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(54) Title: MOLTEN MAGNESIUM COVER GAS USING FLUOROCARBONS

(57) Abstract: This invention relates to a method for preventing the ignition of molten magnesium by contacting the molten magnesium with a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof.



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MOLTEN MAGNESIUM COVER GAS USING FLUOROCARBONS

Field of the Invention

This invention relates to a method for preventing the ignition of molten magnesium
5 by contacting the molten magnesium with a gaseous mixture comprising a fluorocarbon
selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures
thereof. This invention also relates to molten magnesium and solid magnesium
comprising a film formed on a surface of the magnesium. This film is comprised of a
reaction product of molten magnesium and a fluorocarbon selected from the group
10 consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof. The solid
magnesium may be in the form of ingots or castings. The invention also relates to
extinguishing a fire on the surface of magnesium by contacting the surface with the
gaseous mixture described above.

Background of the Invention

Molded parts made of magnesium (or its alloys) are finding increasing use as
components in the automotive and aerospace industries. These parts are typically
manufactured in a foundry, where the magnesium is heated to a molten state in a crucible
to a temperature as high as 1400 °F (760 °C), and the resulting molten magnesium is
20 poured into molds or dies to form ingots or castings. During this casting process,
protection of the magnesium from atmospheric air is essential to prevent a spontaneous
exothermic reaction from occurring between the reactive metal and the oxygen in the air.
Protection from air is also necessary to minimize the propensity of reactive magnesium
vapors to sublime from the molten metal bath to cooler portions of a casting apparatus. In
25 either situation, an extremely hot magnesium fire can result within a few seconds of air
exposure, causing extensive property damage and, most tragically, serious injury to and
devastating loss of human life.

Various methods have been investigated to minimize the exposure of molten
magnesium to air. See J. W. Fruehling et al., *Transactions of the American Foundry*
30 *Society, Proceeding of the 73rd Annual Meeting*, May 5-9, 1969, 77 (1969). The two most

viable methods for effectively separating molten magnesium from air are the use of salt fluxes and the use of cover gases (sometimes referred to as "protective atmospheres"). A salt flux is fluid at the magnesium melt temperature and it effectively forms a thin impervious film on the surface of the magnesium, thus preventing the magnesium from reacting with oxygen in the air. However, the use of salt fluxes presents several disadvantages. First, the flux film itself can oxidize in the atmosphere to harden into a thick oxychloride deposit, which is easily cracked to expose molten magnesium to the atmosphere. Second, the salt fluxes are typically hygroscopic and, as such, can form salt inclusions in the metal surface which can lead to corrosion. Third, fumes and dust particles from fluxes can cause serious corrosion problems to ferrous metals in the foundry. Fourth, salt sludge can form in the bottom of the crucible. Fifth, and not least, removal of such fluxes from the surface of cast magnesium parts can be difficult.

As a result, there has been a shift from using salt fluxes to using cover gases to inert molten magnesium. Cover gases can be described as one of two types: inert cover gases and reactive cover gases. Inert cover gases can be non-reactive (e.g., argon or helium) or slowly reactive (e.g., nitrogen, which reacts slowly with molten magnesium to form Mg_3N_2). For inert cover gases to be effective, air must be essentially excluded to minimize the possibility of metal ignition, i.e., the system must be essentially closed. To utilize such a closed system, workers either have to be equipped with a cumbersome self-contained breathing apparatus or they have to be located outside of the dimensions of the processing area (e.g., by using remote control). Another limitation of inert cover gases is that they are incapable of preventing molten metal from subliming.

Reactive cover gases are gases used at low concentration in a carrier gas, normally ambient air, that react with the molten magnesium at its surface to produce a nearly invisible, thermodynamically stable film. By forming such a tight film, the aerial oxygen is effectively separated from the surface of the molten magnesium, thus preventing metal ignition and minimizing metal sublimation.

The use of various reactive cover gases to protect molten magnesium from ignition has been investigated as early as the late 1920s. An atmosphere containing CO_2 is innocuous and economical yet forms a protective film on a magnesium surface which can prevent ignition for over 1 hour at 650 °C. However, the CO_2 -based films formed are dull

in appearance and unstable, especially in the presence of high levels of air, and consequently offer little protection for the magnesium surface from ambient oxygen. In effect, the CO₂ behaves more like an inert cover gas than a reactive cover gas.

SO₂ has been investigated in the past as a reactive cover gas, as SO₂ reacts with
5 molten magnesium to form a thin, nearly invisible film of magnesium oxysulfides. SO₂ is low in cost and is effective at levels of less than 1% in air in protecting molten magnesium from ignition. However, SO₂ is very toxic and consequently requires significant measures to protect workers from exposure (permissible exposure levels are only 2 ppm by volume or 5 mg/m³ by volume). Another problem with SO₂ is its reactivity with water in humid
10 air to produce very corrosive acids (H₂SO₄ and H₂SO₃). These acids can attack unprotected workers and casting equipment, and they also contribute significantly to acid rain pollution when vented out of the foundry. SO₂ also has a tendency to form reactive deposits with magnesium which produce metal eruptions from the furnace (especially when SO₂ concentrations in the air are allowed to drift too high). Though SO₂ has been
15 used commercially on a large scale for the casting of magnesium alloys, these drawbacks have led some manufacturers to ban its use.

