Development of Fe Base Phase Change Materials for High Temperature Using Solid–Solid Transformation

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Fe base Phase Change Materials (PCM) for high temperature around 953–1 273 K using multiple solid–solid transformations were developed. The amount of latent heat of PCM samples were measured by Differential Scanning Calorimetry. The amount of latent heat of Fe–xCo samples increased with increasing Co addition. The reducing atmosphere was suitable for the samples developed in this work. The durability performance of samples was confirmed by heat treatment experiments. From the viewpoint of heat accumulation/supply ability, cost and durability performance, Fe–Co(–Cr) system alloy is one of the most suitable Phase Change Materials for heat recovery from high temperature exhaust gases.

KEY WORDS: phase change materials; high temperature; solid–solid transformations; latent heat; iron base.

1. Introduction

Iron and steelmaking companies consume about 11% of total primary energy and emit about 5% of the energy without recovery in the form of waste heat in Japan. Many papers have been reported the method of recovering these unused energies to suppress carbon dioxide emissions. However, in many cases, such as high temperature exhaust gas from LD converter, recovery of the waste heats is still very difficult because these energies or high temperature exhaust gases are emitted discontinuously. In addition, these waste heats are very unstable heat source.

A heat storage material for efficient heat recovery of the intermittently emitted high temperature waste heat such as combustion waste gas has been reported by Maruoka et al. In the companion paper, they reported a new heat storage material with large latent heat, so-called Phase Change Material (PCM), and examined the encapsulation technology of copper sphere with nickel film based on an electroplating method. PCM, which utilizes solid–liquid transformation, should be encapsulated to keep the liquidus PCM at/above the liquidus temperature of the PCM as reported in the papers. In most situations, reactivity of the capsule with the PCM or atmosphere, durability of the capsule and the heat capacity of the capsule will be serious and irresoluble problems in the recovery of energy at high temperatures such as the waste gases from LD converters.

Therefore, the purpose of this work is development of new Phase Change Materials for efficient heat recovery of the intermittently emitted high temperature waste heat without capsule, which utilize one or two solid–solid transformations at high temperatures.

2. Samples Preparation

Solid–solid transformations include magnetic transformations, crystallographic structure transformations, order–disorder transformations, transformations between amorphous structure and crystal structure and so on. Generally speaking, the amounts of latent heats of solid–solid transformations are small compared to those of solid–liquid transformations. Therefore several numbers of transformations should occur simultaneously to obtain huge amount of latent heat or heat storage/discharge at a specific temperature by solid–solid transformations; however, materials which have multiple and reversible solid–solid transformations at close temperatures are very limited. Transformations between amorphous structure and crystal structure are not reversible transformations as solid–solid transformations. In the solid–solid transformations, crystallographic structure transformations and magnetic transformations have relatively large amount of latent heat. Of course, various metals show crystallographic structure transformation, however, typical metals which show magnetic transformation are limited to Fe, Co and Ni. The temperature of crystallographic structure transformation between ferrite and austenite of Fe and that of magnetic transformation of Fe are very close. These transformation temperatures can be controlled by the Co concentration in Fe–Co binary system. Therefore, in this work, we used ‘crystallographic structure transformation between ferrite and austenite of Fe’ and ‘transformation between the ferromagnetic and paramagnetic phases of Fe’ to develop Fe base Phase Change Materials which have huge amount of latent heat. The phase diagram of Fe–Co binary system is shown in Fig. 1. An increase of Co addition into Fe causes an increase of magnetic transformation temperature. More
than about 15 mass% Co addition results in the coincidence of the α–γ transformation temperature and magnetic transformation temperature. On the other hand, Phase Change Materials have to have a certain level of oxidation resistance because Phase Change Materials might be used under oxidizing atmospheres. Therefore, in this work, samples of Fe–xCo (mass%, x is 15–40), Fe–10Co–5Cr (mass%), Fe–7Si (mass%) and Fe–10Al (mass%) were prepared from reagent grade Fe (99.99%), Co (99.93%), Cr (99.3%), Si(11N) and Al (99.99%) powders because there is a report that addition of Cr, Si, and Al improve the oxidation resistance of iron at high temperatures.13)

Weighed mixtures of Fe, Co, Cr, Si and Al were melted in crucibles in Ar for 300 s at 1 773 K by a high-frequency induction heating furnace and poured into a mold. The bulk samples were cut into die about 1 cm\(^3\) and some die of each sample were crushed into powders for the measurements of the amount of latent heat by Differential scanning calorimetry (DSC). Compositions of the samples are shown in Table 1.

