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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Development of high temperature sensible/thermochemical heat storage system for high efficiency solar thermal power generation

研究課題名（英文）Development of high temperature sensible/thermochemical heat storage system for high efficiency solar thermal power generation

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研究成果の概要（和文）：実験室規模の熱化学反応器貯蔵システムが設計され、太陽光シミュレータを使用して金属酸化物粒子の還元ステップを実行するために構築されました。空気は熱伝達流体および反応物として使用されます。異なるモル比の Fe/Mn 粒子が合成されました。合成された材料は、X 線回折によって特性評価されました。熱重量分析装置（TGA）を使用して、反応速度論を研究しました。

研究成果の学術的意義や社会的意義
Thermal energy storage (TES) plays a vital role in concentrated solar thermal power (CSP) plants to generate electricity beyond on sun hours. A high-energy-density TES system has been developed in this research to operate at temperatures between 800 °C-1000 °C to enhance the efficiency of CSP plants.

研究成果の概要（英文）：A lab scale thermochemical reactor-storage system has been designed and constructed to perform the reduction step of the metal oxide particles using solar simulator. Air is used as heat transfer fluid as well as reactant. Fe/Mn particles with different molar ratios (2:1) and (1:3) have been synthesized. The synthesized materials were characterized by X-ray diffraction. Thermogravimetric analyzer (TGA) was used to study the reaction kinetics. Then, to obtain detailed heat transfer characteristics between the bed and heat transfer fluid, to analyze reaction rate and apply shrinking core model, an 1D numerical model has been developed. Moreover, a kinetic analysis of the charging mode has been conducted at different heating rates to derive the kinetic equation and describe the reaction mechanism by determining the appropriate reaction model. The activation energy of iron-manganese oxide has been obtained using four isoconversion methods (KAS, OFW, Starink, Friedman) and Arrhenius plots.

研究分野：Solar thermal energy

キーワード：Thermal energy storage　Concentrated solar power　Thermochemical storage

１．研究開始当初の背景

In recent years, research and developments on renewable energy technologies are very active to substitute fossil fuels to reduce CO_2 emissions and global warming. Among them, concentrated solar power (CSP) technology has various advantages, including thermal energy storage (TES) systems. During daylight hours and sunny days, the thermal energy obtained from concentrated sunlight is stored in TES system; and the stored energy can be retrieved during the night hours and cloudy days [1-2]. Since the TES capable to enhance the power production dispatchability by storing excess energy during the low electricity demand period and powering the network when energy is needed, it is recognized as a key feature of CSP plants. Currently, various TES strategies have been explored including sensible, latent and thermo-chemical heat storage techniques. Among these, thermochemical storage has been considered as one of the promising systems due to high storage density and high operating temperature. This technique is based on the reversible chemical reactions. During periods of high solar insolation, the heat energy from sun is employed to drive an endothermic reaction and store the energy in chemical bonds. The reverse exothermic reaction is performed (when the energy is needed) to release the stored energy by recombining the chemical reactants. The general form of reaction is

$$A + \Delta h_r \leftrightarrow B + C \quad (1)$$

the reactant (A) is separated into (B) and (C) products during the charging step by endothermic reaction. By reverse reaction, the initial reactant (A) is formed during the discharging step, through an exothermic reaction by mixing the products (B) and (C) together.

At present, to improve the solar-to-electricity efficiency, high temperature (1000 °C) receivers and storage systems are under development to enable advanced power cycle (Brayton cycle). However, it is at the development phase, most of the investigations have been carried out at laboratory scale only. Numerous solid-gas reversible reactions have been examined for TCS applications [5]. Pure and mixed metal oxides can be used for redox TCS. Some recent studies reported that compared to pure metal oxides, some binary metal oxides provide better results and material properties such as higher reaction rates and better microstructural stability, which in turn enhance the long-term cycling stability [3-4]. Mn_2O_3 /Mn_3O_4 redox pair is a remarkable candidate due to its abundance, low toxicity and cost.

