_2F_2 not observed outside of pot
  (at operator positions)
- Effective blanketing achieved:
  - good metal quality obtained
- Head-to-head comparison of SO_2F_2 and SF_6 shows a usage ratio SO_2F_2/SF_6 of 0.1 to 0.5 (volume)
- Technical feasibility of using SO_2F_2 established

Lab Evaluations of SO_2F_2

- Compare videos from laboratory:
  - Pure Mg – SO_2F_2
    - @ 825 °C (1517°F)
    - under 1000 ppm SO_2F_2 in 33% CO_2 / air
  - Pure Mg – SF_6
    - @ 760 °C (1400°F)
    - under 2500 ppm SF_6 in 33% CO_2 / air

AP Experimental Setup



Mg under SO_2F_2 in CO_2/Air

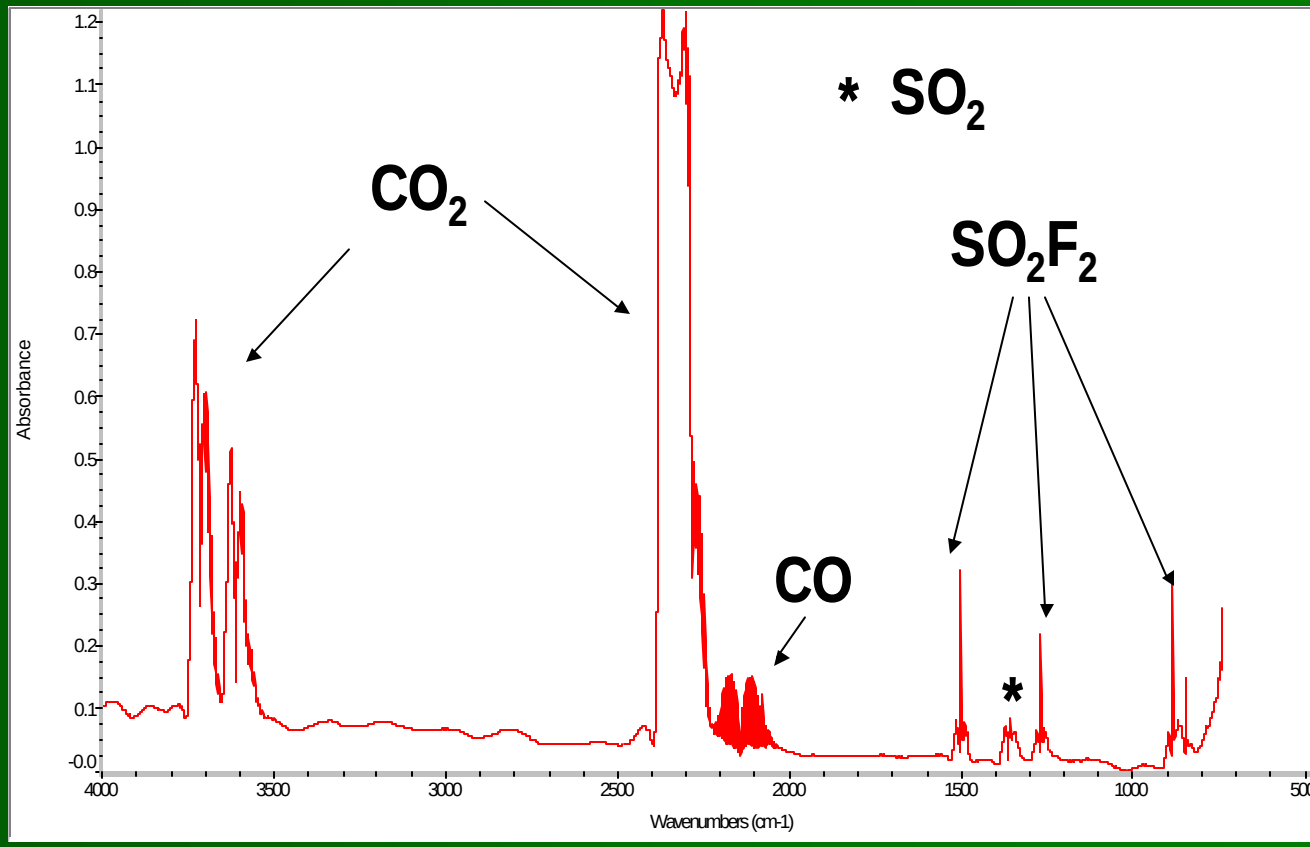
- 1000 PPM SO_2F_2
- 33% CO_2 & Air
- 825 °C (1517 °F)
- No Flares
- Exposed surface retains shine

