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The Phase Equilibria and Seebeck Coefficient of $(Co,M)_3AlC$ (M = Fe or Ni)

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The phase equilibria and the Seebeck coefficient were measured at the vicinity of the carbide $(Co,M)_3AlC$ (M = Fe or Ni) in the Co-Al-C, Co-Fe-Al-C and Co-Ni-Al-C systems. The samples were well annealed at 1473 K and examined through X-ray diffraction measurements, energy dispersive X-ray analysis and carbon analysis. Co_3AlC with a perovskite structure did not exist at its stoichiometric composition, but was located within a narrow compositional range near $Co_3AlC_{0.67}$. The maximum Seebeck coefficient was 23.3 μV/K at 873 K for $Co_3AlC_{0.63}$. The replacement of a small amount of Co by Fe resulted in the expansion of the single-phase area of $(Co,Fe)_3AlC_x$, and the Seebeck coefficient of the single phase reached its maximum, 32.6 μV/K, at 873 K and $Co_{3.506}Fe_{0.025}AlC_{0.77}$ in the quaternary Co-Fe-Al-C system. The addition of Ni did not stabilize this carbide, and the maximum Seebeck coefficient in the quaternary Co-Ni-Al-C system was 26.9 μV/K at 873 K.
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Keywords: *Seebeck coefficient, thermoelectric property, phase equilibria, carbide, energy density of states*

1. Introduction

Metallic oxides,[1,2] silicides[3–5] and aluminides[6–8] have been studied as good thermoelectric materials, in addition to the well-known semiconductors.[9] However, the thermoelectric behavior of metallic carbides has rarely been investigated. Only SiC and BC have been studied for their potential use in high-temperature applications.[10,11] The current area of interest for the authors is the thermoelectric properties of metallic carbides, and in this study they examined the thermoelectric property of Co_3AlC. Co_3AlC with a Perovskite structure, shown in Fig. 1, is stable and potential for high temperature structural application.[12,13] This carbide's elements are environmentally sound and cheaper than those constituting semiconducting materials. These characteristics recommend this carbide as a suitable material for the thermoelectric power generation.

Ohtani, *et al.*[14] have calculated the energy density of states (DOS) of stoichiometric Co_3AlC, as shown in Fig. 2, and shown that it reached the minimum value at the Fermi energy (E_F) level. According to the transport theory by Mott and Johns,[15] the Seebeck coefficient, α, of an isotropic substance can be obtained through the following equation:

$$\alpha = \frac{\pi^2}{3}\frac{{k_B}^2 T}{e}\left[\frac{\partial(\ln\sigma(E))}{\partial E}\right]_{E=E_F}, \quad (1)$$

where e, k_B, T and E are the charge of the carrier, the Boltzmann constant, the temperature and the energy, respectively. The conductivity, $\sigma(E)$, can be obtained using the following equation:

$$\sigma(E) = \frac{e^2}{\hbar^2}\tau D(E)\left(\frac{\partial E}{\partial k_x}\right)^2, \quad (2)$$

where τ and k_x are the relaxation time and the k-spacing in the k-space, respectively. Therefore, in order to obtain a high α, the DOS, $D(E)$, should be minimized at E_F.[6–8,15] The $D(E)$ value shown in Fig. 2 suggests that Co_3AlC may have a high Seebeck coefficient. This kind of argument is valid for Heustler alloys such as Fe_2VAl,[6–8] where $D(E)$ reaches its minimum at E_F and $\partial D(E)/\partial E$ is very large near E_F.

If we replace some of Co in the metallic carbide Co_3AlC by other elements such as Fe or Ni, which are the neighboring elements of Co in the periodic table, an electric charge transfer will occur between the metallic elements. This causes a shift in the $D(E)$ value at E_F, and a high Seebeck coefficient can probably be achieved in Co_3AlC as well.

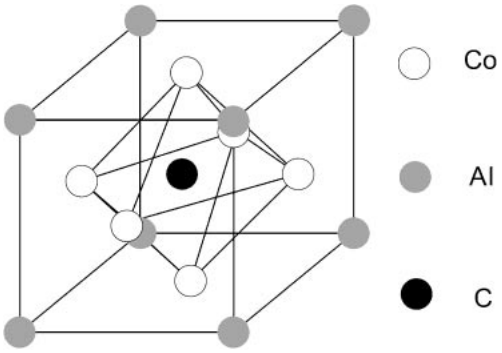

Fig. 1 Crystal structure of stoichiometric Co_3AlC.