２．研究の目的

The main aim of this research is to develop a high-energy-density TES system to operate at temperatures between 800°C-1000°C for higher thermal efficiency and lower electricity cost. Iron-manganese oxide is considered as a promising TCS material because of it's low cost, nontoxic, and higher reaction enthalpy than pure manganese oxide. Thus, this research aims at developing a lab scale cavity type thermochemical reactor and heat storage system to obtain detailed knowledge on particle-flow, heat transfer and reaction characteristics of moving/packed bed of Fe/Mn particles with different molar ratios, (2:1) and (1:3). Furthermore, one of the main objectives of this research is to develop a numerical model to refine the main designing parameters.

３．研究の方法

(1) Experimental method:

A lab scale thermochemical reactor and storage system has been designed and constructed to perform the reduction step of the metal oxide particles using beam-down solar simulator. The schematic and snapshot of the reactor is shown in Figure 1. A packed bed configuration has been considered initially to analyze the main influencing parameters, by considering batch mode operation. The reactor consisted of tubular type cavity with frustum shape aperture, particle feeder, storage tank. Air is used as heat transfer fluid as well as reactant to enable the direct contact heat transfer between the gas and solid phases. The particle bed is heated by the concentrated radiation created by solar simulator, as shown in the schematic figure. In order to prepare Iron–manganese oxide granular $(Mn_{0.33}\ Fe_{0.67})_2\ O_3$ with a molar ratio of Fe/Mn 2:1, Mn_3O4 and Fe_2O_3, both less than 30μm particle diameter, were used. Iron oxide and manganese oxide powders, with molar ratio of 2:1, and along with 3.5 wt% cornstarch solution were mixed together using a magnetic mixer. Then, 50 wt% maltodextrin solution organic binder was added and mixed at the same rotation speed for hours. Subsequently, the material was recovered from the mixer and dried using a drying

oven (Axone DO-450C). Then, the material was calcined for 12 h in air atmosphere at 850 °C using a furnace. Subsequently, the material was sieved in different sizes of granular particles to investigate the effect of particle size. The right hand side of fig. 2 shows the image of prepared pellets, size range approximately between 2 mm to 5mm diameter. The redox reaction of this sample stores and releases energy according to the following reaction:

$$6(Mn_{0.33}Fe_{0.67})_2O_3(s) + \Delta H_r \leftrightarrow 4(Mn_{0.33}Fe_{0.67})_3O_4(s) + O_2(g) \qquad (2)$$

where $(Mn_{0.33}Fe_{0.67})_2O_3$ is the completely oxidized material whereas $(Mn_{0.33}Fe_{0.67})_3O_4(s)$ is completely reduced state of the material. Then, the material was characterized by X-ray diffraction. The left hand side of fig. 2 shows the X-ray diffraction pattern of the sample with a molar ratio of Fe/Mn 2:1. The crystalline phase composition of the oxidized sample shows a bixbyite phase. Similarly, manganese-iron oxide with a Fe/Mn molar ratio of 1:3 has been synthesized as well. The redox reaction of this sample stores and releases energy according to the following reaction:

$$6(Mn_{0.75}Fe_{0.25})_2O_3(s) + \Delta H_r \leftrightarrow 4(Mn_{0.75}Fe_{0.25})_3O_4(s) + O_2(g) \qquad (3)$$

