4Th International Conference on SF6 and the Environment (EPA Conference 2006)

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"SF6 reduction, Alternatives and Process improvement in the Japan Mg Industry"

Tsutomu Ito (Sp), Hisashi Ohara
Japan Magnesium Association (JMA)

Speaker E-mail:ito-tu-mi@cc9.ne.jp

Comparison of SF6 gas exhaust by Die caster

➢Emission Coefficient of SF6 gas

1. Japan ; [33 companies in 2004, Data by JMA]

Year	2001	2002	2003	2004	2005
SF6 kg/ ton-Mg melting	3.3	2.7	2.3	1.9	2.0

2.Europe; [Report for DG ENV 2003 by Ecofys GmbH]

Year	1995	2001
SF6 kg/t-Mg diecasting	3	1(0.9)

3.US ; [Reports in EPA SF6 Conference and IMA Conference]

Year	1999	2000	2001	2002	2003
SF6kg/t-Mg process	2.3	2.0	0.8		2+

Plan and way to SF6 gas reduction

EU : Regulation

F-gas	Use	Date of use Ban
SF6	Magnesium die- casting	*Entry into force :4 July 2006 *Provision of the regulation will apply with affect:4 July 2006
SF6	Magnesium die-casting if use<850kg per year	January /1 2008

USA : Voluntary partnership between US-EPA and Mg Industry 16 companies

✓Partnership's goal is to eliminate SF6 emission by Dec/31 2010

Japan : Voluntary reduction planning and strengthened by each Mg producers, with cooperatively supporting by JMA and Government

Look at Japan Mg industry on the point of view SF6

➢ **Magnesium market and Recent condition**
of SF6 consumption / GHG exhaust in Japan

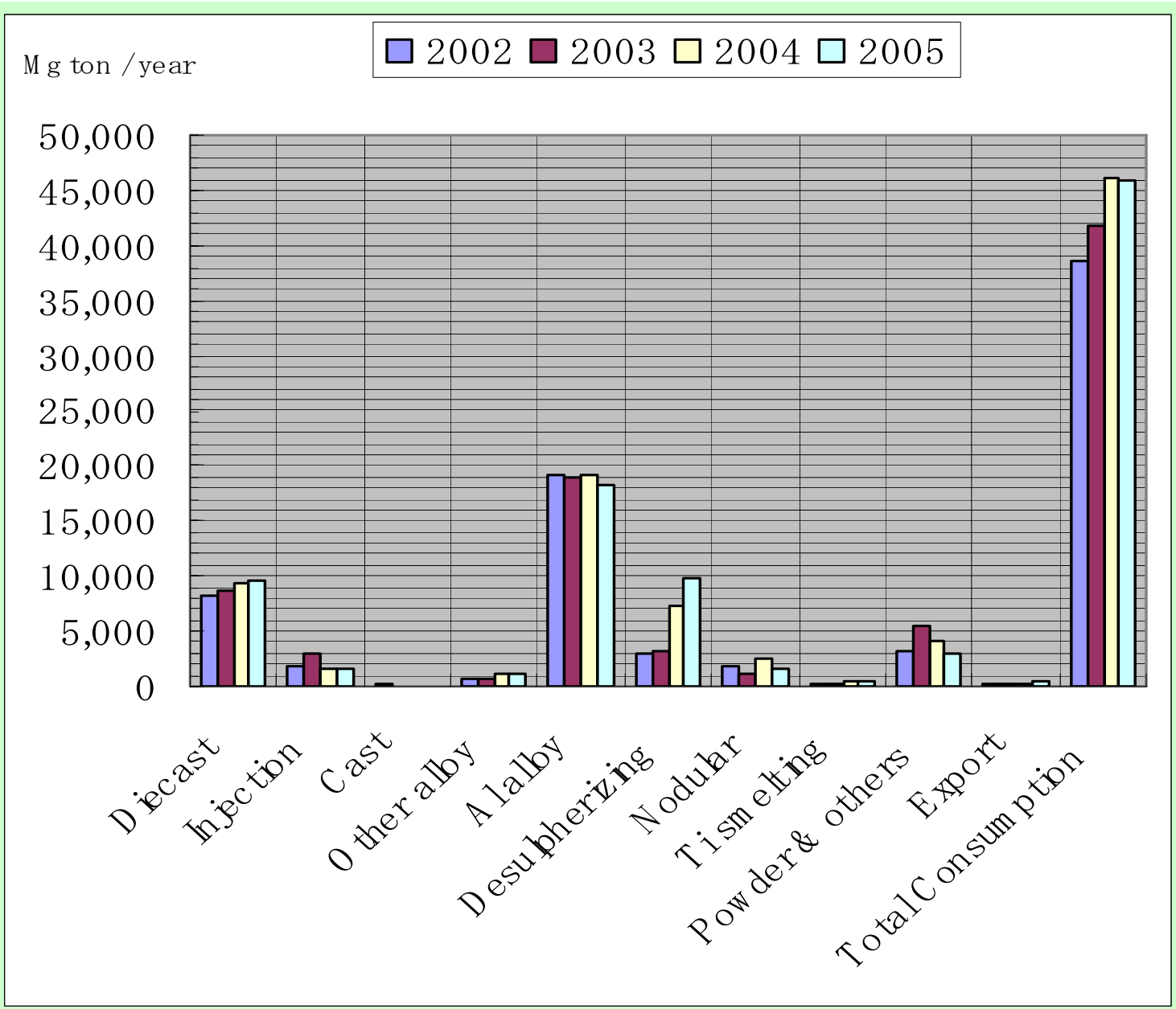
➢ **Technology Road Map in Japan:**
✓Reduction technology system in SF6,
✓Substituting material, (fitted to past equipment or not),
✓ Cover gas free process technology (product development)