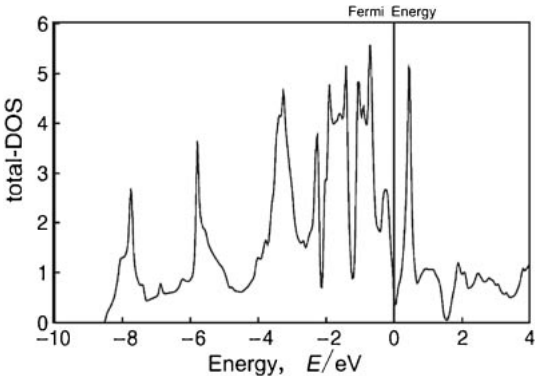

Fig. 2 Energy density of states (DOS) of Co_3AlC.[14]

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Kimura, *et al.*[16] have studied the phase diagram for the Co corner of the ternary Co-Al-C system, including the compositional range where Co_3AlC is stable. They reported that a single phase of Co_3AlC was located within the compositional range where the carbon concentration was lower than that of the stoichiometric Co_3AlC, but slightly carbon richer than that of $Co_3AlC_{0.61}$. Huetter, *et al.* have reported that a single phase with a Perovskite structure (κ phase) was obtained at $Co_3AlC_{0.59}$.[17] The carbide with a Perovskite structure, whose nominal chemical formula is Co_3AlC, will be called the "κ phase" hereafter in this paper. Its crystal structure was analyzed based on the chemical formula $Co_3AlC_{0.5}$.[18] The non-stoichiometry of the κ phase may shift the calculated $D(E)$ value.

The purpose of this study was to investigate the phase equilibria near the κ phase and create a good thermoelectric material with a high Seebeck coefficient by adding Fe or Ni.

2. Experimental Procedure

Highly pure powders of cobalt, aluminum carbide (Al_4C_3) and carbon were mixed in the desired proportion, and the pressed pellets were arc-melted in Ar several times to ensure sufficient homogeneity. The ingots were subsequently annealed at 1473 K for further homogenization. It has been noted that ternary eutectic melting occurs at 1588 K.[16] In the previous study,[16] the samples were annealed at 1273 K for a week, or at 1373 K for 108 ks. Therefore, in this study, our samples were annealed at 1473 K for 259.2 ks in Ar. They were cooled in the furnace and cut into $10 \times 11 \times 12$-mm pieces. The phases in the annealed samples were identified through X-ray diffraction (XRD) measurements, and metallographic observation was conducted using scanning electron microscopy (SEM). The metallic concentrations of the phases were analyzed using an energy-dispersive X-ray (EDX) analyzer equipped with the SEM. Its compositional resolution was calibrated to within 0.2 mol%. Because the carbon concentration could not be analyzed by EDX, the total concentration of carbon in the sample of about 0.2 g was analyzed by using a LECO CS444 carbon analyzer. The Seebeck coefficient of these specimens were measured upon heating from room temperature to 873 K by giving $\Delta T \approx 5$ K in Ar.

3. Results

3.1 Co-Al-C ternary system

A fairly large amount of carbon splashed out from the melt, and a tiny amount of Al evaporated during arc-melting. Table 1 shows the analytical compositions of the annealed samples. The phases were identified using both XRD and EDX analysis. Based both on this phase identification and on the analyzed compositions in the phases co-existing with the κ phase, the phase equilibria near the κ phase in the Co-Al-C ternary system were determined, as summarized in Fig. 3. The reported phase equilibria[16] were considered for the construction of Fig. 3.

Sample 1 ($Co_3AlC_{0.63}$) contained almost exclusively the κ phase; a small amount of Co-rich phase coexisted with the κ phase. The other samples listed in Table 1 clearly contained

Table 1 The analytical compositions and identified phases in the annealed samples.