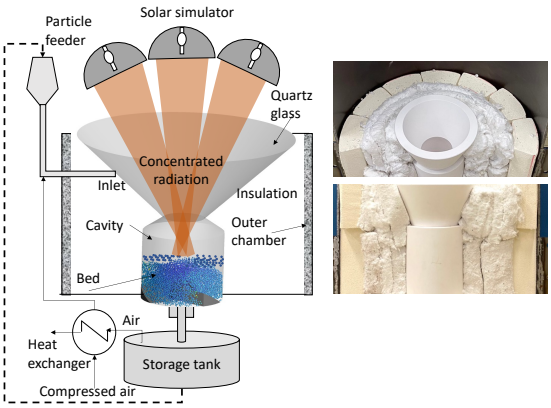

Figure 1. Schematic and image of the experimental setup

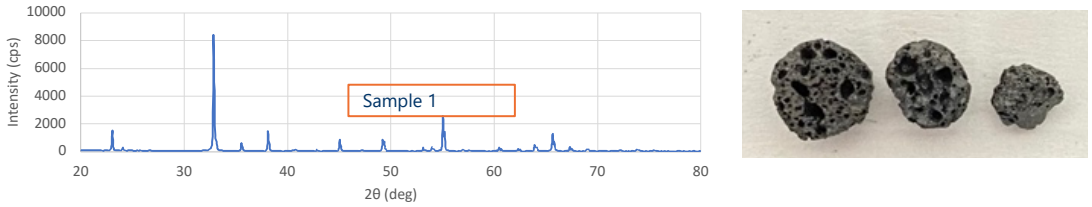

Figure 2. Prepared iron-manganese oxide pellet with a molar ratio of Fe/Mn 2:1 and its X-ray diffraction pattern

Then, the thermal reduction of $(Mn_{0.33}Fe_{0.67})_2O_3$ has been studied by thermogravimetric analysis (TGA) (Rigaku Thermo plus EVO TG-DTA8120). In every cycle, ~33mg of the synthesized sample was placed in a crucible and heated to 150 °C and held for a while to remove the moisture, for 30 minutes. Subsequently, the material was heated up to 1350 °C at 20 °C/min heating rate and held for 10 minutes. The reduction experiments were conducted using nitrogen gas at 300 ml/min flow rate. Fig. 3 shows the temperature and mass change of the sample as a function of time.

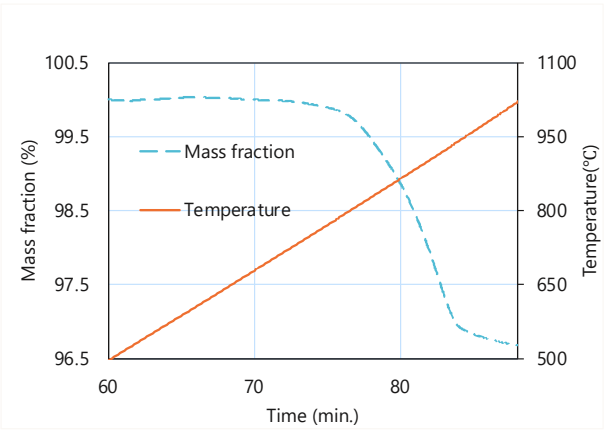

Figure 3. TGA profile of iron-manganese oxide with a molar ratio of Fe/Mn 2:1

(2) Numerical modeling:

In order to obtain detailed heat and mass transfer characteristics of the prepared pellet for packed/moving bed heat storage systems, a simple and computationally fast, 1D conduction model has been developed by the assumption of spherically symmetric, to eliminate other two space coordinates. Moreover, to develop this model, some of the general essential assumptions, including spherical particle with uniform porosity, remained size and shape, no cracks, irreversible and first order reaction, are made. To obtain and analyze the unreacted core and reacted outer layer as a function of time, a spherical pellet of external radius (r_i) is initially kept at initial temperature. The computational geometry is shown in Fig.4. At t=0, the pellet is subjected to heating inside the chamber, by hot heat transfer fluid flow around the pellet. So, the governing equations and boundary conditions can be written as

$$\frac{\partial T}{\partial t} = \left(\frac{k}{\rho C_p}\right)\left[\frac{2}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right} \qquad 0 < r < r_i \tag{4}$$

$$-k\frac{\partial T}{\partial r} = (T - T_{ext})h \quad \text{at } r = r_i \tag{5}$$