➢ **Alternative gas promotion activity:**
✓ Actual continuous operation and expansion,
✓ Typical introducer's support,
✓ Financial supporting system,
✓ New cover gas research

➢ **Process technology**:
✓ Mg alloy (products) developments by SF6 free

➢ **Equipments and process improvement**:
✓ Reviewing

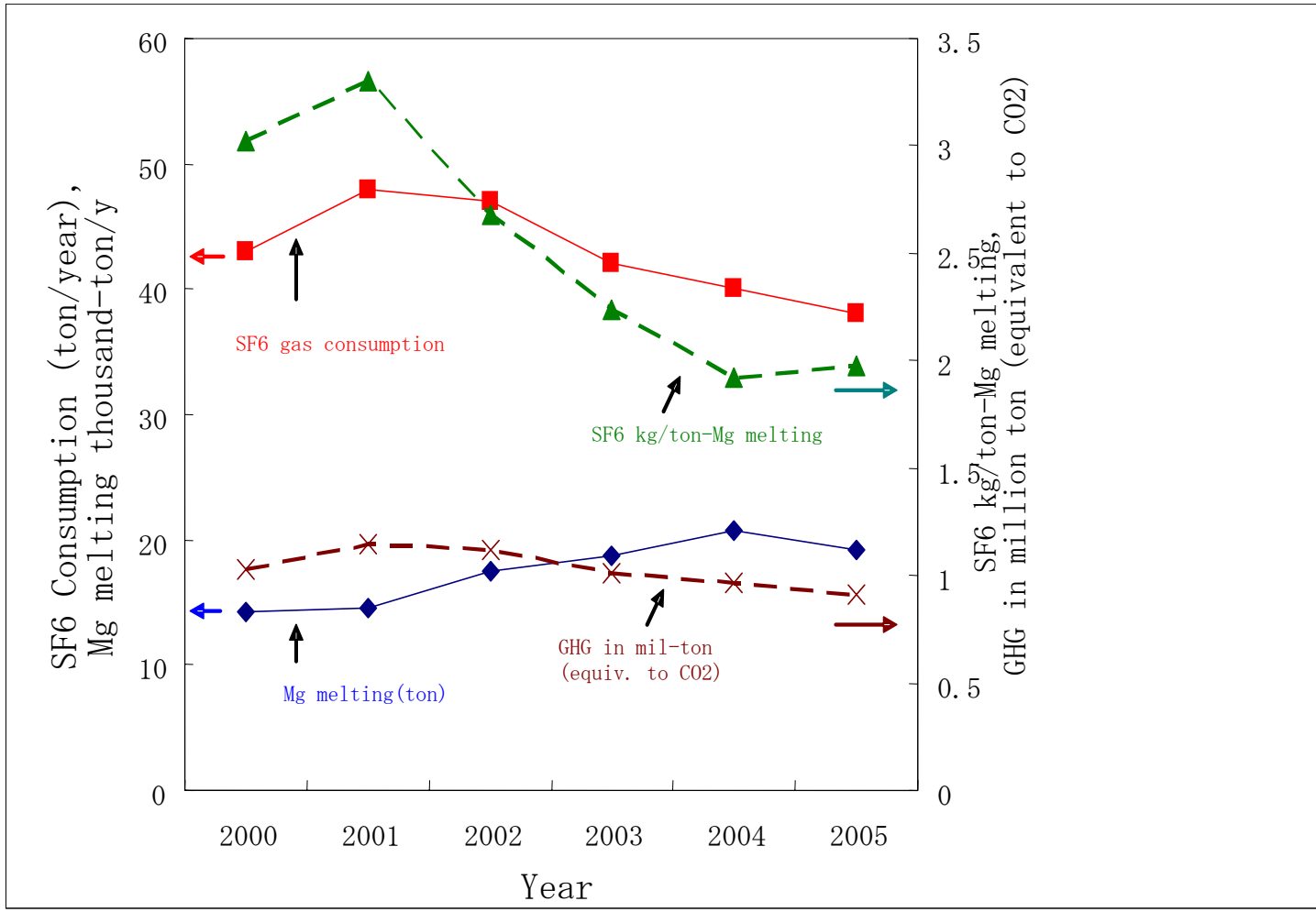
Mg consumption in Japan(2002~2005)