Sample name	Concentration (mol%)			Identified phases
	Co	Al	C	
1	64.71	21.60	13.67	κ + Co?
2	65.84	21.88	12.27	κ + Co
3	66.14	21.70	12.14	κ + Co
4	65.43	20.98	13.58	κ + Co
5	66.16	19.36	14.48	κ + Co + C
6	63.42	19.52	17.04	κ + Co + C
7	62.12	19.92	17.95	κ + Co + C
8	61.76	18.37	19.85	κ + Co + C
9	63.22	24.17	12.59	κ + CoAl
10	61.39	22.98	15.63	κ + CoAl + C

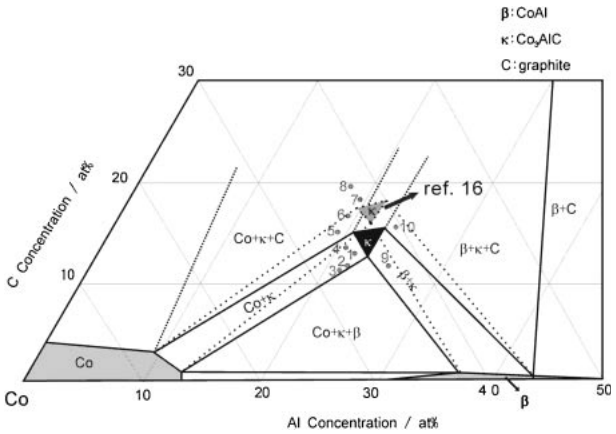

Fig. 3 Phase equilibria in the vicinity of the κ phase in the Co-Al-C ternary system.

phases other than the κ phase. Therefore, the compositional range of the single κ phase was very narrow, and it was located within the compositional range with a slightly larger amount of carbon than $Co_3AlC_{0.63}$, as shown in Fig. 3.

We tried to place some samples within the Al-rich and C-rich compositional range, but precise composition control was not possible. Therefore, many samples were examined to seek for the phase boundaries of the κ phase.

Concerning the molar ratio of Co:Al, the EDX analysis showed that Co:Al at the κ phase was 73.28:26.72 in sample 10 and 76.20:23.80 in sample 5. This suggests that the molar ratio of Co:Al should be brought to precisely 3:1 to obtain the single κ phase. Carbon in sample 10 and 1 were 15.6 and 13.6 mol%, respectively. This suggests that the composition of the κ phase is close to near $Co_3AlC_{0.67}$.

Although a difference was found concerning the carbon concentration in the κ phase, as shown in Fig. 3, the large non-stoichiometry of the κ phase agreed with the previous experimental results.[16,17] The phase boundaries in Fig. 3 did not give any serious conflictions with the experimental data reported by Kimura, *et al.*[16] A slight deviation may be due to the difference in the annealing temperature and cooling rate. Note that the previous study did not examine carbon contents as high as those in samples 6, 7 and 8.

Figure 4 shows the temperature dependencies of the

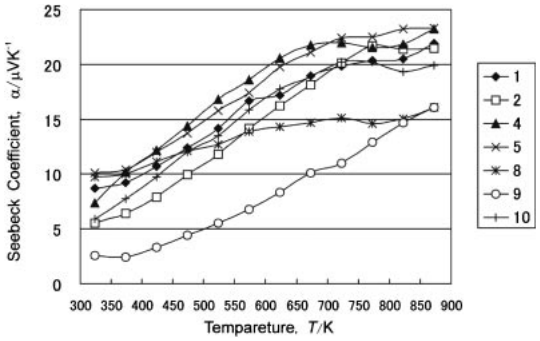

Fig. 4 Seebeck coefficient for the samples with a Co-Al-C ternary system.

Table 2 The analytical compositions and identified phases in the annealed samples in which a part of the Co was replaced by Fe.