Fluorine-containing reactive cover gases provide an inert atmosphere which is normally very stable to chemical and thermal breakdown. However, such normally stable gases will decompose upon contact with a molten magnesium surface to form a thin,
20 thermodynamically stable magnesium oxyfluoride protective film. U.S. Patent No. 1,972,317 (Reimers et. al.) describes the use of fluorine-containing compounds which boil, sublime or decompose at temperatures below about 750 °C to produce a fluorine-containing atmosphere which inhibits the oxidation of molten magnesium. Suitable compounds listed include gases, liquids or solids such as BF₃, NF₃, SiF₄, PF₅, SF₆, SO₂F₂,
25 (CClF₂)₂, HF, NH₄F and NH₄PF₆. The use of BF₃, SF₆, CF₄ and (CClF₂)₂ as fluorine-containing reactive cover gases is disclosed in J. W. Fruehling et al., described *supra*.

Each of these fluorine-containing compounds has one or more deficiencies. Though used commercially and effectively at lower levels than SO₂, BF₃ is toxic and corrosive and can be potentially explosive with molten magnesium. NF₃, SiF₄, PF₅, SO₂F₂
30 and HF are also toxic and corrosive. NH₄F and NH₄PF₆ are solids which sublime upon heating to form toxic and corrosive vapors. CF₄ has a very long atmospheric lifetime.

(CClF₂)₂, a chlorofluorocarbon, has a very high ozone depletion potential (ODP). The ODP of a compound is usually defined as the total steady-state ozone destruction, vertically integrated over the stratosphere, resulting from the unit mass emission of that compound relative to that for a unit mass emission of CFC-11 (CCl₃F). See Seinfeld, J. H. and S. N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, Inc., New York, (1998). Currently, there are efforts underway to phase out the production of substances that have high ODPs, including chlorofluorocarbons and HCFCs, in accordance with the Montreal Protocol. UNEP (United Nations Environment Programme), Montreal Protocol on Substances that Deplete the Ozone Layer and its attendant amendments, Nairobi, Kenya, (1987).

Until recently, SF₆ was considered the optimum reactive cover gas for magnesium. SF₆ is effective yet safe (essentially inert, odorless, low in toxicity, nonflammable and not corrosive to equipment). It can be used effectively at low concentrations either in air (<1%) or in CO₂ to form a very thin film of magnesium oxyfluorides and oxysulfides on the surface of molten magnesium. This magnesium oxyfluoride/oxysulfide film is far superior at protecting the magnesium from a vigorous exothermic oxidation reaction than is the magnesium oxide film inherently present on the metal surface. The magnesium oxysulfide/oxyfluoride film is sufficiently thin (i.e., nearly invisible to the naked eye) that the metal surface appears to be metallic. This superior protection is believed to result from the greater thermodynamic stability of a magnesium oxysulfide and/or magnesium oxyfluoride film as compared to the stability of a thick porous magnesium oxide, sulfide or fluoride film.

In a typical molten magnesium process employing a reactive cover gas, only a small portion of the gas passed over the molten magnesium is actually consumed to form that film, with the remaining gas being exhausted to the atmosphere. Efforts to capture and recycle the excess SF₆ are difficult and expensive due to its very low concentrations in the high volumes of exhaust stream. Efficient thermal oxidizing equipment would be required to remove the SF₆ from the exhaust stream, adding significantly to production costs. Product costs can also be considerable, as SF₆ is the most expensive commercially used reactive cover gas.

However, perhaps the greatest concern with SF₆ is its very significant global

warming potential (3200 year atmospheric lifetime, and about 22,200 times the global warming potential of carbon dioxide). At the December 1997 Kyoto Summit in Japan, representatives from 160 countries drafted a legally binding agreement containing limits for greenhouse gas emissions. The agreement covers six gases, including SF₆, and
5 includes a commitment to lower the total emissions of these gases by the year 2010 to levels 5.2% below their total emissions in 1990. UNEP (United Nations Environment Programme), Kyoto Protocol to the United Nations Framework Convention on Climate Change, Nairobi, Kenya, 1997.

As no new replacement for SF₆ is yet commercially available, efforts are underway
10 to reinvigorate SO₂, as SO₂ has essentially no global warming potential (despite its other considerable drawbacks). See H. Gjestland, P. Bakke, H. Westengen, and D. Magers, Gas protection of molten magnesium alloys: SO₂ as a replacement for SF₆. Presented at conference on Metallurgie du Magnesium et Recherche d'Allegement dans l'Industrie des Transports, International Magnesium Association (IMA) and Pole de Recherche et de
15 Devleoppment Industriel du Magnesium (PREDIMAG) Clermond-Ferrand, France, October 1996.

The data in TABLE 1 summarize selected safety and environmental limitations of compounds currently known to be useful in the protection of molten magnesium.

Numbers followed by an asterisk (*) are particularly problematic with regard to safety
20 and/or environmental effects.

25

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Table 1

Compound	Exposure Guideline ⁽¹⁾	Atmospheric Lifetime ⁽³⁾ (yrs)	Global Warming Potential - GWP ⁽³⁾ (100 yr ITH)	Ozone Depletion Potential - ODP ⁽³⁾ (CFC-11 = 1)
SO ₂	2 ppmv *			
BF ₃	1 ppmv *			
NF ₃	10 ppmv *	740	10800 *	
SiF ₄	2.5 mg/m ³ as F *			
PF ₅	2.5 mg/m ³ as F *			
SF ₆	1000 ppmv	3200	22200 *	
SO ₂ F ₂	5 ppmv *			
(CClF ₂) ₂	1000 ppmv	300	9800 *	0.85 *
HF	3 ppmv ceiling *			
NH ₄ F	2.5 mg/m ³ as F *			
NH ₄ PF ₆	corrosive, causes burns ⁽²⁾ *			
CF ₄	Moderately toxic by inhalation	50000 *	5700*	
CHClF ₂	1000 ppmv	11.8	1900*	0.055 *

⁽¹⁾ The Condensed Chemical Dictionary, edited by Gessner G. Hawley.

5 New York, Van Nostrand Reinhold Co. (1981). Note: ppmv = parts per million by volume.

⁽²⁾ Material Safety Data Sheet for ammonium hexafluorophosphate, Sigma-Aldrich Corporation, Milwaukee, WI.