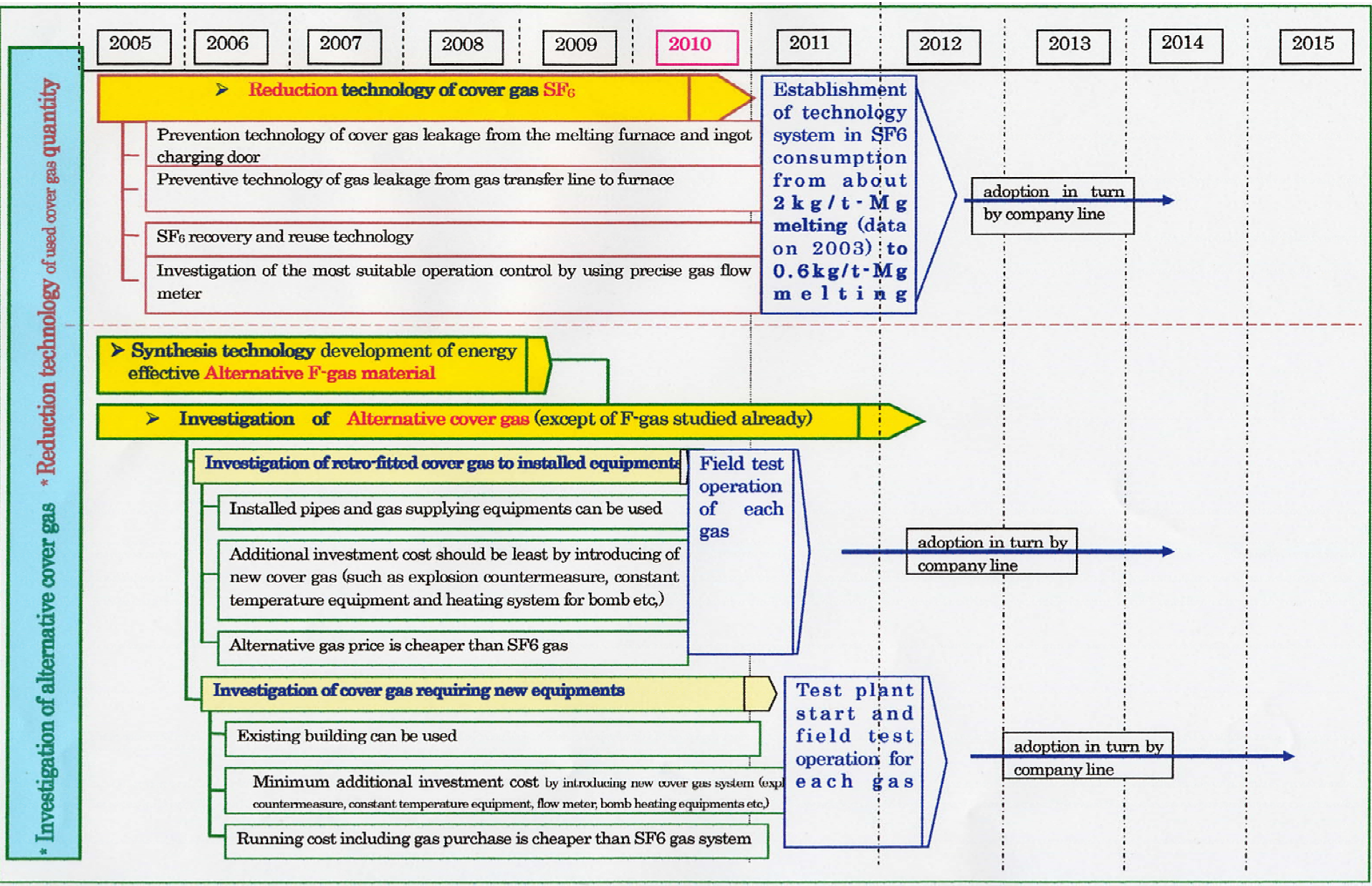
(Memo) :
melting volume is 1.5-2 times of virgin ingot because of re-use of recycled ingot by in-house or recycle shop

Recent trend of SF6 gas Consumption and Mg melting Volume at Die Casters in Japan

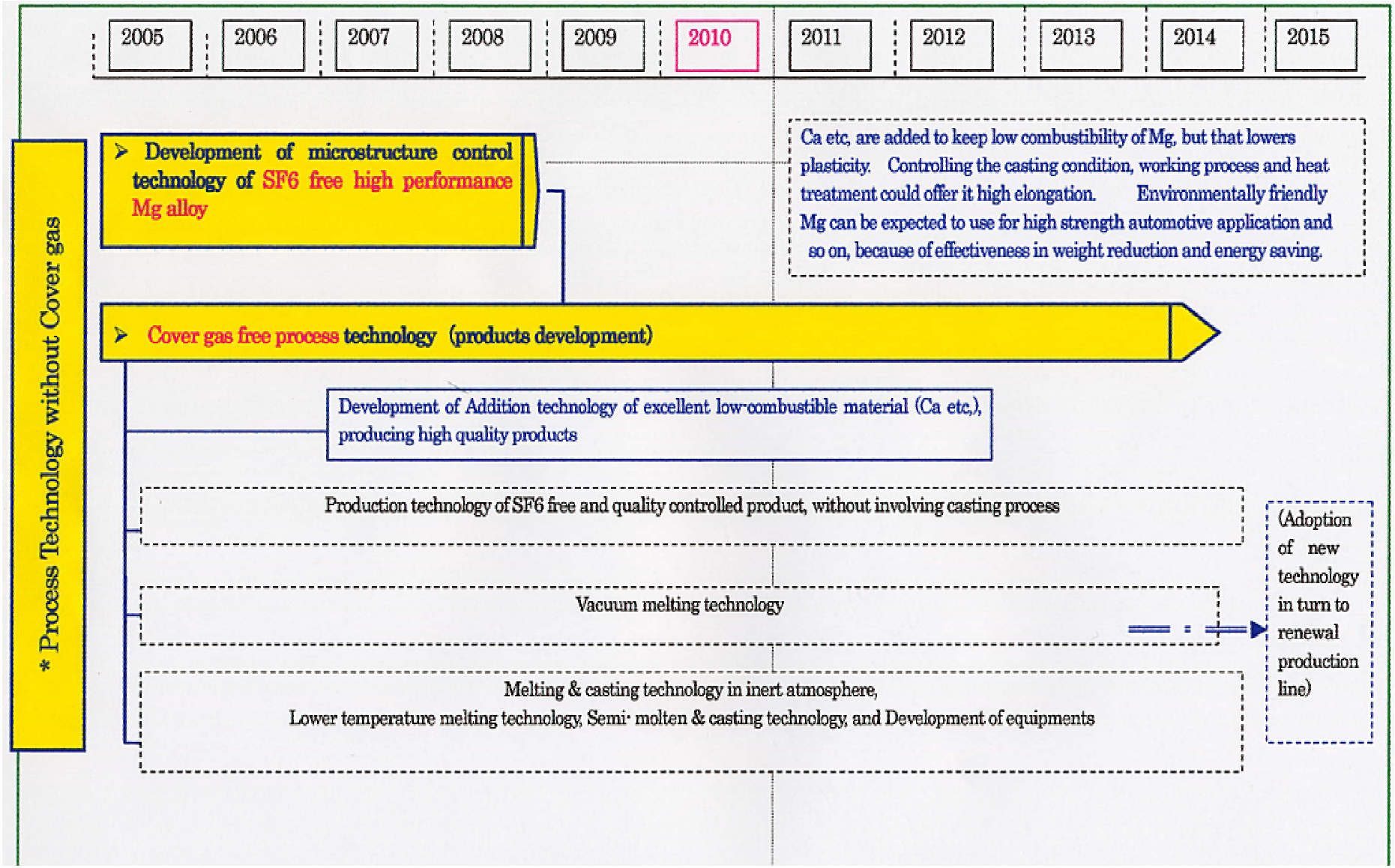
	Year						
	2000	2001	2002	2003	2004	2005	2010(Estimate)
SF6 gas Exhaust (ton)	43	48	47	42	40	38	20
GHG in mil-ton	1.028	1.147	1.123	1.013	0.967	0.913	0.478
Mg melting thousand- ton/ y	14.2	14.5	17.5	18.7	20.7	19.1	40
SF6 kg/t-Mg melting	3.02	3.30	2.68	2.24	1.92	1.98	0.5



