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	Development of New Foaming Agent and Techniques for Cellular Aluminum Production		
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論文内容要旨

Chapter 1. Introduction

Recent developments in metal foams, especially aluminum, have produced a new class of lightweight materials at the side of the traditional ones such as polymers, ceramics or glass. The combination of a metallic character together with a cellular structure gives an interesting potential for a wide application of this material, particularly for high volume markets such as the automotive industry. Increased demands concerning cost economy, passenger safety in automobiles and materials recycling all bring constructors now to use metal foams and develop production techniques.

In the present research on aluminum foaming the route of gas-releasing agents is selected to produce bubbles in the melt. To reduce a production costs and develop a technique applicable for the production of aluminum foam with uniform cellular structure a new widely available, inexpensive and safe foaming agent, calcium carbonate, is suggested instead of the conventional agent, titanium hydride.

In this work, the ion-exchange process was employed for the novel purpose of coating calcium carbonate powder with fluoride. The present study aims to investigate the coating procedure, to compare the foaming ability of the conventional FA (TiH_2) with the new one ($CaCO_3$), and to elucidate the impact of surface phenomena occurring during melt foaming on the structure of solid foam.

To provide insight into the melt foaming process and achieve the present purposes the study is carried out and the results are summarized as follows:

Chapter 2. Initial growth of a bubble in a liquid metal around a gas-releasing particle

This process has been studied using both physical and mathematical models. Hydrodynamic, diffusion and capillarity factors have been applied to analyze bubble nucleation from a gas-releasing particle in a melt.

The generalised equation derived in analytical form allows to estimate a bubble growth kinetics in a liquid medium and can be also applied to various combination of GSI material and melts, different external pressure and melt temperature. The condition for microcavity nucleation and bubble growth from GSI in a liquid melt is derived.

The validity of the present theory was tested by calculation of the bubble formation released with Ti-H compounds in Al melt. Analysis of the results shows that the developed theoretical approach is applicable for pore growth study in liquids, particularly at metal foaming by gas releasing agents.

Chapter 3. Development of new foaming agent for aluminum

Improvement of foaming ability of the new foaming agent (FA) in a melt was achieved by enhancing the wetting of particles. An ion-exchange process was employed for coating calcium carbonate powder with fluoride. The coating procedure and a comparative study of the foaming ability of the conventional FA (TiH₂) with the new agent (CaCO₃) have both been carried out.

Surface analysis of the particles revealed the presence of fluoride on the coated particle surface. Effect of coating was considered by the examination of wetting behavior of coated and uncoated CaCO₃ by the Al melt. It was determined that coating of CaCO₃ by the CaF₂ resulted in a decrease in contact angle (~ 15°) in comparison with uncoated carbonate. The possibility of using calcium carbonate as a new foaming agent for aluminum was supported following examination of agent foaming ability. Coated carbonate produced metallic foam with a density comparable to that of samples treated by titanium hydride (~1.0×10³ kg·m⁻³) and much less than uncoated carbonate (1.7×10³ kg·m⁻³). It is believed that this result was caused by wettability enhancement due to the agent coating. For practical use of the new foaming agent, it is important that coated carbonate ensures aluminum foam with smaller pores (1.1×10⁻³ m) than those produced by the conventional FA, titanium hydride (1.8×10⁻³ m). Optimal conditions for agent coating were determined.

Chapter 4. Decomposition of TiH₂ and CaCO₃ foaming agents in liquid aluminum

The present study aims to investigate the decomposition of the foaming agent in liquid aluminium, monitor its foaming behavior and identify the parameters controlling these processes.

The results of the TG and DTA measurements showed that the decomposition of TiH₂ and CaCO₃ occurs in the temperature ranges of 460 to 650 °C and of 650 to 850 °C respectively. It was observed with X-ray apparatus that titanium hydride in tablets and foil decomposed at the constant melt temperature (690°C) for 50 min in similar stages – with intensive bubbling, foaming and slow bubbling. Tablets produced gas much intensively than powder packed into foil. Cellular metal structure was not obtained because of total amount of hydrogen released by TiH₂ was lost to atmosphere when temperature was held at 690°C.