Sample name	Concentration (mol%)					Identified phases
	Co	Fe	Co + Fe	Al	C	
11	64.56	0.53	65.09	22.03	12.87	κ
12	66.13	0.47	66.60	18.86	14.51	κ
13	61.69	0.50	62.09	25.09	12.59	κ + CoAl
14	65.10	0.43	65.53	19.32	15.14	κ + Co + C
15	64.22	0.98	65.20	22.05	12.74	κ
16	65.22	1.15	66.37	18.97	14.64	κ
17	61.40	1.21	62.61	24.78	12.59	κ + CoAl
18	65.46	0.95	66.41	19.71	13.86	κ + Co + C
19	62.48	3.27	65.76	21.50	12.73	κ
20	62.30	3.32	65.53	19.69	14.77	κ
21	59.32	2.95	61.43	23.79	14.77	κ + CoAl
22	63.71	3.31	67.02	19.64	13.32	κ + Co + C

Seebeck coefficient for samples 1, 2, 4, 5, 8, 9 and 10. The compositions of the κ phase in samples 1, 2, 4, 5 and 10 were almost identical, and they all reached a maximum (20–23 μV/K) between 773 and 873 K. The composition of the κ phase in sample 10 deviated slightly from the common trend of the other samples; that is, the Seebeck coefficient of sample 10 was slightly lower than that of the other samples. Because the largest value of the measured Seebeck coefficient was 23.21 μV/K at 873 K (in sample 5), the maximum Seebeck coefficient in the ternary Co-Al-C system can be obtained at the Co-rich compositional boundary of the κ phase.

3.2 $(Co,Fe)_3AlC$

Table 2 shows the analytical compositions of the annealed samples and identified phases in the quaternary Co-Fe-Al-C system. A part of the Co in samples 11–14, 15–18 and 19–22 was replaced by 0.5 mol% Fe, 1.0 mol% Fe and 3.0 mol% Fe, respectively. Due to the splashing of carbon and the evaporation of Al during the arc-melting, the analytical concentrations shifted slightly from the desired compositions. Based on the identified phases and the analyzed compositions of the existing phases in these samples, the phase equilibria were determined, as summarized in Fig. 5 (in reference to Fig. 3). In order to ensure a better understanding of the data, the sum of the Co and Fe concentrations, (Co + Fe), was used as the compositional axis.

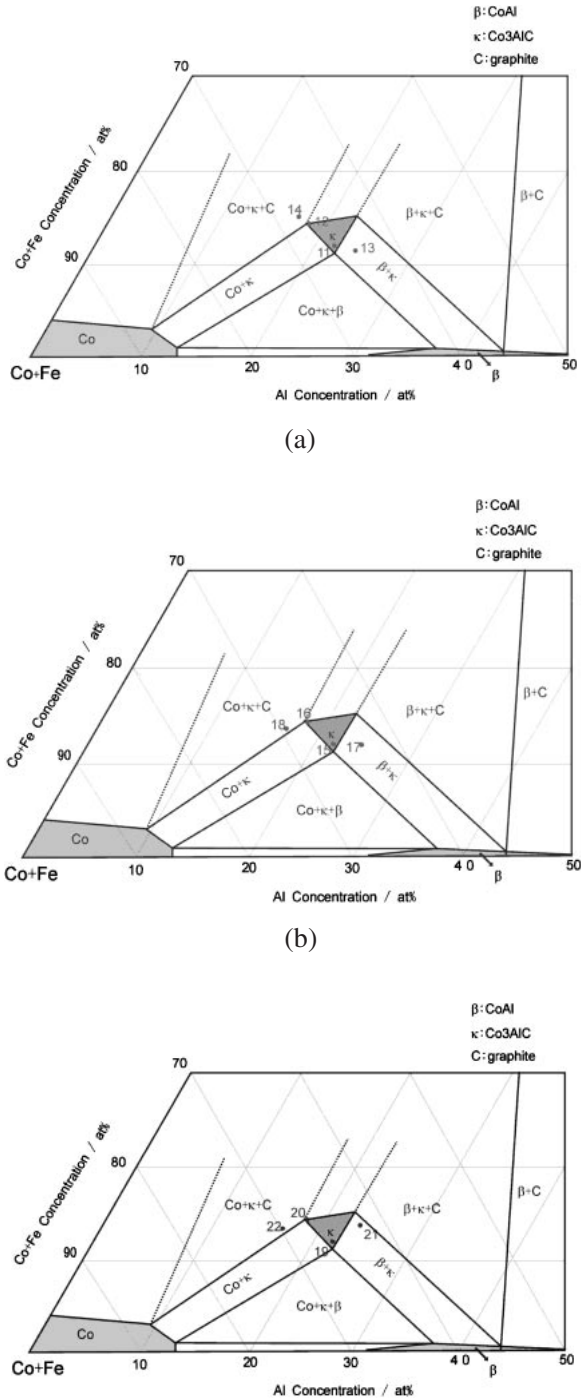

Fig. 5 Phase equilibria in the vicinity of the κ phase in the Co-Fe-Al-C quaternary system. (a) 0.5 mol% Fe addition, (b) 1.0 mol% Fe addition and (c) 3.0 mol% Fe addition.