Road Map(1) in Japan METI & NEDO



Road Map(2) in Japan



Promotion activity: SF6 Substitute, Process and Financial

*Marketing by gas supplier and technology developer

a) Taiyo Nippon Sanso Corporation (TNSC) : Development of MG-Shield gas system in Japan market

b) CSIRO and Advanced Magnesium Technology (AMT) : Introduction of AM-Cover gas system in Japan market

Tokai Rika : Adoption and enlargement plan of Gas System [MG-Shield], in November 2005

Trial Tests
Succeeded but
Not equal with SF6:
Technical support important

✓**Investigation project**: new protective gases with low global warning potential for Mg alloy melt. **New Energy and Industrial Technology Development Organization (NEDO)** proj:2005 Nagaoka Technical University

✓**Process Technology project**: cover gas free process technology, microstructure control, products development. **NEDO** proj: 2005-

✓**Financial support program** : go to start "Equipment for Alternative gas introduction and F-gas reduction" by **Ministry of Economy, Trade and Industry (METI)** :
✧Two years from 2007 to 2008

✧ Max. of 2/3 of the equipment fund, and effective value of gained CO2 equivalent reduction

Actual SF6 Alternatives in Japan(1)

2005/Oct ; Tokai Rika
(Press release)

✓Introduction of "Mg-Shield" gas system in model line

✓Forecast of GHG Reduction equivalent to CO2 gas : about 45,000t- CO2/year

2006/Feb; Tokai Rika
(Environmental white paper 2006)

✓ Expectation of GHG Reduction at Otowa plant, Tokai Rika is 51,800t-CO2 in fiscal year 2007

✓ METI's Financial Support Program for "Business and Area Improvement on the GWP reduction at the year 2005 "

(Properties)	SF6 gas	FK gas
Poisonous	No	No
Gas life (Year)	3,200	0.01 (3-5 days)
GWP	23,900	1
Consumption (ton/y)	2.25 (2004)	0.3 (forecast in 2007)
CO2 Equivalent (ton-CO2)	52,000	200

Alternatives(1):MG-Shield gas by (TNSC)

Special Property of MG-Shield:

✓ **Gas Supply condition: Liq. CO2 + Novec 612**
[Super critical condition; CO2/ +32℃, 7.3MPa]

✓ **Bottle Supply system:**
→ **Easy handling of small quantity**
→ **Precise and stable concentration control**
→ **Easy exchange from SF6 system**
→ **Operation continue in case of power failure**

Property of Novec 612 developed by 3M:

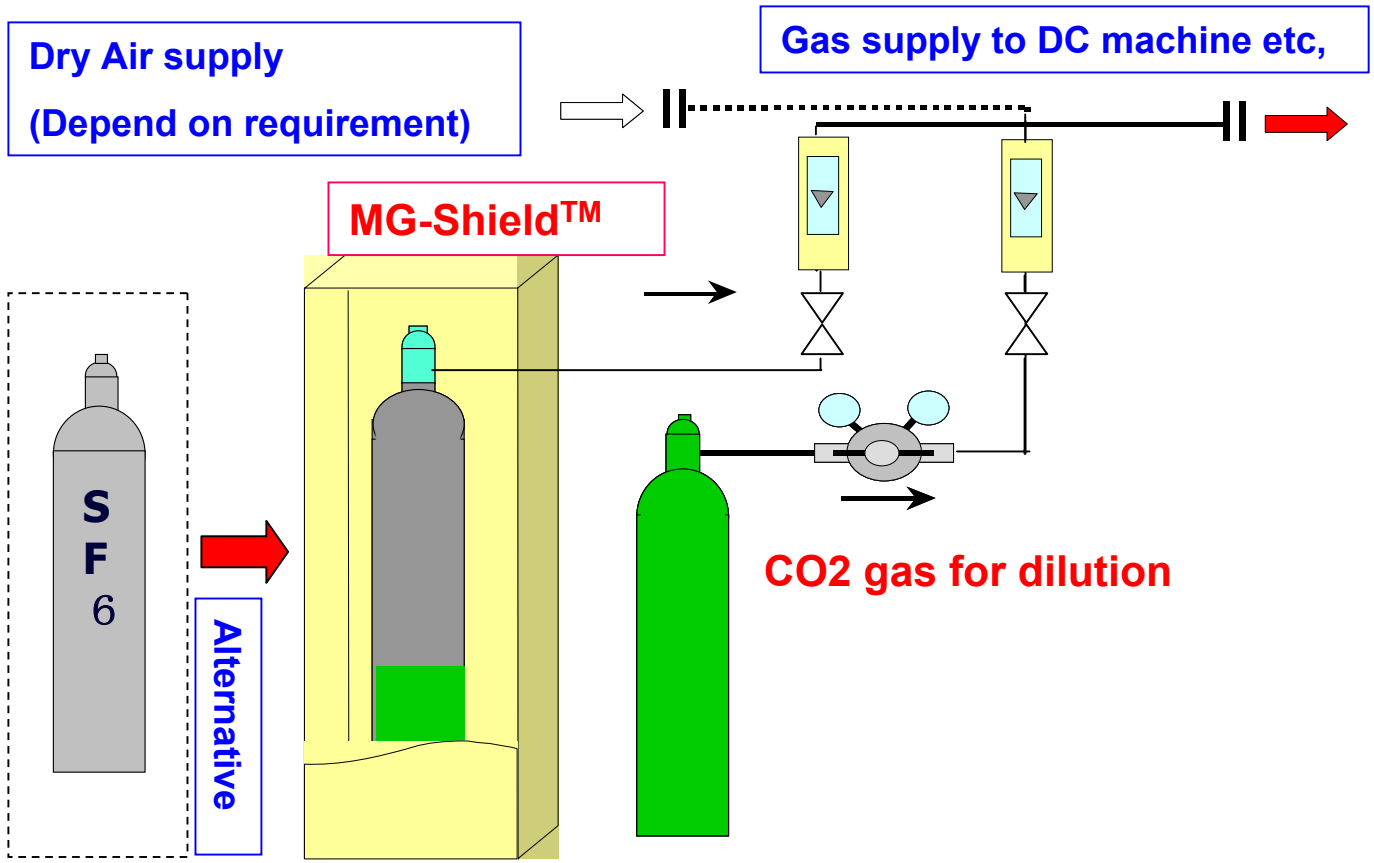
✓ **GWP: about 1 (Lowest level)**
✓ **Practically Harmless:**
LC50 ⩾100,000 ppm
✓ **Molecular Wt.:316**
✓ **No Sulfur Contained**
✓ **Liquid at room temp.: b.p. 48 ℃**

