1 **High Thermal Conductivity Phase Change Composite with a**
2 **Metal-Stabilized Carbon-Fiber Network**

3 Takahiro Nomura^{1*}, Chunyu Zhu¹, Sheng Nan¹, Kazuki Tabuchi¹,
4 Shuangfeng Wang², and Tomohiro Akiyama¹

5
6 ¹ Center for Advanced Research of Energy and Materials, Faculty of Engineering,
7 Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan

8
9 ² Key Laboratory of Enhanced Heat Transfer and Energy Conservation of the Ministry
10 of Education, School of Chemistry and Chemical Engineering, South China University
11 of Technology, Guangzhou 510640, China

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13
14 **Corresponding author*

15 *Tel.: +81 11 706 6842; fax: +81 11 706 6849*

16 *E-mail address: nms-tropy@eng.hokudai.ac.jp (T. Nomura)*

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21 **Keywords:** Phase change material, Network structure, Latent heat storage, Thermal
22 conductivity

24 **Abstract**

25 To enhance the thermal conductivity of phase change materials (PCM) such as sugar
26 alcohol and molten salts, the preparation of a phase change composite (PCC) with a
27 PCM and a filler with high thermal conductivity has been widely investigated. Although
28 many reported PCCs have high thermal conductivity, the stability during thermal
29 cycling endurance is often too low for practical use. This paper describes the
30 development of a PCC with both high thermal conductivity and high cyclic durability.
31 The PCCs were prepared by a hot-pressing method. Erythritol (melting point: 118°C,
32 thermal conductivity: 0.73 Wm⁻¹K⁻¹) was used as a PCM, and carbon fiber (thermal
33 conductivity: 900 Wm⁻¹K⁻¹ in the fiber direction) and indium particles (thermal
34 conductivity: 82.8 Wm⁻¹K⁻¹) were used as the high thermal conductivity fillers. The
35 effective thermal conductivity of the PCC was measured using the laser flash method
36 and the network structures were analyzed using energy dispersive spectroscopy and
37 scanning electron microscopy. Thermal cycling tests through the melting and
38 solidification phases of the erythritol were performed to investigate the cyclic durability
39 of the PCCs. We found that the indium particles melted during hot pressing, welding
40 together the carbon fiber to produce a stable percolating network, which significantly
41 enhanced the thermal conductivity and cyclic endurance of the PCCs.

42 **1. Introduction**

43 To effectively exploit solar energy and achieve reduced fossil fuel consumption,
44 advanced thermal energy systems are required. Such systems should have high-heat
45 capacity, a high heat exchange rate, and long-term durability. Conventional sensible heat
46 storage (SHS) technology has been widely applied in various fields and in fact, is the
47 foundation of the current industry. However, SHS technology is not suitable for future
48 thermal energy storage (TES), which require high heat capacity materials.

49 Latent heat storage (LHS) using phase change materials (PCM) is a promising
50 technology which can satisfy the high-performance requirements of future TES
51 applications. LHS is typically based on the storage or release of latent heat during a
52 solid-to-liquid phase transition of a PCM. The use of latent heat allows LHS systems to
53 achieve higher heat capacities than SHS, the ability to convert intermittent heat sources
54 to constant ones, and excellent long-term durability. These advantages have allowed
55 LHS systems to be applied in many fields [1], such as building materials [2], battery
56 thermal management [3], solar heat utilization (including concentrated solar power) [4],
57 and industrial exhaust heat recovery [5-7].

58 A low heat transfer rate, which is caused by low thermal conductivity of
59 common PCM materials such as sugar alcohol and molten salts, is a major drawback for

60 LHS systems [8]. Generally, heat conduction is dominant for typical indirect-contact
61 LHS heat exchangers, such as shell-tube and packed-beds of encapsulated PCM.
62 However, common PCM candidates such as paraffin [9, 10], salt-hydrates [11], sugar
63 alcohol [12, 13], and molten salts [14, 15] have thermal conductivities that are too low
64 for practical application in TES systems. Generally, organic PCMs have conductivity
65 values less than $0.4 \text{ Wm}^{-1}\text{K}^{-1}$ and those of inorganic PCMs are less than $1.0 \text{ Wm}^{-1}\text{K}^{-1}$ [8].
66 Although using high thermal conductivity metals as a PCM is attractive [16-20], there
67 are few candidate materials in the temperature range below 300°C . Therefore,
68 identifying and investigating PCMs with high thermal conductivities is an important
69 area of research.