Mg under SF_6 in CO_2/Air

- 2500 PPM SF_6
- 33% CO_2 & Air
- 760 °C (1400 °F)
- No Flares
- Skin tarnishes slowly

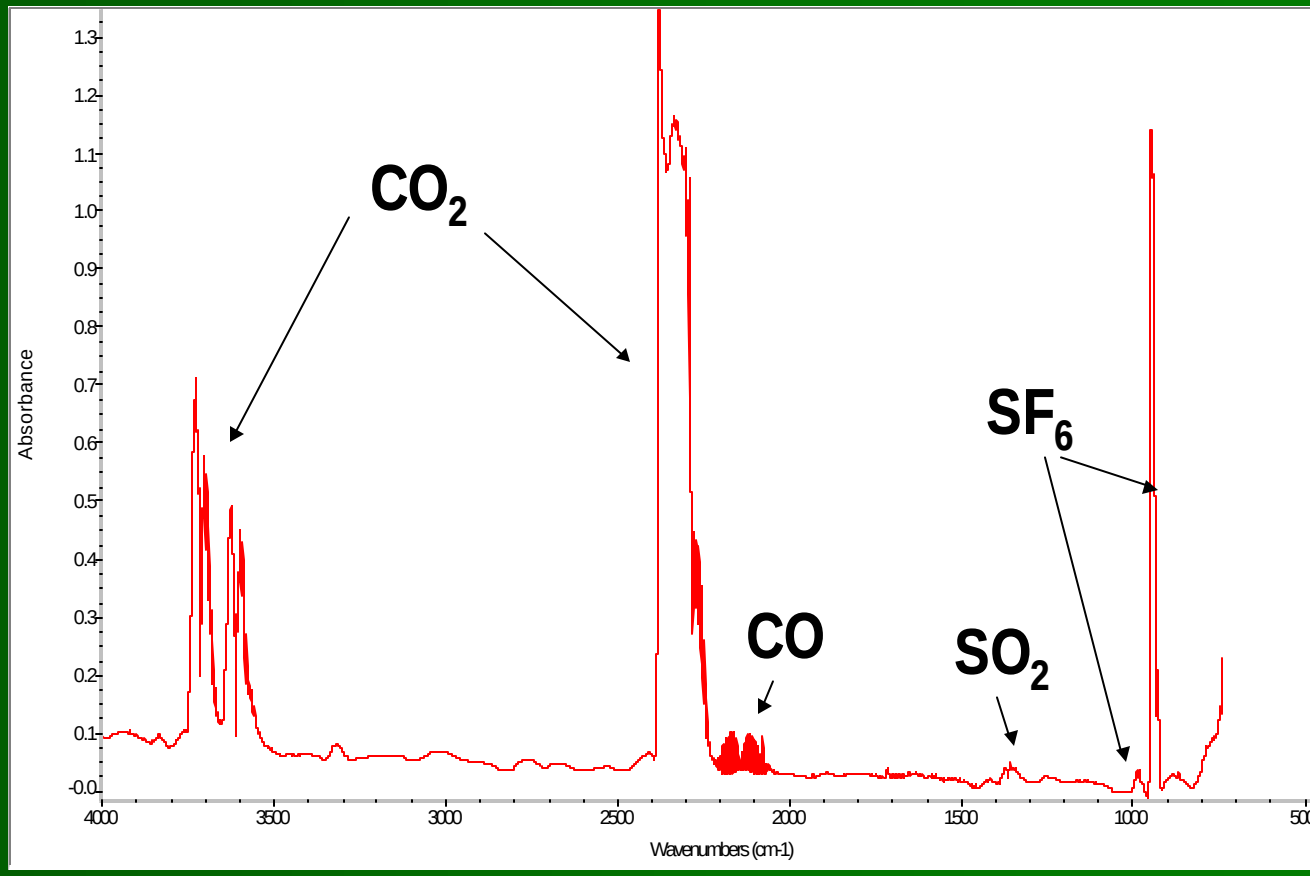
Mg - Exhaust Gas for SO_2F_2 in 33% CO_2 and Air