Evaluation as Cover gas :

✓**Gas Flow :Suitable Concentration Control and Dilution**
✓ **Combustion Preventing property**
✓ **Safety of Exhaust gases**

Source: TNSC

MG-Shield gas Flow System



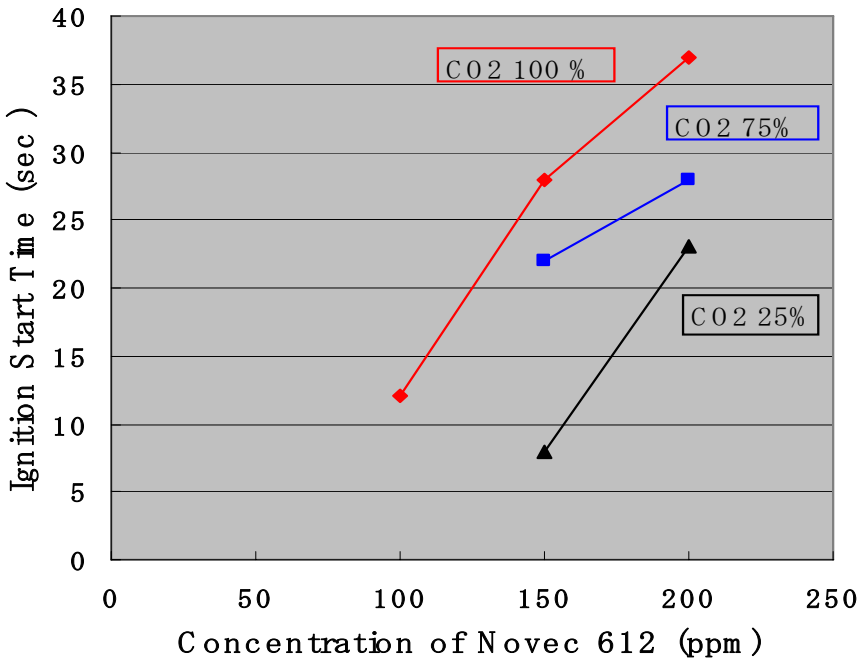
Exclusive Supply Equipment

Super Critical condition(35-39℃)

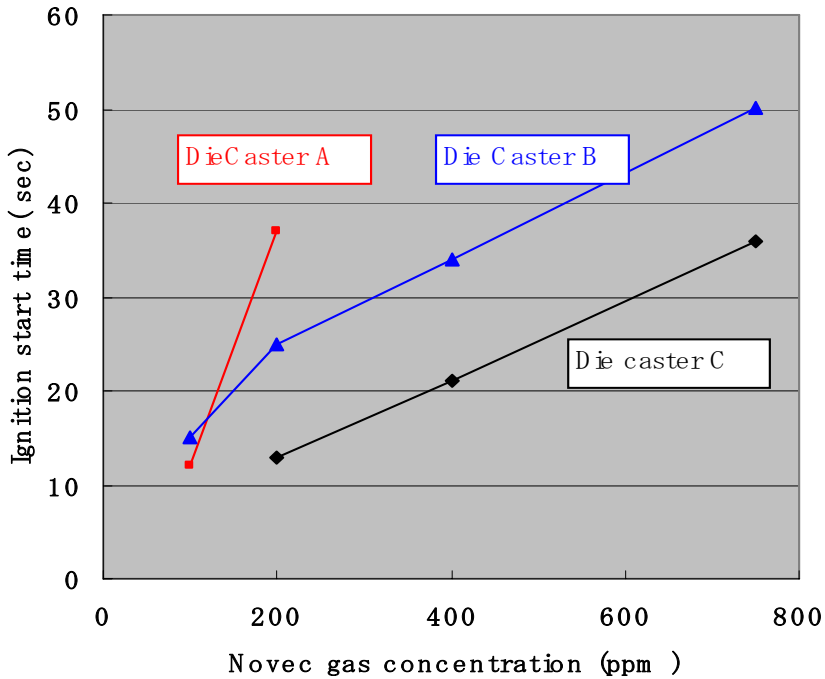
Gas flow:200 liter/min,Max

Operation Condition of MG-Shield gas

- ✓ Novec gas density : 100～400ppm(0.01-0.04%)
- ✓ Mixing gas flow volume： Equal to twice of SF6 cover gas
- ✓ Carrier gas ：Add CO2 ⩾25%（100% CO2 Recommended）
- ✓ Lowering of Gas density or Flow Volume : Reducing Air Invasion ;Tighten the Furnace Sealing and Short Time Opening of Furnace Door **(depend on furnace and operation condition)**