70 Several studies have focused on developing phase change composites (PCC)
71 with high thermal conductivities. Recently, Zhang et al. [8] reviewed state-of-the-art
72 PCC technologies from over 200 studies presented in the literature. They broadly
73 classified the fabrication methods for high thermal conductivity PCCs into three groups:
74 simple mixing, impregnation, and compression. The most important step for enhancing
75 the thermal conductivity of any PCC is forming a percolating network of a high thermal
76 conductivity material [12].

77 With respect to the heat transfer network of a PCC, impregnating a porous

78 material (such as a metal or carbon foam) with a liquid PCM has many advantages [8],
79 as the foam has a high quality percolating network. It has been shown that the effective
80 thermal conductivity of PCMs can be enhanced by 1–2 orders of magnitude using metal
81 or carbon foams [17]. Unfortunately, foam substrates such as porous metals (usually Cu
82 [21, 22], Al [23, 24], and Ni [21, 25]) and carbon [26-29] are difficult to process, and
83 are usually too expensive to use as PCM supports.

84 The compression method [12, 30, 31] is also promising for enhancing the
85 thermal conductivity of PCCs by forming efficient heat transfer networks. In this
86 method, solid PCM particles and fillers such as carbon fiber are mixed and then
87 compressed with or without heating. Our previous study revealed that the fillers occupy
88 the voids between the PCM particles during compression treatment, and this
89 phenomenon accelerates the formation of a percolating network of filler [12]. In
90 addition, fillers with anisotropy thermal conductivity, such as carbon fiber, become
91 vertically oriented with respect to the direction of the press in the final PCC. This
92 orientation enhances the drastic increase of the effective thermal conductivity of the
93 PCC [12, 30, 32-34]. In addition, this method has economic advantages related to facile
94 processing and the use of inexpensive carbon materials, such as expanded graphite [30,
95 32-34].

96 However, the PCC prepared by the compression method would have a fatal
97 problem that fillers in the PCC just contacts to each other. This condition of filler
98 network in the PCC caused two challenges for practical use of the PCC. The first is that
99 the stability under thermal cycling of PCCs prepared by compression is often too low
100 for practical use. The second is that thermal conductivity of the PCC is still low with
101 respect to the quite high thermal conductivity of filler materials; e.g. carbon fiber: 900
102 W m⁻¹K⁻¹ [12]. This was because the condition that filler just contacts to each other
103 would cause the increase of thermal contact resistance.

104 Therefore, this study attempts to solve the two challenges simultaneously and
105 to develop PCCs with both high thermal conductivity and high cyclic durability, using a
106 hot-press method. Erythritol was used as the PCM, and carbon fiber and indium
107 particles were used as the high thermal conductivity fillers. Here, Indium particles
108 would be expected as a welding material for carbon fibers. The effective thermal
109 conductivity of the PCC was measured using the laser flash method and the network
110 structures were analyzed using energy dispersive X-ray spectroscopy (EDS) and
111 scanning electron microscopy (SEM). In addition, cyclic melting and solidification tests
112 were performed to investigate the cyclic durability of the PCCs.

113

115 **2. Materials and Methods**

116 **2.1 Materials**

117 Table 1 shows the thermophysical properties and specifications of the PCM and
118 filler materials used in this study. Erythritol ($C_4H_8O_4$) was selected as a PCM; it has a
119 melting point of $118^{\circ}C$, a latent heat of 340 Jg^{-1} , and a thermal conductivity of 0.73
120 $Wm^{-1}K^{-1}$ [35]. Particles of erythritol were used as a raw material for the preparation of
121 PCCs. Fig. 1 shows the particle distribution of the PCM. The average particle size and
122 packing ratio was $614\text{ }\mu m$ and 0.66 , respectively. Note that the particle distribution is
123 controlled as relatively broad to get high packing ratio of PCM.

