Development of PCM for Recovering High Temperature Waste Heat and Utilization for Producing Hydrogen by Reforming Reaction of Methane

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For efficient heat-recovery of high temperature waste gas such as LDG in the form of latent heat, the utilization technology of phase change material, PCM, was experimentally studied. Copper balls as the PCM were encapsulated by nickel film with/without an insertion of carbon or ruthenium as an inhibition layer, based on an electro-plating method. Then, the effect of the film thickness on the strength of capsules was experimentally examined. As a result, the obtained PCM had enough strength by increasing the film thickness and showed an excellent catalytic property for reforming reaction from methane to hydrogen. In conclusion, the copper PCM with the thick film of nickel and an inactive layer between nickel and copper was available for producing hydrogen by recovering high-temperature waste heat efficiently.

KEY WORDS: steelmaking; heat recovery; phase change material; latent heat; encapsulation; high temperature; electro-plating; hydrogen production.

1. Introduction

The high-temperature industry, such as the steelmaking industry and cement industry, emits essentially a half of input energy in the form of waste heat. Some processes have still high temperature waste heat. For example, a LD converter of steelmaking periodically releases waste gas (LDG) above 1 873 K in the interval of fifteen minutes. However, thermal energy of its sensible heat is rarely recovered in spite of its large potential. This is mainly due to technical difficulty for applying a conventional heat recovery method based on sensible heat, such as steam generation, to the high temperature waste heat intermittently generated. In other words, we should realize the limitation of sensible heat utilization from the viewpoint of low storage density.

An alternative concept of heat recovery process by using latent heat, not sensible heat, has been proposed from high storage density and already realized for the low temperature application. It is one typical example that in order to save electricity at daytime, ice is produced during night and utilized for air conditioning. In this method, the heat storage material with large latent heat, like ice, is called as a phase change material (PCM) and is still under developing for the high temperature application.

The requirement of the latent heat utilization as a heat storage device is as follows:

1) Waste heat is efficiently recovered by melting a PCM with melting point close to the waste heat temperature and the thermal energy is supplied as heat source at fixed temperature by freezing it,
2) density of latent heat storage is over fifty times larger than that of sensible heat,[*1]
3) the PCM is repeatedly usable without losing its property, and
4) the system is relatively cost-effective.

The PCMs have been already proposed for the middle-temperature application from 300 to 1 200 K,[1–7] in which the PCM recovered the waste heat and then can be reused as the thermal energy at fixed output temperature. However, as far as we know, the PCM for high temperature above 1 200 K has never been proposed, although such waste heat of high temperature with high potential exergy still exists within the steelworks.[5] There is, however, no practical design of the PCMs for the high temperature applications and many questions exist. For example, what kind of a material is available as the PCM? How can we encapsulate the PCM? What is cyclic property of the PCM at the operations of heat storage and release? How can we reuse the heat stored?

Therefore, the purpose of this study is to select the PCM and to develop the manufacture technology of the encapsu-

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[*1] For instance, water's latent heat is 80 times larger; 336 kJ/kg, in comparison to its sensible heat; 4.2 kJ/kg.

Table 1. Candidates of PCM for high-temperature waste heat recovery from 1 200 to 1 800 K.