Calcium carbonate decomposed at 720 °C not so intensively as titanium hydride without foam formation for 10 min. Cross section of the samples showed no pores in the metal. It is not reasonable to use for foaming compacted agent because tablet can not ensure uniform bubble distribution in the melt. Moreover the tablet remains in metal making the properties of metal worse.

Actual foaming by TiH₂ agent starts in semiliquid melt at 630°C while cooling with bubble redistribution and growth. Hydrogen pressure and cooling rate of the melt are to be very important parameters to control cell size. To obtain the cellular structure it is necessary to cool melt down while treating by TiH₂ agent or to use

foam stabilising additives.

Metal foam treated by CaCO_3 can be obtained only using melt thickening (for example by Ca addition) and vigorous stirring of the melt during agent introduction as was ensured in Section 3.

Comparison of different agents decomposition allowed to distinguish the foaming mechanism. Melt foaming by CaCO_3 took place while melt cooling to temperature higher than that reached in the case of TiH_2 agent. Calcium oxide particles are supposed to restrict bubble expansion and coalescence causing smaller pores compared with that obtained by TiH_2 .

Chapter 5. Influence of wetting conditions on bubble formation at orifices in an inviscid liquid

Since wettability is found to be a substantial criterion to control bubble size it plays an increasingly important role in making of a new class of lightweight materials such as metallic foams. Both the gas injection technique and foaming agent usage to produce foamed metal deal with bubble formation at the solid (nozzle, gas releasing particle) - liquid (melt) interface.

Bubble formation at single orifice (1 mm diameter) submerged in water with air blowing at an extremely small flow rate (0.033 cc/s) has been studied at a wide range ($68^\circ \leq \theta_0 \leq 110^\circ$) of wetting contact angles. Bubble shape and volume variations were properly described considering the bubble configuration and the key geometrical parameters (V, S, Ro, D), and criteria relations D/d , V/Ro and S/V . Mechanism of bubble growth was described for orifices with different wettability.

The difference between bubble formation at extremely small flow rates and geometrical assumptions of the two-stage mechanism excepted previously by different theoretical models is pointed out. The study conforms importance of wetting conditions in bubble formation. Wettability enhancing (from 110° to 68°) results in bubble volume decrease by more than half.

Chapter 6. In situ bubble formation at nozzles in liquid aluminum

The effect of wettability during the injection of argon into molten aluminum on bubble formation with foaming purpose was in situ studied. In the experiments X-ray fluoroscope was used to observe gas behavior directly at the nozzle tip with different wetting.

It was determined that a bubble produced by steel and silica nozzles (relatively good wettability) is smaller than that formed from an alumina tip (poorer wettability). The examination revealed similar stages of bubble evolution, named growth and necking while detaching. It has been shown that bubble volume increase with contact angle both for aqueous and metallic systems. It was also indicated that bubbling mode turn into jet mode when gas flow rate exceeds the range of 2.5–6.5 cc/s depending on diameter and nozzle material. The present study shows that injection devices wetted by liquid melt are reasonable to use, particularly in metal foaming techniques, for producing small bubbles in the melt.

Chapter 7. Conclusions

The present work has focused on the development of the new foaming agent for aluminium, calcium carbonate. Its foaming ability was improved by wetting enhancement and compared with conventional titanium hydride foaming agent. Bubble formation in liquids (water and aluminum melt) was studied both mathematically and experimentally.