124 We selected carbon fiber (CF, XN-100, Nippon Graphite Fiber Co., Ltd) and
125 micro-particles of indium (In, Kojundo Chemical Laboratory Co., Ltd) as the high
126 thermal conductivity filler The CFs had an average diameter of $10\text{ }\mu m$, average length
127 of $64\text{ }\mu m$, and density of 2220 kgm^{-3} . The anisotropic thermal conductivity in the fiber
128 direction was $900\text{ Wm}^{-1}K^{-1}$ and $10\text{ Wm}^{-1}K^{-1}$ in the direction normal to the fiber. The
129 indium had an average particle size of $45\text{ }\mu m$, a melting point of $156^{\circ}C$, a latent heat of
130 28.7 Jg^{-1} , and a thermal conductivity of $82.8\text{ Wm}^{-1}K^{-1}$. Note that both the erythritol and
131 the carbon fiber were the same materials as used in our previous study [12].

Table 1 Thermophysical properties and specifications of a PCM and fillers used in this study.

Material	Classification	k [W m ⁻¹ K ⁻¹]	T _m [°C]	C _p [J g ⁻¹ K ⁻¹]	L [J g ⁻¹]	ρ [kg m ⁻³]	D _{ave} [μm]	Diameter [μm]	Length [μm]
Erythritol	PCM	0.73	118	1.68	340	1450	614	-	-
Carbon fiber (CF)	Filler	900	-	0.69	-	2220	-	10	64
Indium	Filler	82.8	156	0.24	28.6	7030	-	-	-

k: Thermal conductivity, T_m: Melting point, C_p: Specific heat, L: Latent heat, ρ: Density, D_{ave}: Average particle size

Figure 1: Particle distribution of the erythritol used in this study.

137 **2.2 Preparation of the PCCs**

138 We prepared PCCs by hot-pressing (HP), as described in detail in our previous
139 study [12]. First, the PCM particles, CF, and indium particles were wet-mixed in 99.9%
140 acetone at 1500 rpm with a stirrer, for 30 min at room temperature. Then, the
141 well-mixed wet samples were dried in air at room temperature. Next, about 3 g of the
142 dry sample was packed into a carbon mold with a diameter of 12.7 mm and then placed
143 in a compression machine with an electric heater. The samples were pressed at 10 kN
144 with heating at a rate of 10 °Cmin⁻¹ from room temperature to 160°C; the pellets were
145 kept at this temperature for 1 h. The hot-pressed samples with diameters of 12.7 mm
146 and thicknesses around 10 mm were cooled in the furnace, and then removed from the
147 mold. Finally, samples with a size of 10 × 10 × 1 mm were cut from the horizontal
148 direction to the press-direction and carefully polished using #2000 emery paper.

149 **2.3 Thermal cycling tests**

150 Thermal cycling tests were undertaken on the as-prepared PCCs in a furnace
151 with forced air cooling to evaluate their cyclic durability during the melting and
152 solidification. One cycle consisted of heating the furnace to 125°C, where it was kept
153 for 15 min, and then cooling to room temperature. Tests were undertaken for up to 10
154 cycles.

156 2.3 Characterization

157 The density of the PCC samples was measured using a pycnometer
158 (Quantachrome Instruments, Ultrapycnometer 1000). The accuracy of the instrument
159 was $\pm 0.02\%$. The measurement was repeated five times for each specimen and the
160 average calculated; the standard deviation was within $\pm 0.01\%$. The average value of the
161 measurement was applied. The real volume fraction of CF; $V_{f,CF}$ and that of indium;
162 $V_{f,In}$ in the final PCC was calculated based on the measured density of the PCC. Note
163 that the real amount of CF and indium in the final PCC differed from the initial amounts
164 of them weighed for preparing PCC, since a part of the fillers were attached on wall of a
165 beaker during mixing, leading to the loss of the fillers. The real volume fraction, $V_{f,CF}$
166 and $V_{f,In}$ in PCC was calculated using the following Eqs. (1) and (2):

167

$$168 \quad 1 = V_{f,PCM} + V_{f,CF} + V_{f,In} \quad (1)$$

169

$$170 \quad \rho_{PCC} = V_{f,PCM} \rho_{PCM} + V_{f,CF} \rho_{CF} + V_{f,In} \rho_{In} \quad (2)$$

171

172 Where $V_{f,PCM}$, ρ_{PCC} , ρ_{PCM} , ρ_{CF} , and ρ_{In} are the volume fraction of PCM in the PCC,
173 and the density of the PCC, PCM, CF, and indium, respectively.