Material	Comp. [mol%]	T_{mp} [K]	ΔH [kJ/mol]	M [g/mol]	ΔH [KJ/kg]	Density [kg/m³]	ΔH [kJ/m³]	Price* [¥/kg]	[kJ/¥]	k [W/m·k]
Ag	–	1235	11.3	108.0	104.6	10500	1.099E+06	22,600	0.005	377
NaF	–	1269	–	42.0	796.0	2780	2.213E+06	40,000	0.020	–
MgF₂–NaF	64–36	1273	–	55.0	794.0	3017	2.395E+06	15,000	0.053	–
KF–MgF₂	31–69	1281	–	61.0	710.0	2943	2.089E+06	20,000	0.036	–
Au	–	1337	12.7	197.0	64.5	19300	1.244E+06	10,000,000	0.000	272
Sm	–	1345	8.6	150.0	57.5	7700	4.430E+05	2,500,000	0.000	–
Cu	–	1357	13.3	63.5	209.4	8930	1.870E+06	255	0.821	354
Na₂O	–	1405	–	62.0	770.0	2390	1.840E+06	–	–	–
MgF₂–MgO	91.5–8.5	1502	–	60.4	922.0	3187	2.938E+06	12,000	0.077	–
Mn	–	1517	14.6	55.0	265.5	7420	1.970E+06	170	1.561	8
MgF₂	–	1536	–	62.3	942.0	3150	2.967E+06	11,200	0.084	–
Be	–	1560	15.8	9.0	1754.4	1840	3.228E+06	2,200,000	0.001	200
Gd	–	1585	10.1	157.0	64.0	7870	5.038E+05	2,500,000	0.000	–
Si	–	1685	39.6	28.0	1414.3	2340	3.309E+06	6,000	0.236	148
Co	–	1767	17.2	59.0	291.5	8800	2.565E+06	6,900	0.042	99

∗ : 13599 chemical goods (1999),[Kagaku–Kougyou–Nippou–sha]

lated PCM. In the experiments, the selected PCMs were coated by nickel based on an electro-plating method and their strength and catalytic property for reforming reaction of methane were examined. The results will show a possibility for promoting the energy saving by recovering the high temperature waste heat and using for producing hydrogen from methane.

2. Sample

Table 1 lists candidates of the PCM for the high-temperature waste heat recovery from 1 200 to 1 800 K, which were selected from several published database.[8] Thermophysical data of latent heat and thermal conductivity, molecular weight, density, price, heat storage amount, *etc.*, were provided in the table. From the heat storage amount per unit volume and price, copper was finally determined as a PCM used in this study.

Figure 1 shows comparison of heat stored by latent heat and sensible heat, in which ΔT means temperature difference of solid copper. In using copper as PCM, the heat storage by latent heat was absolutely huge, in comparison to the sensible heat. The former was approximately five hundred times larger than the latter. When we use only sensible heat without latent heat, it has to be heated and cooled by ΔT of 500 K.

Figure 2 shows a comparison between conventional and new processes for the PCM encapsulation. The conventional method was really complicated, requiring many procedures of shaping, welding, pouring of liquid PCM and vacuum sealing. As a result, this method is quite time-consuming and expensive. In contrast, the method using electroplating is very attractive from simplicity because it has only one procedure.

In the experiments, commercially available copper balls, 99.9 mass% in purity, with 3 mm of diameter were used for the recovery of high temperature waste heat over 1 400 K, because the melting point of copper was 1 356 K. They were thinly coated by nickel; a melting point of 1 723 K, by an electroplating method. The obtained PCM is suitable for recovery of the waste heat from 1 400 to 1 700 K. Significant
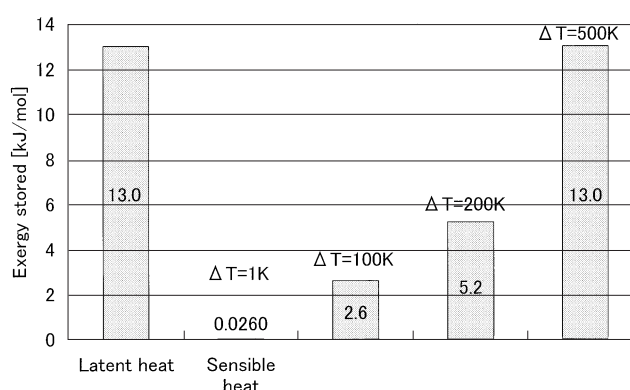
Fig. 1. Comparison of heat stored by latent heat and sensible heat, in which ΔT means temperature difference of solid copper.