$$\frac{\partial T}{\partial r} = 0, \ at \quad r = 0 \tag{6}$$

Where *T, ρ, Cp and k* are temperature, density, specific heat, thermal conductivity respectively. The convective heat transfer condition at the external surface of the PCM capsule is calculated by the Nusselt number as given below

$$Nu = \frac{hd}{k} \tag{7}$$

Where *d* is the diameter of the pellet and heat transfer coefficient *h* is calculated by the reported correlations. The radiation effects present in the pellet at high temperature is included by using the concept of effective thermal conductivity coefficient in the energy equation [3]. The aforementioned governing equations have been solved by using Comsol Multiphysics code.

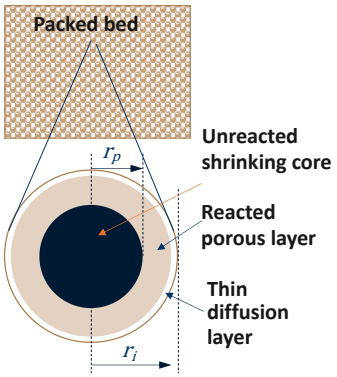

Figure 4. Computational domain

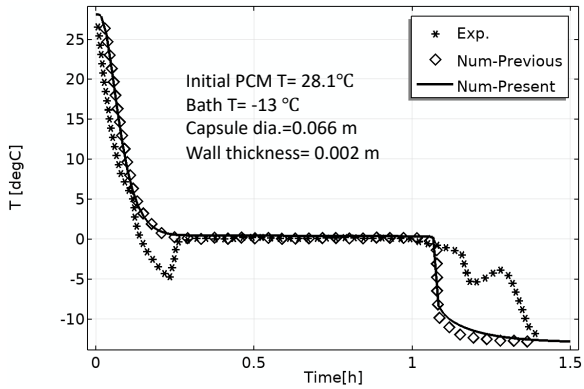

Figure 5. Temperature at the center of the capsule measured by experiments, predicted by the previous model Ismail et al., [6] and the present model

4．研究成果

Initially, to verify the model, the developed model has been applied to predict the temperature and phase change process inside a spherical shell, made of Pyrex glass, external diameter of 0.066 m, wall thickness of 0.002 m. Initially, the capsule was filled with water at 28.1°C and placed in a cool Ethanol bath at constant temperature of -13 °C. For this operating conditions, temperature at the center of the capsule measured by experiments, predicted by the previous model [6], and the present model are compared in Fig. 5. As can be noticed a degree of supercooling is observed in experimental profile. It should be noted that the present model is not able to predict the supercooling process. As can be seen, a relatively good agreement has been observed between the present model and previous experimental and numerical models results. Then, to investigate the effect of pellet size on the heat transfer characteristics, initially two different sizes of pellets, 1.5 and 3mm diameter, were considered at completely reduced state. Initially, the pellet was in room temperature. Then the external

wall of the pellet was subjected to hot nitrogen gas flow around the pellet (at 1350 °C). For these conditions, simulations were conducted. Fig.6 shows temperature distribution of the pellet, from external surface to the core, as a function of time for different pellet sizes. Every line represents an increment of 1 s from the preceding line. In order to compare and show the difference between the two cases, profile at 50 s is plotted in both cases. It is noted that, initially there is significant difference between the outer surface and core whereas it gradually decreases as time progresses. The difference is expected to increase when considering the reduction/oxidation reaction due to enthalpy of reaction and reacted/unreacted regions, as schematically shown in Fig. 4. As can be seen in Fig. 7, 1.5 mm pellet reached almost steady state around 50 s whereas the 3 mm pellet has not reached steady state.