⁽³⁾ World Meteorological Organization Global Research and Monitoring Project – Report

No. 44, "Scientific Assessment of Ozone Depletion: 1998," WMO (1999).

As each of these compounds presents either a significant safety or an environmental concern, the search continues to identify new reactive cover gases for protecting molten magnesium which are simultaneously effective, safe, environmentally acceptable, and cost-effective.

Summary of the Invention

This invention relates to a method for treating molten magnesium to protect the magnesium from reacting with oxygen in air. The method comprises providing molten magnesium and exposing the magnesium to a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof.

The gaseous mixture may further comprise a carrier gas. The carrier gas may be selected from the group consisting of air, carbon dioxide, argon, nitrogen and mixtures thereof.

This invention also relates to a method for protecting molten magnesium from reacting with oxygen in air. In this method the exposed surface of molten magnesium is exposed to or contacted with a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof. The gaseous mixture can react with the molten magnesium at its exposed surface to produce a nearly invisible, thermodynamically stable film. By forming this film, the oxygen in air can be effectively separated from the surface of the molten magnesium and thus can prevent metal ignition and can minimize metal sublimation.

This invention also relates to molten magnesium protected from reacting with oxygen in air in accordance with the method of the present invention.

In addition, this invention relates to molten magnesium wherein a protective film is formed on a surface of the magnesium. This film is formed by a reaction of the magnesium with a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones and mixtures thereof. This film can be nearly invisible and thermodynamically stable and can effectively separate oxygen in air

from the surface of the magnesium and thus can prevent metal ignition and can minimize metal sublimation.

In another embodiment, this invention relates to solid magnesium comprising a film formed on a surface of the magnesium. This film is comprised of a reaction product
5 of molten magnesium and a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof. This solid magnesium may be in the form of ingots or castings.

In yet another embodiment, this invention relates to a method for extinguishing a fire on the surface of magnesium comprising contacting a gaseous mixture comprising a
10 fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof, with said surface of said magnesium.

In this application, "magnesium" means magnesium and all alloys formed therefrom.

One advantage of the present invention over the known art is that the Global
15 Warming Potentials of perfluoroketones and hydrofluoroketones are quite low. Therefore, the present inventive process is more environmentally friendly.

Detailed Description of the Invention

Fluorocarbons of the present invention include perfluoroketones (PFKs), and
20 hydrofluoroketones (HFKs) which incorporate limited amounts of hydrogen in their structures. These fluorocarbons can be effective as reactive cover gases to protect reactive molten reactive metals such as molten magnesium from ignition. As is the case with known fluorine-containing reactive cover gases, these fluorocarbons can react with the molten metal surface to produce a protective surface film, thus preventing ignition of the
25 molten metal.

For the protection of molten magnesium from ignition, fluorocarbons of the present invention are desirable alternatives to the most commonly used cover gas currently, SF₆. The fluorocarbons of the present invention are low GWP fluorocarbon alternatives to SF₆, i.e., the fluorocarbons of the present invention have measurably lower global warming
30 potential relative to SF₆ (i.e., significantly less than 22,200) and are not significantly worse in atmospheric lifetime, ozone depletion potential, or toxicity properties.

Perfluorinated ketones (PFKs) useful in the present invention include ketones which are fully fluorinated, i.e., all of the hydrogen atoms in the carbon backbone have been replaced with fluorine atoms. The carbon backbone can be linear, branched, or cyclic, or combinations thereof, and will preferably have about 5 to about 9 carbon atoms.

- 5 Representative examples of perfluorinated ketone compounds suitable for use in the processes and compositions of the invention include $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_5\text{C}(\text{O})\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, perfluorocyclohexanone, and mixtures thereof. In addition to demonstrating reactive cover gas performance,
- 10 perfluorinated ketones can offer additional important benefits in safety of use and in environmental properties. For example, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ has low acute toxicity, based on short-term inhalation tests with mice exposed for four hours at a concentration of 100,000 ppm in air. Also based on photolysis studies at 300 nm $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ has an estimated atmospheric lifetime of 5 days. Other perfluorinated ketones show similar
- 15 absorbances and thus are expected to have similar atmospheric lifetimes. As a result of their rapid degradation in the lower atmosphere, the perfluorinated ketones have short atmospheric lifetimes and would not be expected to contribute significantly to global warming (i.e., low global warming potentials). Perfluorinated ketones which are straight chain or cyclic can be prepared as described in U.S. Patent No. 5,466,877 (Moore et al.)
- 20 which in turn can be derived from the fluorinated esters described in U.S. Patent No. 5,399,718 (Costello et al.). Perfluorinated ketones that are branched can be prepared as described in U.S. Patent No. 3,185,734 (Fawcett et al.).

- Hydrofluoroketones (HFKs) that are useful in the present invention include those ketones having only fluorine and hydrogen atoms attached to the carbon backbone. The
- 25 carbon backbone can be linear, branched, or cyclic, or combinations thereof, and preferably will have about 4 to about 7 carbon atoms. Representative examples of hydrofluoroketone compounds suitable for use in the processes and compositions of this invention include: $\text{HCF}_2\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CF}_3$, $\text{C}_2\text{H}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{CH}_3$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{F}$,
- 30 $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_3$,