174 The thermal diffusivity (α_{PCC}) and specific heat ($C_{P,PCC}$) of the PCCs, was
175 measured using the laser flash method with a thermal constant measurement system
176 (ULVAC Inc. TC-7000) at room temperature. The accuracy of the thermal diffusivity
177 measurement was $\pm 5.0\%$ and that of specific heat was $\pm 7.0\%$. The measurement was
178 repeated ten times for each specimen and the average value calculated; the standard
179 deviation was 5.5%.

180 The effective thermal conductivity of the PCCs ($k_{ef,PCC}$) was evaluated based
181 on the following relationship [25]:

182

$$183 \quad k_{ef,PCC} = \alpha_{PCC} \cdot \rho_{PCC} \cdot C_{P,PCC} \quad (2)$$

184

185 where ρ_{PCC} is the measured density of the PCC. Note that the real volume fractions of
186 CF ($V_{f,CF}$) and indium ($V_{f,In}$) in the final PCC was calculated from the measured density
187 and specific heat values of the PCC. The actual amounts of CF and indium in the final
188 PCC differed slightly from the weighed amounts (due to loss of material during mixing,
189 e.g. particles attached to the walls of the beakers).

190 To analyze the filler network structure, elemental distribution mapping of PCC
191 cross sections were imaged using an energy dispersive spectroscopy system integrated

192 into a scanning electron microscope (JEOL, JSM-7400F).

193 **3. Results**

194 **3. 1 Effective thermal conductivity**

Figure 2 shows the effective thermal conductivities of PCC-CF (only CF used as filler) and PCC-CF/In (both CF and In particles used as filler), prepared by hot pressing. Note that the volume fraction of CF ($V_{f,CF}$) in PCC-CF/In samples was a constant 20–21 vol.%. The x-axis shows the total volume fraction ($V_{f,Total}$) of filler for both PCC-CF and PCC-CF/In, i.e., the sum of $V_{f,CF}$ and $V_{f,In}$. The effective thermal conductivity of PCC-CF increased with increasing $V_{f,Total}$. The effective thermal conductivities of the PCC-CF samples were similar to those presented in our previous study [12], which is reasonable considering that the materials (PCM and CF), hot-pressing method, and preparation conditions were the same. This shows that our

204 results have good reproducibility. The effective thermal conductivity of PCC-CF/In also
 205 increased with increasing $V_{f,Total}$, in other words, that of PCC-CF/In increased with
 206 increasing $V_{f,In}$ as $V_{f,CF}$ of PCC-CF/In samples is constant. Interestingly, the effective
 207 thermal conductivity of PCC-CF/In was slightly higher than PCC-CF, even though the
 208 thermal conductivity of In ($80 \text{ Wm}^{-1}\text{K}^{-1}$) is much lower than that of CF ($900 \text{ Wm}^{-1}\text{K}^{-1}$).

209 3. 2 Cyclic tests

210 Figure 3 shows the temperature profiles of the furnace and a PCC during a
 211 cyclic heating and cooling test, where the sample temperature increased with the
 212 furnace temperature. When the furnace temperature was kept at 125°C for 15 min, the

Figure 2: Effective thermal conductivities of PCC-CF prepared by hot-pressing. Black circles: only CF filler, red diamonds: CF and In filler. The volume fraction of CF was a constant 20-21 vol.%.

213 PCC temperature exceeded the melting temperature(T_m) of the PCM, although it did not

Figure 3: Temperature profiles of the furnace and a PCC sample during a cyclic heating and cooling test.

Figure 4: Ratio of effective thermal conductivity as a function of volume fraction for samples after 5 and 10 thermal cycles for PCC-CF/In after 5 and 10 cycles, together with data for PCC-CF with a $V_{f,CF}$ of 20-21vol.% (i.e. no added In, $V_{f,In}$ of 0 vol.%.)

215 quite reach the set point. During the cooling period, the PCC temperature decreased a
216 little slower than the set rate, reaching room temperature after about 30 min. These
217 results show that the PCC passed through both the melting and solidification phases
218 during the cyclic tests.