A) Conventional Manufacturing Process

B) Proposed Electroplating Mass Production Process
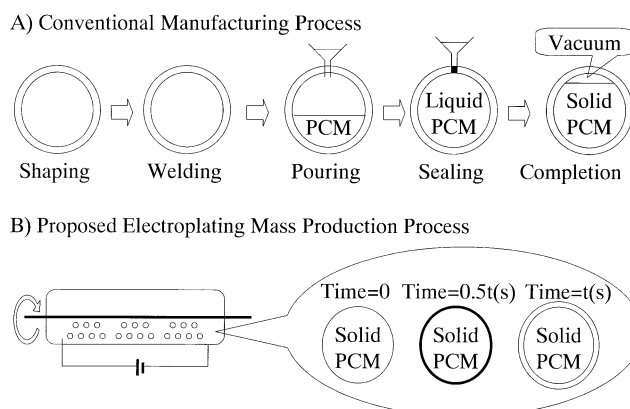
Fig. 2. Comparison between conventional and proposed processes for the PCM encapsulation.

benefit of this method is that thickness of the nickel layer was very easily controllable by changing operating time. Table 2 is the specification of electroplating equipment. At temperature of 323 K, electricity has been charged during desired period. Table 3 gives chemical compositions of aqueous solution for electroplating. For shinning the surface of sample and avoiding the sintering, a commercially available organic material*² was added. The operating con-

*² 2-Butyne-1, 4-diol is usually used.

Table 2. Specification of an electro-plating equipment.

Rotaring rate of barrel	8	rpm
Bath temperature	323	K
Electric current	0.2	A
Cu electrode	15 x 20	mm
Barrel size	200 x 400	mm
Bath size	800 x 500 x 450	mm

Table 3. Chemical compositions of aqueous solution for electro-plating.

composition	Concentration	Comment
$NiSO_4$	$250 kg/m^3$	Ni plating
$NiCl_2$	$50 kg/m^3$	Ni plating
H_3BO_3	$50 kg/m^3$	PH stabilizer
Organic material	$10 dm^3/m^3$	Surface shining

Table 4. Manufacture conditions of the PCM encapsulation.

Material	Cu	
Melting point	1356K(1083°C)	
Diameter	ca.3mm	
First layer **	C	(0 ~ 0.053 μm)
	Ru	(0 ~ 1000 μm*)
Second (main) layer	Ni	(90 ~ 950 μm*)
Method	Electro-plating	

* Thickness of layers is control-able by changing operating time in the electroplating method.

** First layer is needed for avoiding melting between copper and nickel.

ditions were described in the previous study in detail.[4]

Two types of samples were prepared; one is only nickel film and another, nickel-carbon or ruthenium double films. The carbon or ruthenium layer was selected as an inhibition layer for avoiding the direct solution between copper and nickel, because they have complete solubility in the phase diagram at the operating temperature. **Table 4** gives the manufacture conditions of the encapsulated PCMs. Here, the thickness of nickel film ranged from 91 to 940 μm, and ruthenium, 1 mm. The carbon film of 53 μm in thickness was made by a commercially available spray.*3 Averaged thickness of the films was evaluated from the cross sectional view of several balls by scanning electron microscope (SEM).