$\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_3$,
 $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_2\text{F}$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CHF}_2$,
 $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CH}_2\text{F}$, and
 $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CF}_3$. Some hydrofluoroketones can be prepared by reacting a
5 fluorinated acid with a Grignard reagent such as an alkylmagnesium bromide in an aprotic
solvent, as described in Japanese Patent No. 2,869,432. For example $\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{CH}_3$
can be prepared by reacting pentafluoropropionic acid with magnesium methyl bromide in
dibutyl ether. Other hydrofluoroketones can be prepared by reacting a partially fluorinated
acyl fluoride with hexafluoropropylene in an anhydrous environment in the presence of
10 fluoride ion at elevated temperature, as described in U.S. Patent Application Ser. No.
09/619306. For example, $\text{HCF}_2\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ can be prepared by oxidizing
tetrafluoropropanol with acidic dichromate, then reacting the resulting $\text{HC}_2\text{H}_4\text{COOH}$ with
benzotrichloride to form $\text{HC}_2\text{H}_4\text{C}(\text{O})\text{Cl}$, converting the acyl chloride to the acyl fluoride
by reaction with anhydrous sodium fluoride, and then reacting the $\text{HC}_2\text{H}_4\text{C}(\text{O})\text{F}$ with
15 hexafluoropropylene under pressure.

The gaseous mixture that comprises a fluorocarbon selected from the group
consisting of perfluoroketones and hydrofluoroketones further comprises a carrier gas or
carrier gases. Some possible carrier gases include air, CO_2 , argon, nitrogen and mixtures
thereof. Preferably, the carrier gas that is used with the perfluoroketones is dry air.

20 The gaseous mixture comprises a minor amount of the fluorocarbon and a major
amount of the carrier gas. Preferably, the gaseous mixture consists of less than about 1%
of the fluorocarbon and the balance carrier gas. More preferably, the gaseous mixture
contains less than 0.5% by volume (most preferably less than 0.1% by volume)
fluorocarbon, selected from the group consisting of perfluoroketones, hydrofluoroketones
25 and mixtures thereof.

In order to keep the protective layer on the magnesium, the gaseous mixture is
continuously, or nearly continuously, fed to the surface of the magnesium. Small breaks in
the thin protective layer can then be healed without the possibility of such small breaks
exposing molten magnesium to the air and initiating a fire.

30 A cover gas composition is of low toxicity both as it is applied to the molten
magnesium and as it is emitted from the process in which it is used. Cover gases

comprising low toxicity hydrofluoroketones and perfluoroketones, and mixtures thereof, will be safe mixtures as applied to magnesium. However, all fluorine containing cover gas composition produce measurable amounts of hydrogen fluoride upon contact with the molten magnesium due to some level of thermal degradation and reaction with magnesium
5 at temperatures of 650 to 750°C. Hydrogen fluoride is corrosive and toxic and its concentration in the emitted gas should be minimized. A preferred cover gas composition will, therefore, produce minimal hydrogen fluoride. *See Examples, below.*

Atmospheric lifetimes and global warming potentials for several fluorocarbons used in accordance with this invention, along with compounds currently known to be
10 useful in the protection of molten magnesium as comparative examples, are presented in TABLE 2.

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TABLE 2

Compound	Atmospheric Lifetime (years) ⁽¹⁾	Global Warming Potential (GWP) (100 year ITH) ⁽¹⁾	GWP relative to SF ₆
Hydrofluoroketone			
HCF ₂ CF ₂ C(O)CF(CF ₃) ₂	≤ 0.1 ⁽⁴⁾	≤ 10 ⁽⁴⁾	0.0005
Perfluoroketone			
C ₂ F ₅ C(O)CF(CF ₃) ₂	0.02 ⁽²⁾	1 ⁽²⁾	0.00005
Comparative Compounds:			
Hydrofluorocarbons			
FCH ₂ CF ₃	13.6	1600	0.07
CF ₃ CHFCHFCF ₂ CF ₃	17.1	1700	0.08
CF ₃ CHFCF ₃	36.5	3800	0.17
HCF ₂ CF ₃	32.6	3800	0.17
Segregated Hydrofluoroethers			
C ₄ F ₉ OCH ₃	5.0	390	0.02
C ₄ F ₉ OC ₂ H ₅	0.8	55	0.002
C ₃ F ₇ CF(OC ₂ H ₅)CF(CF ₃) ₂	2.5 ⁽²⁾	210 ⁽²⁾	0.01
Non-Segregated Hydrofluoroethers			
HCF ₂ OCF ₂ CF ₂ OCF ₂ H	7 ⁽³⁾	1725 ⁽³⁾	0.08
HCF ₂ OCF ₂ OC ₂ F ₄ OCF ₂ H	7.1 ⁽³⁾	1840 ⁽³⁾	0.08
Other Fluorochemicals			
SF ₆	3200	22200	1.00
NF ₃	740	10800	0.49
CClF ₂ CClF ₂	300	9800	0.44
CF ₄	50000	5700	0.26
C ₂ F ₆	10,000	11,400	0.51

- (1) World Meteorological Organization Global Research and Monitoring Project – Report No. 44, “Scientific Assessment of Ozone Depletion: 1998, Vol. 2,” Chapter 10, Table 10-8, pp. 10.27 to 10.28.
- (2) Unpublished data, 3M Company, St. Paul, MN.
- 5 (3) Marchionni, G., *et al.*, *Journal of Fluorine Chemistry*, **95**, (1999), 41-50.
- (4) Estimated, as described below.

The perfluoroketones and hydrofluoroketones of the invention have much lower global warming potential (GWP) than the fluorocarbons known in the art such as SF₆, hydrofluorocarbons, and hydrofluoroethers. As used herein, "GWP" is a relative measure of the warming potential of a compound based on the structure of the compound. The GWP of a compound, as defined by the Intergovernmental Panel on Climate Change (IPCC) in 1990 and updated in Scientific Assessment of Ozone Depletion: 1998 (World Meteorological Organization, *Scientific Assessment of Ozone Depletion: 1998*, Global Ozone Research and Monitoring Project – Report No. 44, Geneva, 1999), is calculated as the warming due to the release of 1 kilogram of a compound relative to the warming due to the release of 1 kilogram of CO₂ over a specified integration time horizon (ITH).

$$GWP_x(t') = \frac{\int_0^{ITH} F_x C_{ox} e^{-t/\tau} dt}{\int_0^{ITH} F_{CO_2} C_{CO_2}(t) dt}$$

20 where F is the radiative forcing per unit mass of a compound (the change in the flux of radiation through the atmosphere due to the IR absorbance of that compound), C is the atmospheric concentration of a compound, τ is the atmospheric lifetime of a compound, t is time and x is the compound of interest.