Ignition start time delayed by CO2 addition increase in air



Ignition start time depend on operation condition

Alternatives(2):AM-cover gas
by Advanced Magnesium Technology(AMT)

➢ Special properties of AM-cover :

✓ Mixing gas of HFC 134a : (CF3CH2F:b.p:-26.5) + Carrier gas(N2, CO2 etc)
✓ GWP: 1,300(17 times less than SF6:22,600)
✓ Gas concentration recommended : 0.3 % (depend on furnace operation condition)
✓ Gas Available in the market

➢ Comparison to SF6 gas system

✓ Melt protection level: Equivalent or superior

✓ Reduction in dross and sludge formation

✓ Reduction burning of molten metal adhering to handling tools

✓ Significant reduction in Green House Gas Emissions (>97 %)

✓ Cost reduction in operation(need License fee)

➢ Commercial results at Die Casters:

✓Example of melt temperature at large diecasting plants in USA and Europe:

USA - Hot chamber, AM50A 652° C
Cold chamber, AZ91D 695° C

Europe -Cold chamber, AZ91D 690° C

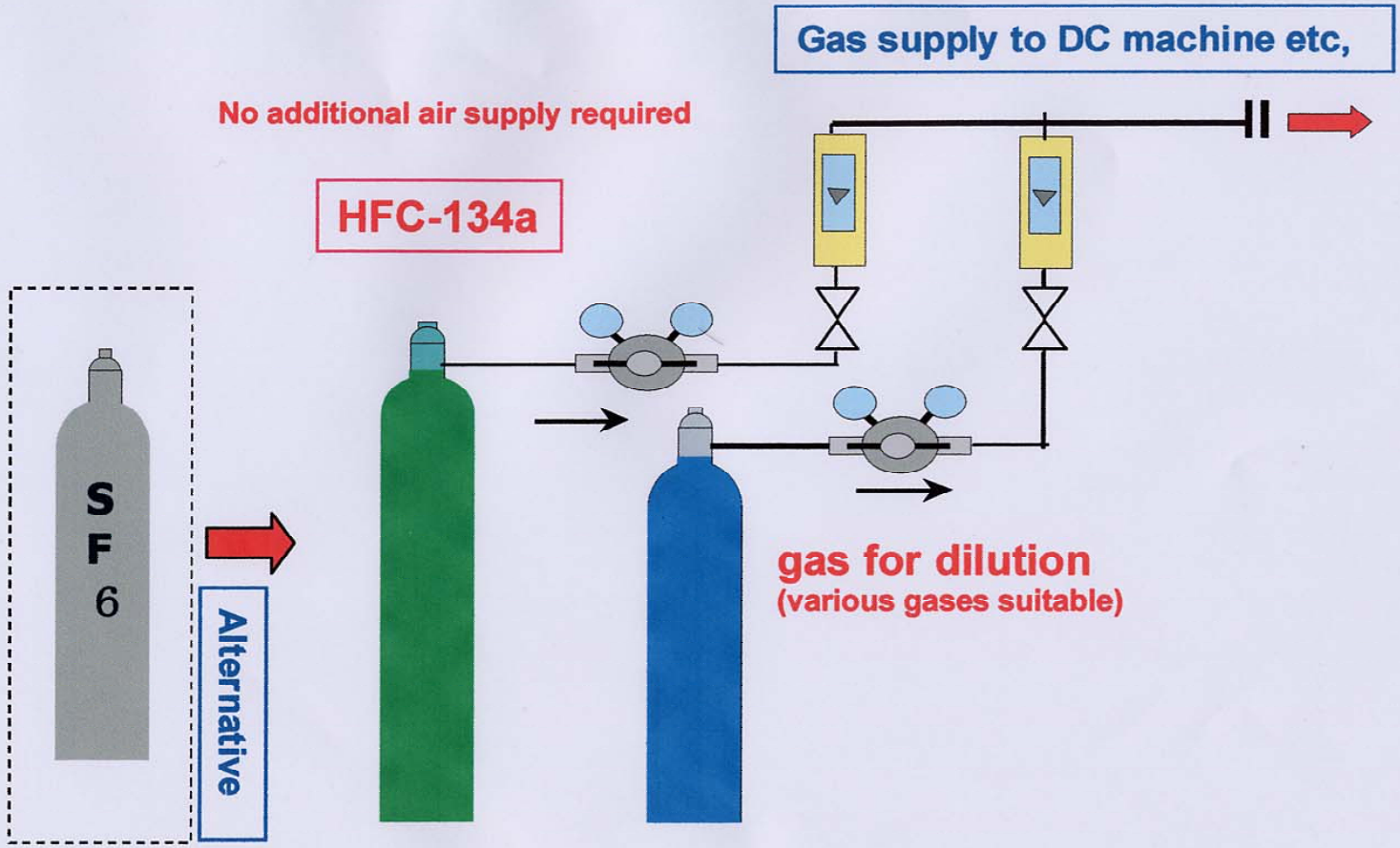
➢ Marketing in Japan

✓ Evaluation trial have been succeeded and under investigation of installing:
Several companies