3. Method

3.1. Durability Experiment

For examining high-temperature durability of the encapsulated PCMs, heating and cooling experiments were conducted. The experimental procedure is that four to six samples were 1) placed on the ceramic boat with the dimensions of $15 \times 13 \times 90$ mm, 2) heated from a room temperature to 1 373 K in air atmosphere by using an electric furnace, 3) kept for one hour as a heat storage step and 4) naturally cooled after being taken out. Both outside view and cross-sectional view of the sample were carefully observed and recorded by a digital camera after each heat cycle in order to examine the crack formation. The procedure was repeated up to fifty times, if no defect was detected.
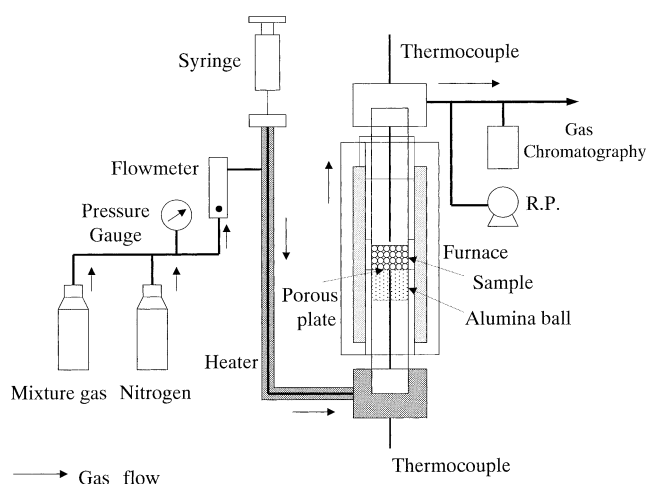
Fig. 3. Schematic diagram of an experimental apparatus for catalytic reaction.

3.2. Catalytic Experiment

The PCM ball, after recovering waste heat at high temperature, can supply thermal energy at constant temperature of 1 356 K, which corresponds to the melting point of copper. Under such high temperature, several endothermic reactions can proceed by utilizing the evolved heat. For studying a possibility that the latent heat stored can be transferred to chemical energy through the endothermic reaction,[7] the catalytic property of nickel coated on the surface of the PCM, was examined. The experimental apparatus, as shown in **Fig. 3**, was used. The nickel-coated PCM balls were packed in the alumina tube of 22 mm in inner diameter and then heated to 1 473 K at nitrogen after being evacuated. Then, the mixture of methane-containing gas corresponding to a coke oven gas (COG: $H_2/CO/CO_2/N_2/CH_4 = 58.22/7.78/1.96/2.84/29.2\%$) and steam was introduced to the reactor at rate of 7.1×10^{-3} Nm^3/s. The concentration of steam added was controlled by a syringe. The mixing ratio of methane and steam was 1 : 1 in the molar ratio. The chemical composition of outlet gas was analyzed by a gas chromatography directly connected to the gas waste line. The experiments were continued until the steady state was attained. To confirm the catalytic ability of nickel, alumina balls of 3 mm in diameter were packed instead of the PCM balls.

4. Results and Discussion

4.1. Durability

Figure 4 shows the appearance and the cross sectional view of the PCM with the two layers of nickel and ruthenium. The color changed from reddish to silver due to the nickel plating. The nickel layer was successfully fixed to the PCM ball tightly and uniformly without any pores. The observed film thickness of 940 μm was the same as the one predicted from faraday's law.[4]

Table 5 gives the physical data of the PCM balls after the single heating cycle. The strength of the balls was signifi-

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*3 Main component is colloidal graphite powder, which is packed by liquefied petroleum gas.

cantly dependent on the preparation conditions. The balls with thin layer less than 100 μm were easily broken or partially cracked. In contrast, the balls with thicker layer showed strength against the heating tests. This is probably because the thin layer was not physically tough enough for

Appearance

Cross sectional view

Fig. 4. Photographs of encapsulated PCMs before heating tests; appearance and cross section view.

Table 5. Results of the observation of PCMs after the heating test.

	Cu-Ni	Cu-C-Ni	Cu-Ru-Ni
$\theta < 100\,\mu$m	×	△	×
$\theta > 940\,\mu$m	×	○	○

○; No breakage △; Partial crack ×; Breakage
θ; Thickness of Ni layer

the copper volumetric expansion due to melting.

Regarding to the film structure, the two layer structure with C or Ru showed an advantage in the strength of the ball. They did not get any breakage when the film thickness is greater than 940 μm. It is evident that the inserted film of C or Ru was extremely effective for avoiding the solution reaction between nickel and copper. There is no significant effect of number of heat cycle on the crack formation of PCM with/without an insert material.