25 The commonly accepted ITH is 100 years representing a compromise between short-term effects (20 years) and longer-term effects (500 years or longer). The concentration of an organic compound, x, in the atmosphere is assumed to follow pseudo first order kinetics (i.e., exponential decay). The concentration of CO₂ over that same time interval incorporates a more complex model for the exchange and removal of CO₂ from

the atmosphere (the Bern carbon cycle model).

Carbonyl compounds such as aldehydes and ketones have been shown to have measurable photolysis rates in the lower atmosphere resulting in very short atmospheric lifetimes. Compounds such as formaldehyde, acetaldehyde, propionaldehyde, isobutyraldehyde, n-butyraldehyde, acetone, 2-butanone, 2-pentanone and 3-pentanone have atmospheric lifetimes by photolysis ranging from 4 hours to 38 days (Martinez, R.D., et al., 1992, *Atmospheric Environment*, 26, 785-792, and Seinfeld, J.H. and Pandis, S.N., *Atmospheric Chemistry and Physics*, John Wiley & Sons, New York, p. 288, 1998). $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ has an atmospheric lifetime of approximately 5 days based on photolysis studies at 300 nm. Other perfluoroketones and hydrofluoroketones show similar absorbances near 300 nm and are expected to have similar atmospheric lifetimes.

The very short lifetimes of the perfluoroketones and hydrofluoroketones lead to very low GWPs. A measured IR cross-section was used to calculate the radiative forcing value for $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ using the method of Pinnock, et al. (*J. Geophys. Res.*, 100, 23227, 1995). Using this radiative forcing value and the 5-day atmospheric lifetime the GWP (100 year ITH) for $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ is 1. Assuming a maximum atmospheric lifetime of 38 days and infrared absorbance similar to that of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ the GWP for $\text{HCF}_2\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ is calculated to be 9. The perfluoroketones and hydrofluoroketones of the invention typically have a GWP less than about 10.

As a result of their rapid degradation in the lower atmosphere, the perfluoroketones and hydrofluoroketones have short lifetimes and would not be expected to contribute significantly to global warming. The low GWP of the perfluoroketones make them well suited for use as an environmentally preferred cover gas.

Also, the PFKs and HFKs of this invention can react more fully with molten magnesium than does SF_6 . As a result less unreacted cover gas can be emitted to the atmosphere; less cover gas can be required to produce a comparably performing protective film; or both. Consequently, useful concentrations of the cover gas can be lowered, thus reducing the global warming impact. The full substitution of fluorocarbons of the present invention for SF_6 can be accomplished without increasing the risk to worker safety since these materials (PFKs, and HFKs) are of low toxicity, are non-flammable, and are generally very innocuous materials.

Substitution for SF₆ with a PFK, or HFK, alone or as a mixture thereof, can provide protection of molten magnesium in various processes, such as magnesium refining, alloying, formation of ingots or casting of parts. This substitution can be straightforward and can provide the same utility as a reactive cover gas that only SF₆ does
5 currently. Surface films produced with the fluorocarbons of the present invention can be more stable to higher temperatures than those formed with SO₂, enabling work with higher melt temperatures (e.g., additional alloys, more complex casting parts). Improvements realized through the use of fluorocarbons of the present invention as reactive cover gases can include a significant reduction in the emission of a potent greenhouse gas (i.e., SF₆), a
10 potential reduction in the amount of fluorine-containing reactive cover gas required to provide protection, and a reduction in total emissions. This substitution can be done without increasing risks for workers since the fluorocarbons of the present invention are all safe materials with which to work, have low toxicity, are nonflammable, and are not a detriment to production equipment.

15 The use of perfluoroketones, or hydrofluoroketones, or mixtures thereof, in a gaseous mixture demonstrate the ability to also put out fires that are already occurring on the surface of molten magnesium. Therefore, the gases also may be used to extinguish fires on molten magnesium.

20 Examples

The present invention is further illustrated, but is not meant to be limited by, the following examples. The standard test procedure for evaluating the efficiency of each test fluorocarbon cover gas is given below.

An approximately 3 kg sample of pure magnesium was placed in a cylindrical steel
25 crucible having an 11.4 cm internal diameter and was heated to 680°C. Cover gas was continuously applied to the 410 cm² surface of the molten magnesium through a 10 cm diameter ring formed of 95 mm diameter stainless steel that was placed about 3 cm over the molten magnesium. The tubing was perforated on the side of the ring facing the molten magnesium so that the cover gas flowed directly over the molten magnesium. A
30 square 20 cm x 20 cm, 30 cm high stainless steel chamber with an internal volume of about 10.8 liters was fitted over the crucible to contain the cover gas. The top of the

chamber was fitted with two 8.9 cm diameter quartz viewing ports and ports for a skimming tool and thermocouple. A cover gas inlet, two gas sampling ports and a door for adding fresh magnesium and for removing dross from the chamber were placed on the sides of the chamber.