Source: AMT

Advanced Magnesium Technologies

AM-cover gas flow system



HFC-134a is available from your local gas supplier

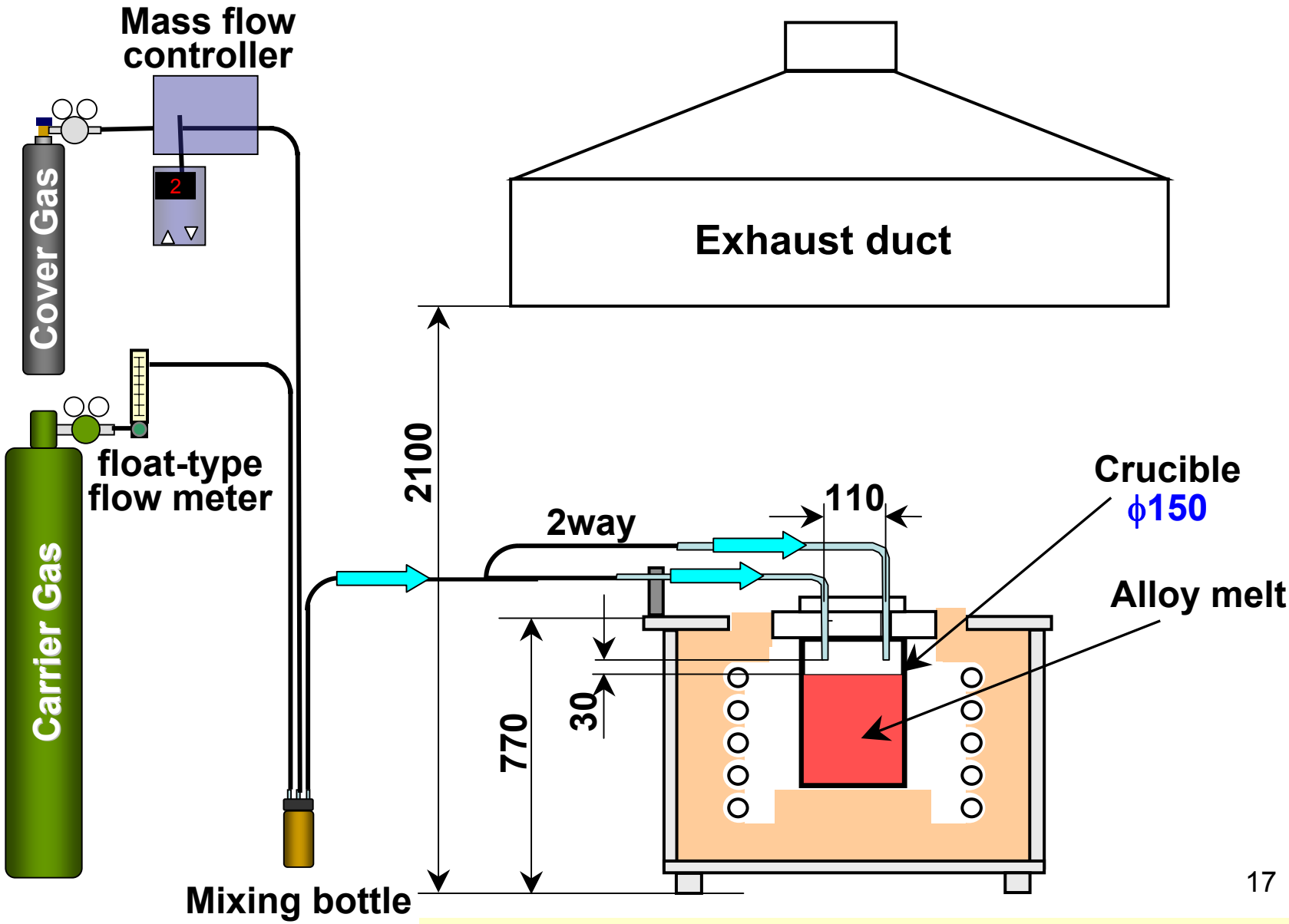
New Cover Gas below GWP 1000

Survey of SF6 gas alternatives in Japan (NEDO project 2005)

Cover gas	Chemical formula	Life (years)	GWP_{100}	Remarks
Conventional cover gas				
SF_6	—	3200	22200	Most used cover gas Extra-large GWP Kyoto Protocol reduction obligation
SO_2	—	—	≒0	Poisonous for men
NOVEC612	$C_3F_7C(O)C_2F_5$	0.014	≒1	Easy to degradation at high Temp.
HFC-134a	CH_2FCF_3	14	1300	Refrigerant Kyoto Protocol reduction obligation
New protective cover gas				
HFC-245fa	$CF_3CH_2CHF_2$	8.4	950	Blowing agent Boiling point: 15℃ Liquid phase at R.T.
OHFC-1234ze	$CF_3CH=CHF$	—	＜10※	By-product gas of HFC-245fa Boiling point: -19℃
HFE-254pc	$CHF_2CF_2OCH_3$	2.4	30	Blowing agent Boiling point: 37℃ Liquid phase at R.T.

※Estimated

Delivery System of Cover Gas Mixture



Source: KAMADO et al. :Internl. Sympo. on Mg Tech. in Glob.Age; Oct.1-4,2006

AZ91D Ingot Surfaces Cast with / without Delivery of Cover Gas

Flow rate: 6l/min
OHFC-1234ze: 0.1%

Outline of Test Results at Survey of SF6 gas alternatives (NEDO project 2005)

✓Ignition preventing properties

・Sufficient effect has from 650 ℃to 800 ℃ as compared gas(SF6, HFC-134a)
・Reduction rate of Green House Gas calculated from Input Gas： OHFC-1234ze andHFE-254pc systems have more than 98% to SF6 gas cover.