Table 1. Composition of Phase Change Materials used in this work.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Fe (mass%)</th>
<th>Co (mass%)</th>
<th>Cr (mass%)</th>
<th>Si (mass%)</th>
<th>Al (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe-15Co</td>
<td>85</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Fe-20Co</td>
<td>80</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Fe-30Co</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Fe-40Co</td>
<td>60</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Fe-10Co-5Cr</td>
<td>85</td>
<td>10</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Fe-7Si</td>
<td>93</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Fe-10Al</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

3. Experiments
3.1. Latent Heat Measurement
3.1.1. Differential Scanning Calorimetry Analysis
The amounts of latent heat of each PCM sample were measured by Differential Scanning Calorimetry (DSC). About 60 mg of samples were pressed into briquettes by a hydraulic press. Aluminum powders were used for a standard specimen. One of the PCM samples and aluminum specimen were put into platinum plates respectively. Analysis of DSC curves which were obtained under Ar atmosphere, at the rate of temperature increase and decrease 10 K/min, from room temperatures to 1 273 K, measured the amounts of latent heat of samples and transformation temperatures.

3.1.2. Results
(1) Fe–Co Binary System PCM
Figure 2 shows an example of DSC curve of Fe–15Co sample. There is one endothermic peak at 1 208 K in the temperature rising period, and one exothermic peak at 1 198 K in the temperature dropping period. It can be confirmed that ‘change in the crystallographic structure between ferrite and austenite of iron’ and ‘transformation between the ferromagnetic and paramagnetic phases of iron’ proceed simultaneously in the sample around the crystallographic structure transformation temperature because there is only one peak in the temperature rising and dropping periods respectively. The amount of latent heat of the sample was almost the same values as the summation of the amount of latent heat of α–γ transformation and that of transformation between the ferromagnetic and paramagnetic phases of iron.

(2) Fe–Co–Cr System PCM
The DSC curve of Fe–10Co–5Cr sample (Fig. 3) is very similar to that of Fe–15Co sample in the point of that each period has only one peak because the both samples have very similar compositions. However, the transformation temperature is slightly lowered compared to the Fe–15Co sample because Fe–10Co–5Cr sample contains 5 mass% less Co than Fe–15Co sample. There is a large difference between the transformation temperatures at temperature rising period and temperature dropping period, which is different behavior from that of the Fe–Co binary system PCM samples. The transformation temperature moves to higher temperature at temperature rising period, and moves to lower temperature at temperature dropping period. The rea-
son is probably that the bcc–fcc structural transformation of this sample needs huge driving force due to slow diffusion rate of Cr atoms in iron.

In general materials, transformation between the ferromagnetic and paramagnetic phases does not proceed only at the Curie point, and the transformation proceeds at a specific temperature range around the Curie point as is well known. In the case of Fe–Co–Cr system PCM, in the temperature rising period, after the temperature reached a certain level of high temperature, magnetic transformation proceeds gradually until the temperature reaches the \(\alpha\)–\(\gamma\) transformation temperature. When the temperature reaches \(\alpha\)–\(\gamma\) transformation temperature, most of the magnetic transformation proceeds at the temperature because \(\gamma\)-Fe is paramagnetic material. In the temperature dropping period, the \(\alpha\)–\(\gamma\) transformation temperature considerably moves to lower temperature by the addition of 5 mass% of Cr, then, the magnetic transformation proceeds at narrower temperature range than Fe–Co system PCM samples.

(3) Fe–Si, Fe–Al System PCM

Fe–7Si and Fe–10Al samples showed lower transformation temperatures than Fe–Co binary system PCM and Fe–Co–Cr system PCM samples. The transformation temperatures of the Fe–Si and Fe–Al samples were almost the same values. The amounts of latent heat of both samples were also almost the same values. These samples only show magnetic transformation and do not show structural transformation, therefore, the amount of latent heat of the samples were lower than that of Fe–Co(–Cr) system PCM samples.