5 A stream of the cover gas was pumped from the chamber into the flow cell of an FTIR spectrophotometer (Midac I2000 Gas Phase FTIR) with a mercury cadmium telluride (MCT) detector. Using Modified Extractive FTIR (EPA Method 320), the volumetric concentration of HF and the test cover gas (in ppmV) were measured continuously during experimentation. Once the mixtures had stabilized, concentrations were measured over a
10 period of 5 to 10 minutes, average values of these concentrations were calculated, and those average values were used to make a relative comparison of the test cover gases.

In all cases, initial magnesium melting was done using a standard cover gas of 0.5% SF₆ in CO₂ at a flow rate of 5.9 L/min. The experimental gas mixture was then substituted for the standard cover gas mixture by utilizing a train of rotameters and valves.
15 Dry air (having a -40°C dew point) at a flow rate of 5.9 L/min was used to create the test cover gas by evaporating a flow of test fluid in it such that a volumetric concentration of 0.03 to 1 volume % fluorocarbon in air was produced.

During testing, the molten magnesium was observed for a period of about 20 to 30 minutes (equivalent to 10 to 15 chamber volumes exchanges of cover gas) to monitor any
20 visible changes to the surface that would indicate the start of magnesium burning. The existing surface film was then removed by skimming the surface for about 3 – 5 minutes. The new surface film that formed was then observed for a period of at 15 – 30 minutes

The concentration of the fluorocarbon component of the cover gas mixture was started at about 1% by volume in air and reduced sequentially in steps of ½ the previous
25 concentration to a minimum fluorocarbon concentration of 0.03 to 0.06%.

Comparative Example C1

C₄F₉OCH₃ (methoxy nonafluorobutane), a hydrofluoroether, has been described as an effective fluorocarbon cover gas for molten magnesium in World Published Application
30 WO 00/64614 (Example 5). In this comparative example, C₄F₉OCH₃ (available as NOVEC™ HFE-7100 Engineering Fluid from 3M Company, St. Paul, MN) was evaluated

as a fluorocarbon cover gas at 1% and at decreasing volumetric concentrations in air. In all cases, the volumetric flow rate for the cover gas/air mixture was 5.9 L/min. At nominal concentrations of about 1, 0.5, 0.25 and 0.125% (corresponds to 10000, 5000, 2500 and 1250 ppmV, respectively), C₄F₉OCH₃ produced a thin flexible surface film on molten magnesium immediately after skimming so that no evidence of metal burning was observed. When the concentration of C₄F₉OCH₃ was reduced to 0.0625% (i.e., 625 ppmV), some evidence of burning was observed on the molten magnesium surface as white blooms, but no fire resulted. Exposure to fresh molten magnesium during skimming caused the HF concentration to remain essentially unchanged or to be increased at all volumetric concentrations of C₄F₉OCH₃ tested.

The HF concentrations measured at the various volumetric concentrations of C₄F₉OCH₃ tested are presented in TABLE 3.

TABLE 3

Concentration of C ₄ F ₉ OCH ₃ in Air Over Molten Magnesium (ppm by volume)	Concentration of Hydrogen Fluoride over Stable Surface Molten Magnesium Film (ppm by volume)	Concentration of Hydrogen Fluoride over Fresh Molten Magnesium Film (ppm by volume)
8300	4500	4100
4100	2000	2200
2000	980	1000
800	590	480

The data in TABLE 3 show that significant hydrogen fluoride is produced at 800 ppm volumetric concentration of C₄F₉OCH₃ (i.e., 480-590 ppm HF), the minimum concentration required to protect molten magnesium from ignition.

Example 1

CF₃CF₂C(O)CF(CF₃)₂ (1,1,1,2,4,4,5,5,5-nonafluoro-2-trifluoromethyl-pentan-3-one), a perfluoroketone, was evaluated as a cover gas to protect molten magnesium from

ignition using essentially the same procedure as described in Comparative Example C1 using $C_4F_9OCH_3$. The $CF_3CF_2C(O)CF(CF_3)_2$ was prepared and purified using the following procedures.

Into a clean dry 600 mL Parr reactor equipped with stirrer, heater and
5 thermocouple were added 5.6 g (0.10 mol) of anhydrous potassium fluoride and 250 g of anhydrous diglyme (anhydrous diethylene glycol dimethyl ether, available from Sigma Aldrich Chemical Co.). The anhydrous potassium fluoride was spray dried, stored at 125°C and ground shortly before use. The contents of the reactor were stirred while 21.0 g (0.13 mol) of C_2F_5COF (approximately 95.0 percent purity) was added to the sealed
10 reactor. The reactor and its contents were then heated, and when a temperature of 70°C had been reached, a mixture of 147.3 g (0.98 mol) of $CF_2=CF CF_3$ (hexafluoropropylene) and 163.3 g (0.98 mol) of C_2F_5COF was added over a 3.0 hour time period. During the addition of the hexafluoropropylene and the C_2F_5COF mixture, the pressure was maintained at less than 95 psig (7500 torr). The pressure at the end of the
15 hexafluoropropylene addition was 30 psig (2300 torr) and did not change over the 45-minute hold period. The reactor contents were allowed to cool and were one-plate distilled to obtain 307.1 g containing 90.6% $CF_3CF_2C(O)CF(CF_3)_2$ and 0.37% C_6F_{12} (hexafluoropropylene dimer) as determined by gas chromatography. The crude fluorinated ketone was water-washed, distilled, and dried by contacting with silica gel to provide a
20 fractionated fluorinated ketone of 99% purity and containing 0.4% hexafluoropropylene dimers.