219 Figure 4 shows the ratio of the effective thermal conductivity as a function of
220 $V_{f,In}$ for PCC-CF/In after 5 and 10 cycles, together with data for PCC-CF with a $V_{f,CF}$ of
221 20 vol.% (i.e. no added In, $V_{f,CF}$ of 0 vol.%). Note that, $V_{f,CF}$ values in the PCCs-CF/In
222 samples were constant, 20–21 vol.%. The ratio of the effective thermal conductivity
223 increased with increasing $V_{f,In}$. The value for PCC-CF/In with $V_{f,In}$ of 8.8 vol.% (the
224 highest volume) was about 85%, which is 4 times higher than that of the sample with
225 $V_{f,In}$ of 0 vol.%. In addition, the conductivity values after 5 and 10 thermal cycles were
226 similar for all PCCs with different $V_{f,In}$.

227 Figure 5 shows an EDS map from a cross-section of the as-prepared
228 PCC-CF/In with $V_{f,CF}$ of 20–21 vol.% and indium contents of a) 0 vol.%, b) 2.8 vol.%, c)
229 4.4 vol.%, and d) 8.8 vol.%. Note that the erythritol used as a PCM is composed of
230 carbon (C), hydrogen (H), and oxygen (O), while CF contains only carbon. Therefore,
231 we can distinguish the CFs in the PCC by EDS analysis, as indicated by the different
232 colors: C (red) and O (blue). As shown in Fig. 5 a-1), b-1), c-1), and d-1), for all

233 as-prepared PCCs, the fillers appeared to be located close to the PCM particles, and a
234 percolating structure of the fillers was observed. Focusing on the PCCs with 2.2 vol.%
235 of indium, the metal was located in discrete areas of the CF structure. On the other hand,
236 for PCCs with 8.8 vol.% of indium, the CF and indium particles were well-mixed and
237 formed the main structure of the percolating filler network.

238 Figure 6 shows EDS maps of a cross-section of a PCC-CF/In sample with $V_{f,CF}$
239 of 20–21 vol.% and In contents of a) 0 vol.%, b) 2.8 vol.%, c) 4.4 vol.%, and d) 8.8 vol.%
240 after 5 or 10 heating and cooling cycles. For the PCC with no In (only CF filler), the
241 initial CF network partially collapsed after 5 cycles and was completely destroyed after
242 10 cycles (see Figs. 6 a-1) and a-2), respectively). The EDS results after 10 cycles were
243 similar to that of a PCC prepared by a melt-dispersion method discussed in our previous
244 study [12]. Interestingly, for the samples with $V_{f,In} > 0$ vol.%, the network structure
245 could be maintained even after 5 or 10 cycles test, and the morphology was increasingly
246 closer that of the initial network with increasing indium content. For the sample with
247 $V_{f,In} = 8.8$ vol.% (the highest indium content tested), the initial structure was quite well
248 maintained, even after 10 cycles (see Figs. 6 d-1) and d-2)).

249

Figure 5: EDS map of a cross-section of as-prepared PCC-CF/In with $V_{f,CF}$ of 20-21 vol.% and In contents of a) 0 vol.%, b) 2.8 vol.%, c) 4.4 vol.%, and d) 8.8 vol.%)

Figure 6: EDS map of a cross-section of the PCC-CF/In with $V_{f,CF}$ of 20-21 vol.% and In contents of a) 0 vol.%, b) 2.8 vol.%, c) 4.4 vol.%, and d) 8.8 vol.% after 5 or 10 cyclic tests.

251 **4. Discussion**

252 There are two important observations from this study. The first is that the
253 addition of indium particles to a carbon fiber PCC (PCC-CF/In) increased the effective
254 thermal conductivity compared to that of a PCC containing only a similar volume
255 fraction of CF (PCC-CF). This increase occurred even though the thermal conductivity
256 of In is much lower than that of CF. The second interesting result is that the cyclic
257 durability of the PCCs enhanced with increasing indium content; an excellent stability
258 was observed for the PCC-CF/In sample a $V_{f,In}$ of 8.8 vol.%.