Figure 5 shows photographs of PCM capsules after the heating tests, A is the sample without the breakage, and B and C with breakage. They are typical two examples regarding to breakage of the PCM capsule. In the type B, the surface was foam-like shape after the heating. In the type C, all of the surface of the ball was covered by copper. Obviously, their surfaces, with blackish color, were due to different breakage mechanism. The cross sectional view of both type B and C shows a hollow structure of the ball, because the melted copper flowed out.

Spherical capsule with inner pressure can be theoretically designed, based on the following Lame's equation.[9]

$$\sigma = \frac{r_o^3 + 2r_i^3}{2(r_o^3 - r_i^3)} p_i \quad \text{.............................(1)}$$
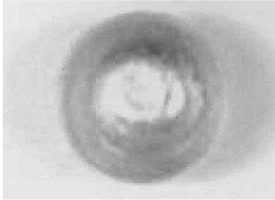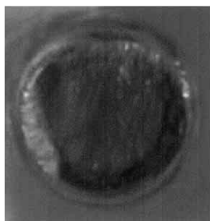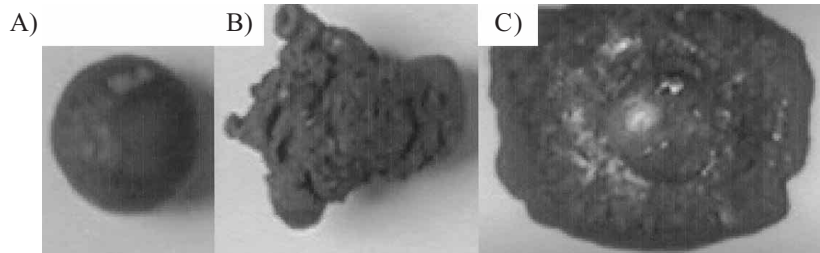
Figure 6 shows stress conditions of the PCM capsule. At 1 273 K, inner pressure is caused by the difference between expansion of copper by melting and thermal expansion of nickel. Volumetric expansion ratio of copper due to the melting is approximately 12.8%.

$$p_i = (\beta - 3\alpha T_{mp})p_0 \text{.............................(2)}$$

The capsule is stable when $\sigma < \sigma_{Ni}$. From the present results, we can understand that the capsule was broken only when σ exceeded σ_{Ni}.

In contrast, regarding to type A without crack, color of the ball surface changed to dark green from silver, due to oxidation. No change in shape of the ball was observed even after heating cycles of fifty times.

Appearance

A)   B)   C)

Cross sectional view
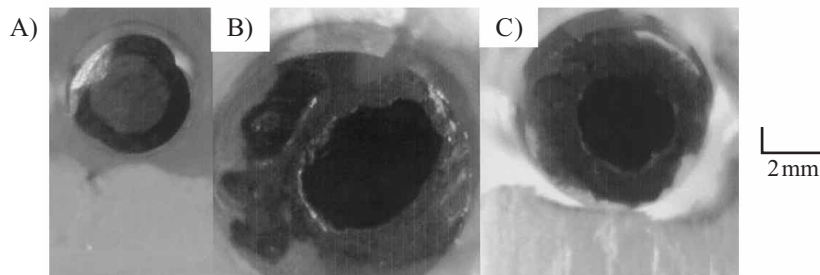
A)   B)   C)

2 mm

Fig. 5. Photographs of encapsulated PCM after heating tests; A-1, B-1: appearance, A-2, B-2: cross section view.
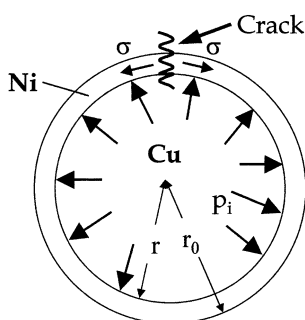
Fig. 6. Mechanism for the crack formation of the PCM capsule.