A sample of fractionated $CF_3CF_2C(O)CF(CF_3)_2$ made according to the above-described procedure was purified of hexafluoropropylene dimers using the following procedure. Into a clean dry 600 mL Parr reactor equipped with stirrer, heater and
25 thermocouple were added 61 g of acetic acid, 1.7 g of potassium permanganate, and 301 g of the above-described fractionated 1,1,1,2,4,4,5,5,5-nonafluoro-2-trifluoromethyl-pentan-3-one. The reactor was sealed and heated to 60°C, while stirring, reaching a pressure of 12 psig (1400 torr). After 75 minutes of stirring at 60°C, a liquid sample was taken using a dip tube, the sample was phase split and the lower phase was washed with water. The
30 sample was analyzed using gas-liquid chromatography ("glc") and showed undetectable amounts of hexafluoropropylene dimers and small amounts of hexafluoropropylene

trimers. A second sample was taken 60 minutes later and was treated similarly. The glc analysis of the second sample showed no detectable dimers or trimers. The reaction was stopped after 3.5 hours, and the purified ketone was phase split from the acetic acid and the lower phase was washed twice with water. 261 g of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ was
5 collected, having a purity greater than 99.6% by glc and containing no detectable hexafluoropropylene dimers or trimers.

The perfluorinated ketone, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, was then evaluated as a fluorocarbon cover gas at 1% and at decreasing volumetric concentrations in air (i.e., at about 1.0, 0.5, 0.25, 0.12, 0.06 and 0.03% by volume; corresponds to 10000, 5000, 2500,
10 1250, 600 and 300 ppm, respectively). At all concentrations tested, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ produced a thin flexible surface film on the molten magnesium during skimming and prevented metal ignition. The film visually appeared to be thinner and more elastic than the surface film produced in the initial molten magnesium protection using SF_6 as a cover gas and in Comparative Example C1 using $\text{C}_4\text{F}_9\text{OCH}_3$ as a cover gas. The silvery-gray
15 film produced was stable and did not change appearance over at least 30 minutes. This is in contrast to the test series using $\text{C}_4\text{F}_9\text{OCH}_3$, where evidence of metal burning was noted when the cover gas concentration was reduced to about 625 ppm.

The HF concentrations measured at the various volumetric concentrations of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ tested are presented in TABLE 4.

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25

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TABLE 4

Concentration of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ in Air over Molten Magnesium (ppm by volume)	Concentration of Hydrogen Fluoride over Stable Surface Molten Magnesium Film (ppm by volume)	Concentration of Hydrogen Fluoride over Fresh Molten Magnesium Film (ppm by volume)
10400	420	670
4800	470	775
2400	360	640
1200	280	370
560	180	120
480	120	100
280	40	40

The data in TABLE 2 show that, at equal volumetric concentrations, significant
5 less hydrogen fluoride is produced using $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ compared to $\text{C}_4\text{F}_9\text{OCH}_3$ as
a cover gas. For example, at 2000 ppm $\text{C}_4\text{F}_9\text{OCH}_3$, 980 ppm of HF was produced over the
stable surface film and 1000 ppm of HF was produced over the fresh molten film. In
contrast, at 2400 ppm $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ (a slightly higher fluorocarbon
concentration), only 360 ppm of HF was produced over the stable surface film and 640
10 ppm of HF was produced over the fresh molten film.

In summary, the perfluorinated ketone outperformed the hydrofluoroether as a
cover gas for molten magnesium (i.e. protected the molten magnesium at lower
concentrations) and also generated less hydrogen fluoride as a degradation product upon
exposure to the molten metal surface.

What is claimed is:

1. A method for treating molten magnesium to protect said magnesium from reacting with oxygen in air which comprises: providing molten magnesium and exposing said magnesium to a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof.
2. The method of claim 1 wherein the fluorocarbon is a perfluoroketone.
3. The method of claim 2 wherein said perfluoroketone is selected from the group consisting of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_5\text{C}(\text{O})\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, perfluorocyclohexanone, and mixtures thereof.
4. The method of claim 1 wherein said fluorocarbon is a hydrofluoroketone that is selected from the group consisting of $\text{HCF}_2\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CF}_3$, $\text{C}_2\text{H}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{CH}_3$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_2\text{F}$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CHF}_2$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CF}_3$, and mixtures thereof.
5. The method of claim 1 wherein the gaseous mixture further comprises a carrier gas.
6. The method of claim 5 wherein said carrier gas is selected from the group consisting of air, CO_2 , argon, nitrogen, and mixtures thereof.
7. A method for protecting molten magnesium from reacting with oxygen in air, said magnesium comprising an exposed surface, comprising:

- (a) providing molten magnesium;
 - (b) contacting said magnesium with a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof; and
 - 5 (c) forming a film on the surface of said magnesium.
8. The method of claim 7 wherein the gaseous mixture further comprises a carrier gas.
 9. The method of claim 8 wherein said carrier gas is selected from the group
 - 10 consisting of air, CO₂, argon, nitrogen, and mixtures thereof.
 10. The method of claim 7 wherein the fluorocarbon is a perfluoroketone.
 11. The method of claim 10 wherein said perfluoroketone is selected from the group
 - 15 consisting of CF₃CF₂C(O)CF(CF₃)₂, (CF₃)₂CFC(O)CF(CF₃)₂, CF₃(CF₂)₂C(O)CF(CF₃)₂, CF₃(CF₂)₃C(O)CF(CF₃)₂, CF₃(CF₂)₅C(O)CF₃, CF₃CF₂C(O)CF₂CF₂CF₃, CF₃C(O)CF(CF₃)₂, perfluorocyclohexanone, and mixtures thereof.
 12. The method of claim 7 wherein said fluorocarbon is a hydrofluoroketone that is
 - 20 selected from the group consisting of HCF₂CF₂C(O)CF(CF₃)₂, CF₃C(O)CH₂C(O)CF₃, C₂H₅C(O)CF(CF₃)₂, CF₂CF₂C(O)CH₃, (CF₃)₂CFC(O)CH₃, CF₃CF₂C(O)CHF₂, CF₃CF₂C(O)CH₂F, CF₃CF₂C(O)CH₂CF₃, CF₃CF₂C(O)CH₂CH₃, CF₃CF₂C(O)CH₂CHF₂, CF₃CF₂C(O)CH₂CHF₂, CF₃CF₂C(O)CH₂CH₂F, CF₃CF₂C(O)CHFCH₃, CF₃CF₂C(O)CHFCHF₂, CF₃CF₂C(O)CHFCH₂F, CF₃CF₂C(O)CF₂CH₃,
 - 25 CF₃CF₂C(O)CF₂CHF₂, CF₃CF₂C(O)CF₂CH₂F, (CF₃)₂CFC(O)CHF₂, (CF₃)₂CFC(O)CH₂F, CF₃CF(CH₂F)C(O)CHF₂, CF₃CF(CH₂F)C(O)CH₂F, CF₃CF(CH₂F)C(O)CF₃, and mixtures thereof.
 13. Molten magnesium protected from reacting with oxygen in air in accordance with
 - 30 the process of claim 7.