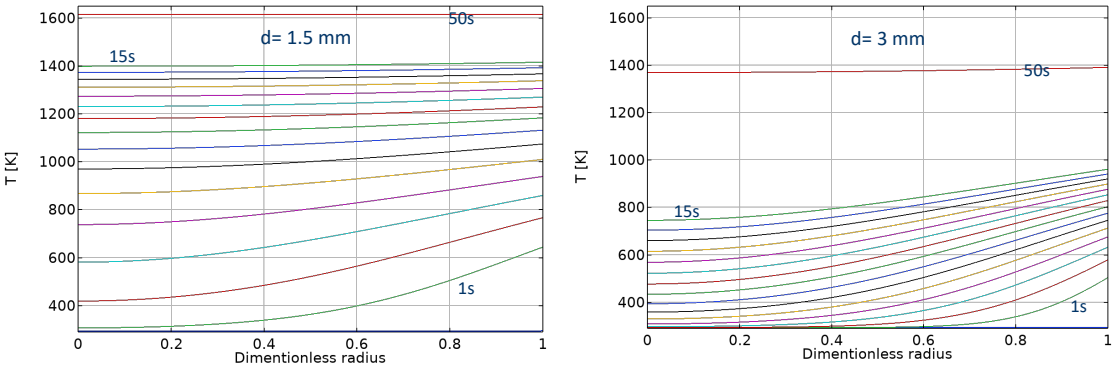

Figure 6. Temperature distribution of the pellet for different cases

Subsequently, kinetic analysis using the TGA results (reduction profiles for various heating rates) was conducted to calculate activation energy and other kinetic parameters using the Arrhenius plots.

References

[1] S. Bellan, T. Kodama, N. Gokon, K. Matsubara, "A review on high-temperature thermochemical heat storage: Particle reactors and materials based on solid–gas reactions" WIREs energy and Environment, 11(2022)e440, https://doi.org/10.1002/wene.440

[2] G. Flamant, B. Grange, J. Wheeldon, F. Siros, B. Valentin, F. Bataille, "opportunities and challenges in using particle circulation loops for concentrated solar power applications", Prog Energy Combust Sci, 94 (2023), p. 101056

[3] M. Hamidi , V. M. Wheeler, X. Gao, J.Pye, K. Catchpole, A. W. Weimer. "Reduction of iron–manganese oxide particles in a lab-scale packed-bed reactor for thermochemical energy storage", Chemical Engineering Science, 221 (2020) 115700

[4] M. Hamidi , A. Bayon, V. M. Wheeler, P. Kreider, M. A. Wallace, A. W. Weimer. "Reduction kinetics for large spherical 2:1 iron–manganese oxide redox materials for thermochemical energy storage", Chemical Engineering Science, 201 (2019) 74-81.

[5] Carrillo, A. J., Gonzalez-Aguilar, J., Romero, M., & Coronado, J. M. "Solar energy on demand: A review on high temperature thermo- chemical heat storage systems and materials" Chemical Reviews, 119 (2019) 4777–4816.

[6] K.A.R. Ismail, J.R. Henríquez, T.M. da Silva. "A parametric study on ice formation inside a spherical capsule" International Journal of Thermal Sciences, 42-9 (2003) 881-887.

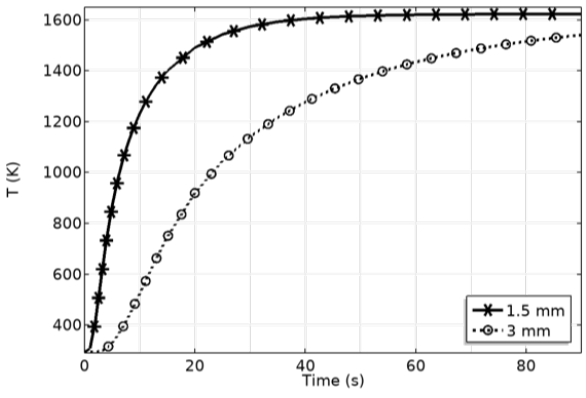

Figure 7. Temperature at the center of the pellet as a function of time for different cases