論文審査結果の要旨及び学力確認結果の要旨

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論文題目	Development of New Foaming Agent and Techniques for Cellular Aluminum Production (発泡アルミニウム製造における新規発泡剤および製造法の開発)
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論文審査結果の要旨

炭酸ガス削減は、地球環境問題を解決ための大きな課題であり、各方面で種々の努力がなされている。自動車の燃費向上もその一つでそのための軽量化の研究開発が求められている。軽量化と衝撃特性の向上を目指し、アルミニウムの発泡金属部品の使用が提案されているが、高コストのために量産される自動車には採用されていない。低コストの発泡金属量産プロセスの開発が望まれている。本論文はプロセス開発の基礎研究をまとめたものであり、全7章より構成される。

第1章は緒論であり、従来の発泡金属製造法についてその製造法、製品の特徴まとめたものであり、特にプロセスの鍵となる点を物理化学の原理から記述している。さらに、本研究の目的と本論文の各章を概説している。

第2章では、熔融金属の中で固体発泡剤からの気泡発生・成長を検討するために、その初期気泡の初期核生成、成長と固体発泡剤からの気泡の離脱を数学モデル化し、シミュレーションを行った。

第3章では、高コストの原因の一つになっている高価で危険な発泡剤である TiH_2 の代わりに炭酸塩系の発泡剤を開発した。従来から炭酸カルシウムなどの炭酸塩を使用する試みはなされていたが、熔融アルミニウムと固体炭酸塩との濡れ性が悪く、熔融アルミニウム中に分散しないために発泡剤として使用できなかった。そこで本研究では、熔融アルミニウムとの濡れ性を改善するために表面を F コーティングすることを提案し、具体的に数十ナノの CaF_2 層をコーティングすることに成功した。また、コーティングした炭酸カルシウム粉末の焼結体は熔融アルミニウムに対し、 TiH_2 焼結体とほぼ同程度の濡れ性を持つことを実験的に明らかにした。

第4章では、今回の研究で開発した F コーティング炭酸カルシウム発泡剤は種々の基礎的特性で TiH_2 に劣らないことを確認し、最終的に新開発発泡剤を用いて発泡アルミニウムを製造した。その結果従来の TiH_2 を使用した場合と変わらない発泡率を得ることならびに従来品より均一で細かい気泡による発泡が可能であることを見出した。

第5章では、気泡吹き込みにより発泡金属を製造するプロセスの基礎となるオリフィスからガスが離脱する際のガス気泡の離脱機構を界面化学的に解明した。具体的には水モデルを用い、オリフィス材と水の濡れ性を変化させながら低流量ガスを送りこみ、そのガスの離脱挙動を高速ビデオで観察し、濡れ性の違いによる離脱挙動、特に気泡径が異なることを明らかにした。また、気泡径をオリフィス径、流量、オリフィス材と水の濡れ性をパラメータとして推測する式の導入に成功した。

第6章では、第5章において水モデルで明らかにした気泡のオリフィスからの離脱機構と気泡径推定式が熔融アルミニウム中で適応できるかどうかを、高温透過 X 線装置を用いて実験的に確認した。オリフィス材料には、熔融アルミニウムとの濡れ性が異なる鉄、アルミナ、シリカを用いた。実験の結果、水モデルにおける結果と定性的に同じように、熔融アルミニウムと濡れ性が高い材料ほど微細気泡が発生し、定性的に水モデルと同じ傾向を示した。

第7章では、結論であり、上記各章を総括している。

以上、要するに本論文は、気泡吹き込み法、ならびに発泡剤添加法のいずれの方法に対しても使用する材料と熔融金属の界面化学特性が重要であることを示し、実際に従来の TiH_2 に代わる安価で安全な新発泡剤の開発し成功した。界面化学ならびに工業材料の開発に大きく貢献した。

よって、本論文は博士（工学）の学位論文として合格と認める。

学力確認結果の要旨

平成14年2月21日、審査委員ならびに関係教官出席のもとに、学力確認のための試問を行った結果、本人は地球工学に関する十分な学力と研究指導能力を有することを確認した。

なお、英学術論文に対する理解力から見て、外国語に対する学力も十分であることを認めた。