259 As presented in the results, the addition of indium improved the thermal
260 conductivity and stability of the PCCs, and here we discuss the mechanisms for this
261 behavior. In the PCCs-CF, the carbon fibers are simply in contact with each other, as
262 sintering would not occur until a temperature around 1000°C (half of melting point of
263 CF; over 2000°C), a much higher temperature than that of the hot press (160°C). This
264 poor contact between filler particles would cause high thermal contact resistance and
265 low thermal conductivity of the PCCs. On the other hand, in the PCCs-CF/In samples,
266 the thermal contact resistance from the filler decreased by adding In as a filler. From
267 SEM analyses (not shown here), we observed that indium existed, not as independent
268 particles, but as a continuous phase containing CF and In. This indicates that the In

269 metal melted during hot pressing and the CF networks were welded together, improving
270 the contact between the filler particles, resulting in a low thermal contact resistance and
271 high thermal conductivity. It is therefore understandable that a higher $V_{f,In}$ results in a
272 lower thermal contact resistance and subsequent higher thermal conductivity. Agari et al.
273 [36] reported similar effects of welding by low melting temperature metal, where a
274 decrease in the thermal contact resistance and enhancement of effective thermal
275 conductivity were observed for plastic-carbon composites prepared by a simple melt
276 dispersion method. Comparing the hot-pressing method used in this study and the
277 melt-dispersion technique, it should be emphasized that hot pressing has the advantage
278 of forming a percolating network of filler material, which accelerates the enhancement
279 of the effective thermal conductivity. Therefore, these results are significant and
280 interesting for not only fabrication of PCCs, but also for high thermal conductivity
281 plastic materials.

282 The second achievement of enhancing the cyclic durability of the PCC
283 structure can also be explained by the same mechanisms that improve the thermal
284 conductivity. The PCC-CF/In had more stable filler networks than that of PCC-CF since
285 the CF network of PCC-CF/In was welded and strengthened by the indium.

286 Furthermore, we would like to refer novelty of the results in this study. As

287 shown in the EDS data, the CF and In filler materials were distributed around the PCM
288 particles (as expected) in a percolating network for all PCC samples. Similar
289 morphologies were observed (in this study and our previous study [12]) when using
290 only CF as filler material. Such networks were created because the PCM particles were
291 solid during hot pressing and not mobile. It is considered that the percolating network
292 structure of the filler was easily formed under such conditions, as initially the PCM
293 particles were in good contact with each other and the voids between the PCM particles
294 occupied by the fillers were initially a percolating structure. From these results, we can
295 conclude that the hot-pressing method is promising, for both single- and
296 multi-component filler systems, and can accelerate the formation of percolating
297 structures. Hot pressing is classified as a compression method for fabricating PCCs and
298 there many reports about using this method for carbonaceous materials [12, 30, 31, 37];
299 however, to the best of our knowledge, there are no published studies that focus on
300 metal or multi-component metal/carbon materials as fillers. Therefore, the results of this
301 study are novel, relevant, and interesting for heat storage applications and the wider
302 materials science and composite fields.

303 Finally, future work of the enhancement of effective thermal conductivity of
304 PCC should be mentioned. This study clarified that adding a binder material such as

indium has a great effect to improve effective thermal conductivity and cyclic stability the PCCs prepared by a hot-press method. On the other hand, Ma et al. numerically showed the possibility to achieve higher thermal conductivity PCCs with much smaller volume fraction of fillers, by optimizing filler network structure [38]. In our previous study, a filler network structure can be easily controlled by controlling particle size or shape of PCM and fillers as raw materials, in hot-press method [12]. Therefore, the hot-press method has possibility to achieve the optimizing filler network structure. In the future work, the achievement of optimized filler network structure should be investigated in more details from viewpoint of materials, mixing, and pressing conditions.

Conclusions

This paper describes the preparation of PCCs prepared by hot pressing with a percolating network of CF and indium. The effects of adding indium on the effective thermal conductivity and stability under thermal cycling of the PCC was investigated.

The main conclusions are as follows.

1. Hot pressing is a promising method for the preparation of PCCs, for both single- and multi-component fillers, and it can accelerate the formation of percolating network

323 structures.

324 2. The effective thermal conductivity of a PCC with both indium particles and CF as
325 fillers was slightly higher than that of a PCC with a similar volume fraction of only CF.

326 This was due to a decrease in the thermal contact resistance as a result of the In melting
327 during hot pressing and welding the CF together to produce a homogenous structure.

328 3. The stability of the PCCs during thermal cycling was enhanced with increasing
329 indium content as the CF filler network was stabilized by being welded by the indium.

330 These results indicate the feasibility of producing novel PCCs with high
331 thermal conductivity and high cyclic durability, which will contribute to the efficient
332 use of solar energy and industrial waste heat.

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336 **Acknowledgements**

337 This research was partially supported by the Japan Science and Technology
338 (JST) agency through the Strategic International Collaborative Research Program
339 (SICORP).

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