3.1.3. Summary of Latent Heat Measurement

The composition, type of transformation, transformation temperature and the value of the latent heat of samples used in this work are shown in Table 2. In the Fe–Co binary system PCM, an increase of Co addition provides an increase of the transformation temperature. Therefore, the transformation temperature or the heat accumulation/supply temperature can be controlled by changing the Co composition. Figure 4 shows the effect of Co addition on the latent heat per unit volume of the samples. Increase of the Co addition provides higher transformation temperature and increase of accumulation energy per unit volume.

Fe–40Co and Fe–10Co–5Cr samples have the largest latent heat per unit weight in the samples prepared in this work. On the other hand, Fe–40Co sample has the largest latent heat per unit volume in the samples because the density of Fe–40Co sample is slightly larger than that of Fe–10Co–5Cr. However, the difference of the amount of latent heat per unit volume of the two samples seems to be in an acceptable range (less than 5%).

Metal base PCM, which has generally larger density than organic PCM, is suitable for stationary usage. The evaluation of the metal base PCM should be made by the amount of heat storage per unit volume. The amounts of heat storage per unit volume of Fe–Co binary system PCM and Fe–Co–Cr system PCM in this work exceed that of solid–liquid transformation of water (about 360 J/cm\(^3\)) in Table 2, thus, these samples have enough performance as PCM for high temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transformation</th>
<th>Temperature (K) / Heat storage (kJ/g)</th>
<th>Temperature (K) / Heat discharge (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-15Co</td>
<td>Structural and Magnetic</td>
<td>1208 / 49(368)</td>
<td>1198 / 52(409)</td>
</tr>
<tr>
<td>Fe-20Co</td>
<td>Structural and Magnetic</td>
<td>1223 / 49(368)</td>
<td>1215 / 50(404)</td>
</tr>
<tr>
<td>Fe-30Co</td>
<td>Structural and Magnetic</td>
<td>1250 / 51(417)</td>
<td>1238 / 54(442)</td>
</tr>
<tr>
<td>Fe-40Co</td>
<td>Structural and Magnetic</td>
<td>1261 / 53(439)</td>
<td>1252 / 57(472)</td>
</tr>
<tr>
<td>Fe-10Co–5Cr</td>
<td>Structural and Magnetic</td>
<td>1117 / 56(441)</td>
<td>1076 / 57(489)</td>
</tr>
<tr>
<td>Fe-7Si</td>
<td>Magnetic</td>
<td>966 / 34(289)</td>
<td>958 / 32(252)</td>
</tr>
<tr>
<td>Fe-10Al</td>
<td>Magnetic</td>
<td>953 / 34(289)</td>
<td>955 / 32(252)</td>
</tr>
</tbody>
</table>

Table 2. Heat storage/discharge and transformation temperature of Phase Change Materials.

![Fig. 4. Effect of Co addition on the accumulation heat (latent heat) per unit volume.](image)

The transformation temperatures in Table 2 are structural transformation temperatures, because the magnetic transformation is occurred at a wide range of temperature around the transformation temperatures. The amount of latent heat in the table shows the summation of amount of absorption/generation heat between room temperatures and 1 273 K. In Fe–10Co–5Cr sample, structural transformation and magnetic transformation proceed at relatively narrow temperature range simultaneously, as mentioned in the Sec. 3.1.2. (2). Therefore, Fe–10Co–5Cr sample is the most useful PCM composition in the samples of this work.

3.2. Effect of Atmosphere

Phase Change Material will be often used under oxidizing/reducing atmospheres at high temperatures. For example, oxidative products will be generated under oxidizing atmospheres. Even under reducing atmospheres for iron, oxidative products of additive elements will be generated depending on the oxygen potential, and then, the behavior of transformations and the amount of heat storage/discharge will be changed from those observed in this work under the inactive atmosphere. Therefore, at first, we investigated the effect of oxidizing atmosphere on the PCM samples, and then, investigated the effect of the reducing atmosphere on the PCM samples.