✓Emission gas (Gas Chromatography / Mass Spectrometer and ion-exchange chromatography method)

・Crucible cover closed：large amount of hazard gas（HF, CO, COF2)detected.
・Outside furnace,1.5m worker's height： less than1ppm HF only detected （less than tolerance limit specified by ACGIH）

Corrosion of tool (OHFC1234a + CO2 gas mixture)

Austenite st.steel(SUS304, SUS316): no color changed, corrosion resistant

Investigation of protective film (OHFC1234a + CO2 gas group)

Double layer films: outer MgF2 + inner MgO

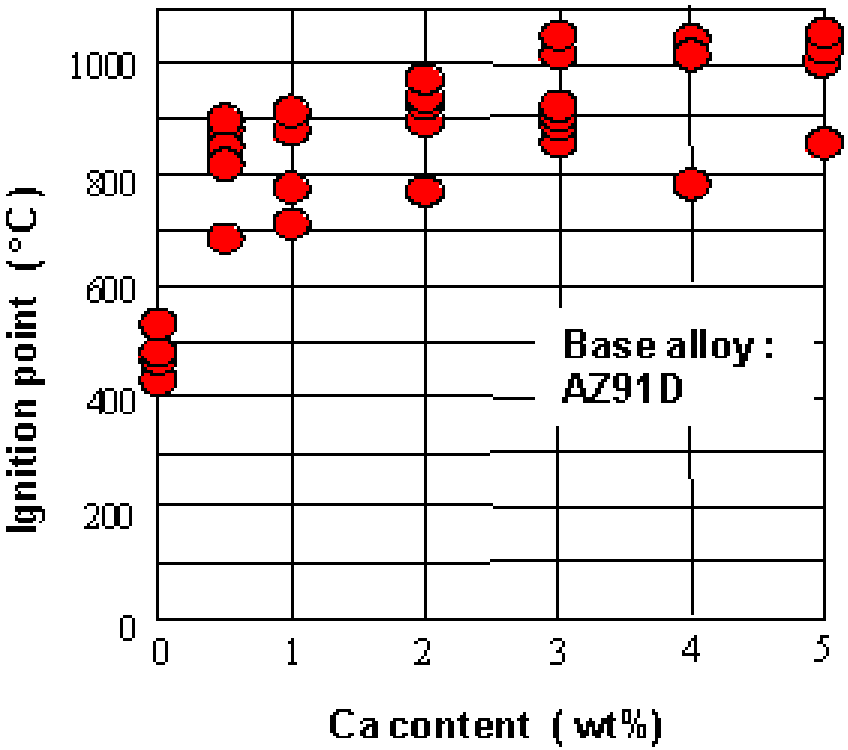
Effect on mech. Property: almost same T.S. and Fatigue limit as SF6 use

New cover gas : Starting of Trial Experiments at Die-casters in Japan

Mg Alloy development for adjustable to environment in Japan

Ref: Home page (Japan) at: **AIST Kyushu**

Mg alloy development : → No use of SF6 gas in melting process



✓Development Target:
Hard or Non-combustible Mg alloy

✓ Ca addition moves the burning temperature 200-300℃ upward of the Mg alloy

✓Recent Technology development :
wrought process, welding such as FSW, quality improvement, high creep alloy, recycling process etc.

✓Example of Application trial and Concept:
Roof box for car;
Toll gate bar;
High speed rotation machine parts,
Ultra rapid train parts etc.

Trial application product : Roof box

Ref: Home page (Japan) at: AIST Chubu

☑ Basic Evaluation of Material Performance:
Mechanical property, Micro structure control and welding property etc.

⇓

- **(Material) : Hard/Non combustible Mg alloy**
- **(Product construction) :** Extrusion plate 100width → FSW & Laser welding
  - ✓**Product size:** 2000L x 670W x 270H
  - ✓ **Weight:** 12.5 kg (normal FRP; 16- 17kg) ; wt. reduction : about 25%

Example of SF6 exhaust gas reduction by equipment improvement

＊ Reduction of SF6 gas supply but Increase of gas flow rate with preventing burning of melt

Trial and recommendation data：Norsk Hydro as. Competence Center

- SF6 gas concentration : 0.2 %
- Surface area : 1 m^2
- SF6 gas flow & Air flow rate : 20cc (or less) SF6 & 10L (or + +)Dry air/min
- Gas flow speed : 10 – 5 m /sec
- Gas injection pore size at distributor : 0.15 - 0.2 mm (multi pore at gas tube)
- Gas distribution over all melt surface: Gas speed & gas distributor

＊Introduction of Precise gas flow meter

①1st generation: Volumetric Flow meter
②2nd generation: Mass Flow meter

＊Introduction of SF6 gas leakage detector

Figure : Polycontrols Technology

SF6 gas reduction: Equipments/ operation

Gas Flow:

✧Small quantity of F-gas

- ✓ High precise SF6 etc. gas flow meter
- ✓ Much mixed gas volume
- ✓ Humidity restricted
- ✓ High gas flow speed to reach melt
- ✓ Uniform gas distribution in furnace
- ✓ Additional gas purge system to keep gas conc. in the furnace

Furnace structure:

✧ Gas leak prevention

- ✓Heat resistant Sealing material and flange structure
- ✓Automatic and sliding door for Ingot charge or de-sludge
- ✓Minimum open door size
- ✓ Air free room for ingot charge
- ✓ Minimize surface agitation and height level change
- ✓ Minimum temp. fluctuation of melt

Operation:

✧ Maintenance of seal, leakage, thermocouple etc.

- ✓Lowest casting temp
- ✓Minimum convection
- ✓Minimum gas supply during holding
- ✓Best operation by continuous 3-shift