Table 6. Chemical compositions of inlet gas and outlet gas in the packed bed of nickel balls at 1 473 K, together with equilibrium compositions.

|	H$_2$	CO$_2$	N$_2$	CH$_4$	CO	H$_2$O	Comment
Inlet	45.06	1.52	2.20	22.60	6.02	22.60	COG+Steam
Outlet	77.27	0.00	1.54	2.48	19.37	0.00	
Equilibrium	76.78	0.10	1.51	0.01	20.65	0.00	

4.2. Catalysis

Table 6 gives chemical compositions of inlet and outlet gas from the packed bed of the PCM balls with Ni layer, together with equilibrium one. It demonstrates that most of methane changed to hydrogen and carbon monoxide due to the following reforming reactions:

$$CH_4 + H_2O = CO + 3H_2 - 206.2\,kJ \quad\quad\quad (3)$$

$$CH_4 + CO_2 = 2CO + 2H_2 - 247.3\,kJ \quad\quad\quad (4)$$
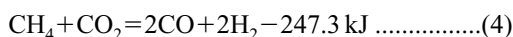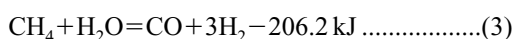
Thermodynamic data show that carbon monoxide and hydrogen increase, and methane, steam and carbon dioxide decrease with elevating temperature. Equilibrium chemical compositions of COG at 1 473 K, calculated by the commercial software code of ASPEN PLUS, was that hydrogen, carbon dioxide, nitrogen, methane and carbon mono-oxide are 76.78, 0.103, 1.51, 0.0061 and 20.65 in molar percent, respectively. The measured compositions of outlet gas agreed reasonably with the equilibrium one. This demonstrated that the nickel surface of the ball was quite an excellent catalyst for methane reforming reaction at 1 473 K.

Instead of the PCM balls with Ni layer, alumina balls were packed for the comparison and outlet gas was also analyzed. However, the analysis of outlet gas was difficult due to severe carbon deposition in the reactor. This phenomena was explained by the following reaction.

$$CH_4 \rightarrow C + 2H_2 \quad\quad\quad (5)$$
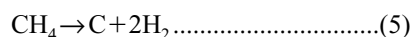
Thus, we conclude that reactions (3) and (4) occurs under the existence of nickel.

This result also demonstrates the possibility of a new process, which recovers waste heat emitted periodically from one process by the PCM balls, reforms methane, and supplies hydrogen and carbon monoxide to another process continuously without introducing additional energy. In the methanol industry, the reformer with Eqs. of (3) and (4) is most energy-consuming step.[10,11] Thus, the PCM developed will have great advantage in reducing the required energy for the production of methanol.

5. Conclusion

The PCM for the high temperature applications over 1 200 K were proposed and examined. The following conclusions were obtained:

1. The copper ball as the PCM was uniformly coated by nickel film by the electroplating method, in which the film thickness was controllable by operating time. The PCM with thick film had enough strength against the heat cycle repeated tests.
2. The two-layer structure of the film by using carbon or ruthenium was definitely effective for avoiding the solution formation between copper and nickel.
3. The nickel film showed an excellent catalytic property against methane reforming reaction at 1 473 K. This suggests a new process of hydrogen generation from hydrocarbon without additional energy.

Nomenclature

h : Thickness of film (m)
p_i : Inner pressure (Pa)
r_i : Inner diameter (m)
r_o : Outer diameter (m)
α : Linear expansion ratio of nickel (K^{-1})
β : Expansion ratio of copper due to melting $(-) = \rho_l/\rho_s$
σ : Stress (Pa)
σ_{Ni} : Tensile stress of nickel at room temperature (Pa)
ρ_l : Liquid density of copper (kg/m^3)
ρ_s : Solid density of copper (kg/m^3)

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