3.2.1. Oxidizing Atmosphere (Air)

Figure 5 shows an experimental apparatus for the experiments under oxidizing atmosphere. The flow rate of the Air in the furnace was maintained at 1.0 NL/min. After a specific temperature distribution in the furnace was confirmed, 10 cycles of heat treatment (1 473 K for 15 min–673 K for 15 min) were applied to the sample by moving the position...
of the sample. After 10 cycles of heat treatment were carried out, the sample was cooled to room temperature. Figure 6 shows an example of the Fe–10Co–5Cr sample before/after oxidizing experiment. The surfaces of all samples were oxidized. Oxide layer was formed on the surface and some of the oxide layer was flaked from the sample. The formation and flare of the oxide layer were probably due to the shortness of the oxidation-resistant element such as Cr, Si, and Al, however, excess of these oxidation-resistant elements prevents the structural and magnetic transformations of PCM. An increase of these oxidation-resistant elements to improve the oxidation-resistant of PCM will decrease/eliminate the heat accumulation/provide ability as PCM. Therefore, the oxidizing atmosphere is not suitable for these Fe base PCM.

3.2.2. Reducing Atmosphere (CO–CO$_2$–N$_2$)

As an example of the system which produces high temperature, discontinuous, reducing exhaust gas, we investigated the probability of heat accumulation/supply system using PCM samples developed in this work intended for the exhaust gas from LD converter. Table 3 shows an example of exhaust gas composition from LD converters. The CO/CO$_2$ ratio of the exhaust gas is about 0.807, and the ratio is reducing atmosphere for iron and iron oxides at 1673 K.

The composition of the reducing gas used in this work is shown in Table 4. The same experimental apparatus shown in Fig. 5 was used in the experiment. The flow rate of the reducing gas in the furnace was maintained at 1.0 NL/min. After a specific temperature distribution in the furnace was confirmed, 10 cycles of heat treatment (1473 K for 15 min–673 K for 15 min) were applied to the sample by moving the position of the sample. After 10 cycles of heat treatment were carried out, the sample was cooled to the room temperature. The cross-sections of the samples were observed by Scanning Electron Microscope (SEM).

Examples of SEM observations are shown in Figs. 7 and 8. There was no obvious change in the structure in the Fe–15Co sample; however, there were coating layer on the surface of the sample and precipitated phase in the Fe–10Co–5Cr sample. As a result of EDX analysis, the existence of the precipitated phase was confirmed to Cr concentrated phase. The position of the Cr concentrated phase does not coincide with the position of the O concentrated phase. Therefore, the Cr concentrated phase is not an oxide of chromium. Considering that the atmosphere is CO–CO$_2$–N$_2$, the Cr concentrated phase is probably chromium carbide such as M$_{23}$C$_6$ which is generated by Fe, Cr and C from CO in the atmosphere. These chromium carbides will solute in the austenite when the sample temperature becomes around/above 1173 K in the temperature rising period, therefore, the precipitation of chromium carbides does not affect heat accumulation/supply ability of the PCM sample. As the results, these samples will be applicable as Phase Change Materials to the heat accumulation/supply system in the atmosphere of LD converters.

4. Conclusions

In this work, we developed Fe base Phase Change Materials, Fe–xCo (x is 15–40), Fe–10Co–5Cr, Fe–7Si, Fe–10Al, then we obtained following results.

(1) Fe base Phase Change Materials, in which structural and magnetic transformations are occurred simultaneously, were developed. Heat accumulation and supply at around 953–1273 K can be available with these Phase Change Materials.

(2) From the viewpoint of heat accumulation/supply

<table>
<thead>
<tr>
<th>Component</th>
<th>CO</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (mol%)</td>
<td>66.5</td>
<td>16.0</td>
<td>18.6</td>
<td>0.90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>CO</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (mol%)</td>
<td>67.0</td>
<td>16.0</td>
<td>17.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3. Example of exhaust gas composition of LD converters.

Table 4. Composition of reducing gas used in this work.
ability, cost and durability performance, Fe–Co(–Cr) system alloy is one of the most suitable Phase Change Materials for heat recovery from high temperature exhaust gases.

3) These Phase Change Materials is preferred to be used under reducing atmosphere due to the formation/flake of metallic oxide layer under oxidizing atmosphere.

REFERENCES