- 1000 PPM SO_2F_2
- 33% CO_2 & Air
- 825 °C (1517 °F)



Mg - Exhaust Gas for SF_6 in 33% CO_2 and Air

- 2500 PPM SF_6
- 33% CO_2 & Air
- 750 °C (1382 °F)



Issues Being Addressed

- Installation of SO_2F_2 Alarms
  - Qualify reliable, cost effective alarm systems
- Delivery-Supply
  - Establish a secure/safe supply chain
- Delivery-Blend/Use
  - SO_2F_2 use concentrations 2-10x lower than SF_6
  - Upgrade or replace equipment

Issue - Detection

- SO_2F_2 Detectors
  - IR
    - Commercial portable unit available (SF_6 issue)
    - 10cm gas cell, <1ppm
  - Electrochemical
    - One system has been evaluated
    - SO_2F_2 is reproducibly detectable to <2.0 ppm
    - Useful well below the PEL of SO_2F_2 (5 ppm)
  - A personal monitor has been identified but needs additional testing
- Odorization of SO_2F_2 is possible – i.e. Banana Oil

Issues - Delivery

- SO_2F_2 Supply
  - Product Stewardship essential
- SO_2F_2 Blend/Point of Application
  - Pressure/Mass flow blenders work
    - on line verification of composition
    - Flow tube blenders generally inadequate
  - Low leakage supply system
  - Adequate local ventilation required

Forward Plan

- Laboratory evaluations completed
- USP 639884: “Blanketing Molten Nonferrous Metals and Alloys with Gases having Reduced Global Warming Potential”
- AP will participate in the IMA program at SINTEF
  - SO_2F_2 has been shipped to Norway
- HGI is actively seeking one or more partners for commercializing this technology

Halide Group, Inc.

Suite 120, Commerce Plaza

5050 Tilghman Street

Allentown, PA 18104

(610) 398-1400

- A private consulting and process development company
- Experienced in design and operation of specialty gas systems for handling high purity, toxic and/or corrosive fluorine based gases and fluorine.

hobbsjp@halidegroup.com

HGI

Thank you

Physical Properties of SO_2F_2

- Thermally stable, non-flammable, non-corrosive, colorless, and odorless gas

  - Vapor density = 4.4 g/l @20°C (0.27 lb/ft3)
    Relative = 3.64
  - Molecular weight = 102
  - Boiling point = -55.4 °C
  - Freezing Point = -137°C
  - Critical Point : T = 91.8°C, P = 50.5 atm (727 psig)
  - Cylinder pressure (liquefied gas) = 217 psig @21.1 °C

Chemical Properties of SO_2F_2

- Solubility in H_2O ~ 750ppm
- Inert:
  - Stable to 400-600°C
  - Does not hydrolyze in neutral water to 150°C
- Hydrolyzed by aqueous base (KOH, NaOH)
- GWP ~ 0
  - t_{50} = 18 min to 3 days

Mg under Stagnant Air

- Stagnant Air
  (low Oxygen)
- 750 °C
  (1382 °F)
- Thick Oxide Layer
- Ignition / Smoke
  (at melt)

Mg under Flowing Air

- Flowing Air
  (~0.75 changes /minute)
- 700 °C
  (1292 °F)
- Thick Oxide Layer
- Ignition / Smoke
  (at melt)

Mg under SF_6 in Air

- 5700 PPM SF_6
- 780 °C
  (1436 °F)
- Flares then
  Extinguishes

Mg under SF_6 in CO_2/Air

- 2820 PPM SF_6
- 50% CO_2 & Air
- 785 °C
  (1445 °F)
- No Flares
- Skin tarnishes rapidly
  May be due to residual oxide layer

Mg under SF_6 in CO_2/Air

- 2820 PPM SF_6
- Air (CO_2 off)
- 785 °C
  (1445 °F)
- Flares

Mg under SO_2F_2 in Air

- 900 PPM SO_2F_2
- 745 °C (1373 °F)
- Flares then extinguishes
- Exposed surface retains shine

Mg under SF_6 in CO_2/Air

- 2500 PPM SF_6
- 33% CO_2 & Air
- 760 °C
  (1400 °F)
- No Flares
- Skin tarnishes slowly

Mg under SO_2F_2 in CO_2/Air

- 1000 PPM SO_2F_2
- 33% CO_2 & Air
- 825 °C (1517 °F)
- No Flares
- Exposed surface retains shine