５．主な発表論文等

〔雑誌論文〕　計4件（うち査読付論文　0件／うち国際共著　4件／うちオープンアクセス　0件）

１．著者名 Selvan Bellan, Tatsuya Kodama, Nobuyuki Gokon, Koji Matsubara	４．巻 11
２．論文標題 A review on high temperature thermochemical heat storage-Particle reactors and materials based on solid-gas reactions	５．発行年 2022年
３．雑誌名 WIRE Energy and Environment	６．最初と最後の頁 e440
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/wene.440　https://doi.org/10.1002/wene.440	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 M Troiano, A Chinnici, S Bellan, GJ Nathan	４．巻 10
２．論文標題 Technological and Fundamental Advances in Production, Storage and Utilization of Fuels	５．発行年 2022年
３．雑誌名 FRONTIERS IN ENERGY RESEARCH	６．最初と最後の頁 830772
掲載論文のDOI（デジタルオブジェクト識別子） 10.3389/fenrg.2022.830772	査読の有無 無
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１．著者名 Genta TSURUMAKI, Selvan BELLAN, Koji MATSUBARA, Tatsuya KODAMA, Mitsuho NAKAKURA, Nobuyui GOKON, Hyun Seok CHO, Karthik MANI, Sakthivel SHANMUGASUNDARAM	４．巻 22
２．論文標題 Fluidization behavior of redox metal oxide and spinel particles to develop high-energy-density thermal energy storage system for concentrated solar power applications	５．発行年 2022年
３．雑誌名 Journal of Thermal Science and Technology	６．最初と最後の頁 61
掲載論文のDOI（デジタルオブジェクト識別子） 10.1299/jtst.22-00061	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 S BELLAN, T KODAMA, HS CHO, JS KIM	４．巻 22
２．論文標題 Hydrogen production by solar fluidized bed reactor using ceria: Euler-Lagrange modelling of gas-solid flow to optimize the internally circulating fluidized bed	５．発行年 2022年
３．雑誌名 Journal of Thermal Science and Technology	６．最初と最後の頁 76
掲載論文のDOI（デジタルオブジェクト識別子） 10.1299/jtst.22-00076	査読の有無 無
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〔学会発表〕　計5件（うち招待講演　0件／うち国際学会　5件）

1．発表者名
Shumpei Fukuda

2．発表標題
Development of Iron-manganese oxide redox material and its reduction kinetics for high temperature thermochemical storage application

3．学会等名
Grand Renewable Energy 2022 International Conference (GRE 2022)（国際学会）

4．発表年
2022年

1．発表者名
Atsushi Kitazawa

2．発表標題
Experimental and numerical study on gas-solid flow in a spout fluidized bed for solar energy conversion

3．学会等名
Grand Renewable Energy 2022 International Conference (GRE 2022)（国際学会）

4．発表年
2022年

1．発表者名
Genta Tsurumaki, Selvan Bellan

2．発表標題
Fluidization Behavior of Redox Metal Oxide and Spinel Particles to Develop High- energy-density Thermal Energy Storage System for Concentrated Solar Power Applications

3．学会等名
11th SOLARIS international symposium on solar energy and efficient energy usage（国際学会）

4．発表年
2021年

1．発表者名
Nobuhiro Okodo, Selvan Bellan

2．発表標題
Numerical Study on the Transient Heat Transfer Behaviour of Packed Bed Thermal Energy Storage System for Concentrated Solar Power Plant

3．学会等名
11th SOLARIS international symposium on solar energy and efficient energy usage（国際学会）

4．発表年
2021年

１．発表者名 Selvan Bellan
２．発表標題 Hydrogen Production by Solar Fluidized Bed Reactor Using Ceria: Euler-lagrange Modeling of Gas-solid Flow to Optimize the Internally Circulating Fluidized Bed
３．学会等名 11th SOLARIS international symposium on solar energy and efficient energy usage（国際学会）
４．発表年 2021年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関