Samples 11, 15 and 19 were in the single-phase area of the κ phase. When their compositions were normalized by Al, the chemical formulas corresponded to $Co_{2.931}Fe_{0.024}AlC_{0.58}$, $Co_{2.91}Fe_{0.04}AlC_{0.58}$ and $Co_{2.90}Fe_{0.15}AlC_{0.59}$, respectively. If we assume that all of the added Fe atoms were able to replace the Co atoms in the lattice, these three compositions match the composition of sample 2 ($Co_3AlC_{0.56}$) with the ternary system. Note that sample 2 contained less carbon and consisted of two phases: a Co-rich phase and a κ phase.

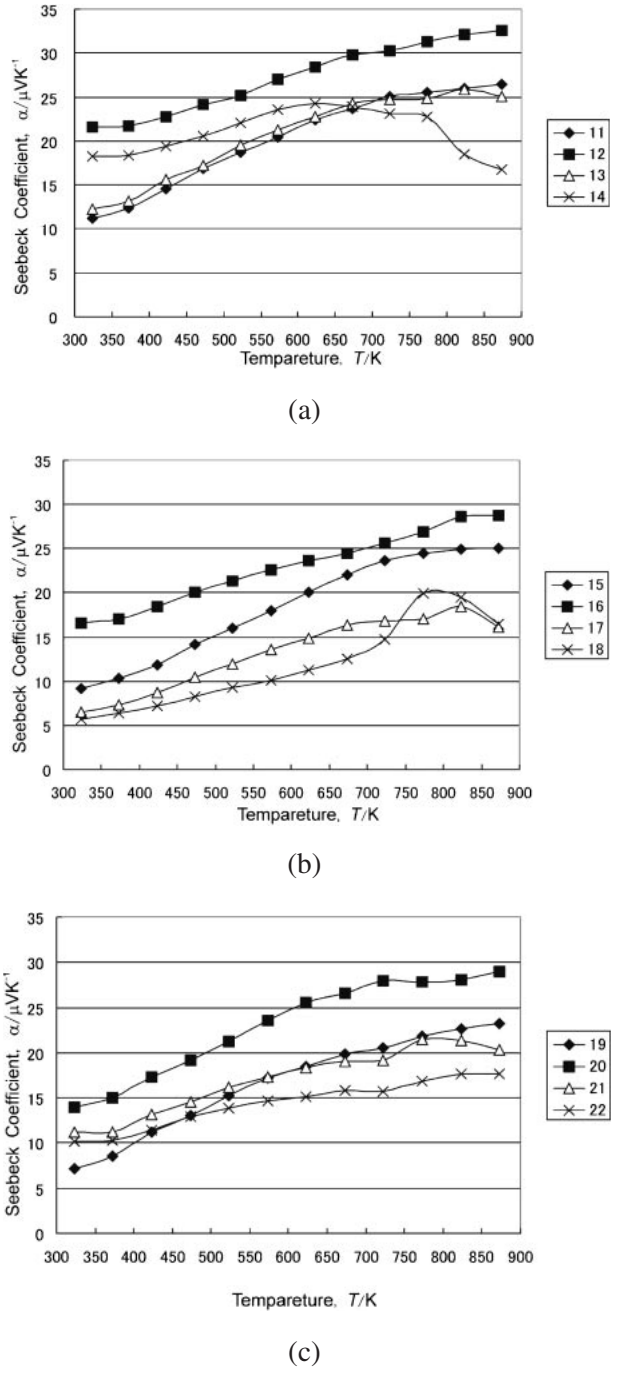

Fig. 6 Seebeck coefficient for the samples in which a part of the Co was replaced by 0.5 mol% Fe (a), 1.0 mol% Fe (b) and 3.0 mol% Fe (c).