14. Molten magnesium wherein a protective film is formed on a surface of said magnesium, said film being formed by a reaction of the magnesium with a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof.
- 5
15. The method of claim 14 wherein the fluorocarbon is a perfluoroketone.
16. The method of claim 15 wherein said perfluoroketone is selected from the group consisting of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$,
 10 $\text{CF}_3(\text{CF}_2)_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_5\text{C}(\text{O})\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_3$, $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, perfluorocyclohexanone, and mixtures thereof.
17. The method of claim 14 wherein said fluorocarbon is a hydrofluoroketone that is selected from the group consisting of $\text{HCF}_2\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CF}_3$,
 15 $\text{C}_2\text{H}_5\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{CH}_3$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_2\text{F}$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CHF}_2$,
 20 $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CF}_3$, and mixtures thereof.
18. Solid magnesium comprising a film formed on a surface of said magnesium, said film comprising a reaction product of molten magnesium and a fluorocarbon selected from
 25 the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof.
19. The method of claim 18 wherein the fluorocarbon is a perfluoroketone.
20. The method of claim 19 wherein said perfluoroketone is selected from the group
 30 consisting of $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_3\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$, $\text{CF}_3(\text{CF}_2)_5\text{C}(\text{O})\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_3$,

CF₃C(O)CF(CF₃)₂, perfluorocyclohexanone, and mixtures thereof.

21. The method of claim 18 wherein said fluorocarbon is a hydrofluoroketone that is selected from the group consisting of HCF₂CF₂C(O)CF(CF₃)₂, CF₃C(O)CH₂C(O)CF₃,
 5 C₂H₅C(O)CF(CF₃)₂, CF₂CF₂C(O)CH₃, (CF₃)₂CFC(O)CH₃, CF₃CF₂C(O)CHF₂,
 CF₃CF₂C(O)CH₂F, CF₃CF₂C(O)CH₂CF₃, CF₃CF₂C(O)CH₂CH₃, CF₃CF₂C(O)CH₂CHF₂,
 CF₃CF₂C(O)CH₂CHF₂, CF₃CF₂C(O)CH₂CH₂F, CF₃CF₂C(O)CHFCH₃,
 CF₃CF₂C(O)CHFCHF₂, CF₃CF₂C(O)CHFCH₂F, CF₃CF₂C(O)CF₂CH₃,
 CF₃CF₂C(O)CF₂CHF₂, CF₃CF₂C(O)CF₂CH₂F, (CF₃)₂CFC(O)CHF₂,
 10 (CF₃)₂CFC(O)CH₂F, CF₃CF(CH₂F)C(O)CHF₂, CF₃CF(CH₂F)C(O)CH₂F,
 CF₃CF(CH₂F)C(O)CF₃, and mixtures thereof.

22. The solid magnesium of claim 18 wherein the magnesium is in the form of ignots or castings.

15

23. A method for extinguishing a fire on the surface of magnesium comprising contacting a gaseous mixture comprising a fluorocarbon selected from the group consisting of perfluoroketones, hydrofluoroketones, and mixtures thereof with said surface.

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24. The method of claim 23 wherein the fluorocarbon is a perfluoroketone.

25. The method of claim 24 wherein said perfluoroketone is selected from the group consisting of CF₃CF₂C(O)CF(CF₃)₂, (CF₃)₂CFC(O)CF(CF₃)₂, CF₃(CF₂)₂C(O)CF(CF₃)₂,
 25 CF₃(CF₂)₃C(O)CF(CF₃)₂, CF₃(CF₂)₅C(O)CF₃, CF₃CF₂C(O)CF₂CF₂CF₃,
 CF₃C(O)CF(CF₃)₂, perfluorocyclohexanone, and mixtures thereof.

26. The method of claim 23 wherein said fluorocarbon is a hydrofluoroketone that is selected from the group consisting of HCF₂CF₂C(O)CF(CF₃)₂, CF₃C(O)CH₂C(O)CF₃,
 30 C₂H₅C(O)CF(CF₃)₂, CF₂CF₂C(O)CH₃, (CF₃)₂CFC(O)CH₃, CF₃CF₂C(O)CHF₂,
 CF₃CF₂C(O)CH₂F, CF₃CF₂C(O)CH₂CF₃, CF₃CF₂C(O)CH₂CH₃, CF₃CF₂C(O)CH₂CHF₂,

- $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_3$,
 $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CHFCH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_3$,
 $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}_2\text{CH}_2\text{F}$, $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CHF}_2$,
 $(\text{CF}_3)_2\text{CFC}(\text{O})\text{CH}_2\text{F}$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CHF}_2$, $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CH}_2\text{F}$,
5 $\text{CF}_3\text{CF}(\text{CH}_2\text{F})\text{C}(\text{O})\text{CF}_3$, and mixtures thereof.