Samples 12, 16 and 20 were also in the single-phase area of the κ phase. When their compositions were normalized by Al, the chemical formulas corresponded to $Co_{3.506}Fe_{0.025}AlC_{0.77}$, $Co_{3.44}Fe_{0.06}AlC_{0.77}$ and $Co_{3.16}Fe_{0.16}AlC_{0.75}$, respectively. If we assume that all of the added Fe atoms were able to replace the Co atoms, these three compositions match the composition of sample 5 ($Co_{3.4}AlC_{0.75}$) with the ternary system. Note that sample 5 consisted of three phases: a Co-rich phase, a C-phase and a κ phase.

These findings of (Co + Fe):Al:C = 3:1:0.56 and 3.4:1:0.75 show the expansion of the stable composition of the κ phase, which is due to the preferential occupation by Fe atoms of the Co sites.

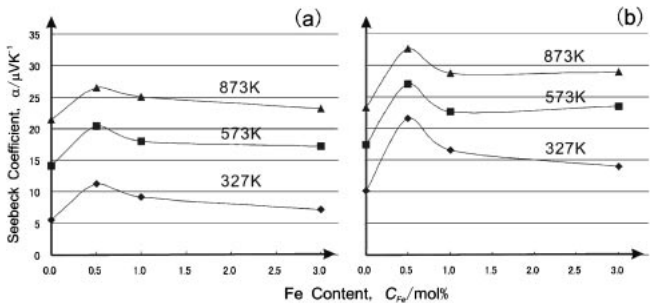

Fig. 7 Dependency of the Seebeck coefficient on Fe addition. (a): (Co + Fe):Al:C = 3.0:1:0.56, (b): (Co + Fe):Al:C = 3.4:1:0.75.

Table 3 The analytical compositions and identified phases in the annealed samples which a part of the Co was replaced by Ni.

Sample name	Concentration (mol%)					Identified phases
	Co	Ni	Co + Ni	Al	C	
23	64.56	0.71	65.27	21.12	13.60	κ + Co?
24	65.96	0.77	66.73	20.94	12.32	κ + Co
25	64.53	0.51	65.04	19.24	15.72	κ + Co + C
26	65.08	0.99	66.07	22.48	11.44	κ + Co
27	64.84	1.34	66.19	21.19	12.61	κ + Co
28	65.56	1.24	66.80	19.32	13.87	κ + Co + C
29	63.25	3.27	66.52	21.44	12.02	κ + Co
30	63.58	3.07	66.65	20.45	12.87	κ + Co
31	63.66	3.31	66.98	19.31	13.69	κ + Co + C

Figure 6 shows the temperature dependencies of the Seebeck coefficients for the samples to which Fe was added. The Seebeck coefficients generally increased as the temperature increased. The Seebeck coefficients of the samples with the single κ phase were higher than those of the non-stoichiometric samples, as shown in Fig. 6. Figures 7(a) and 7(b) show a comparison of the samples with the molar ratios of (Co + Fe):Al:C $\approx$ 3.0:1:0.56 (samples 2, 11, 15 and 19) and (Co + Fe):Al:C $\approx$ 3.4:1:0.75 (samples 5, 12, 16 and 20), respectively. The Seebeck coefficients of the samples containing Fe were larger than those of the ternary samples at any temperature. The Seebeck coefficients of the samples with a molar ratio of (Co + Fe):Al:C = 3.4:1:0.75 (Fig. 7(b)) were larger than those of the samples with a molar ratio of (Co + Fe):Al:C = 3.0:1:0.56 (Fig. 7(a)). This indicates that there exists a distribution of the Seebeck coefficient even inside the single-phase area of the κ phase. Because $Co_{3.506}Fe_{0.025}AlC_{0.77}$ (sample 12) had the largest Seebeck coefficient, 32.56 μV/K at 873 K, the desirable amount of added Fe is less than 0.5 mol% Fe.

3.3 $(Co,Ni)_3AlC$

Table 3 shows the analytical compositions of the annealed samples and the identified phases. A part of the Co in samples 23–25, 26–28 and 29–31 was replaced by 0.5 mol% Ni, 1.0 mol% Ni and 3.0 mol% Ni, respectively. During melting, the concentrations changed slightly from the mixed compositions. As shown in Table 3, all of the annealed samples contained a small amount of Co-rich phase and/or carbon as the minor phases. Based on the identified phases and on the

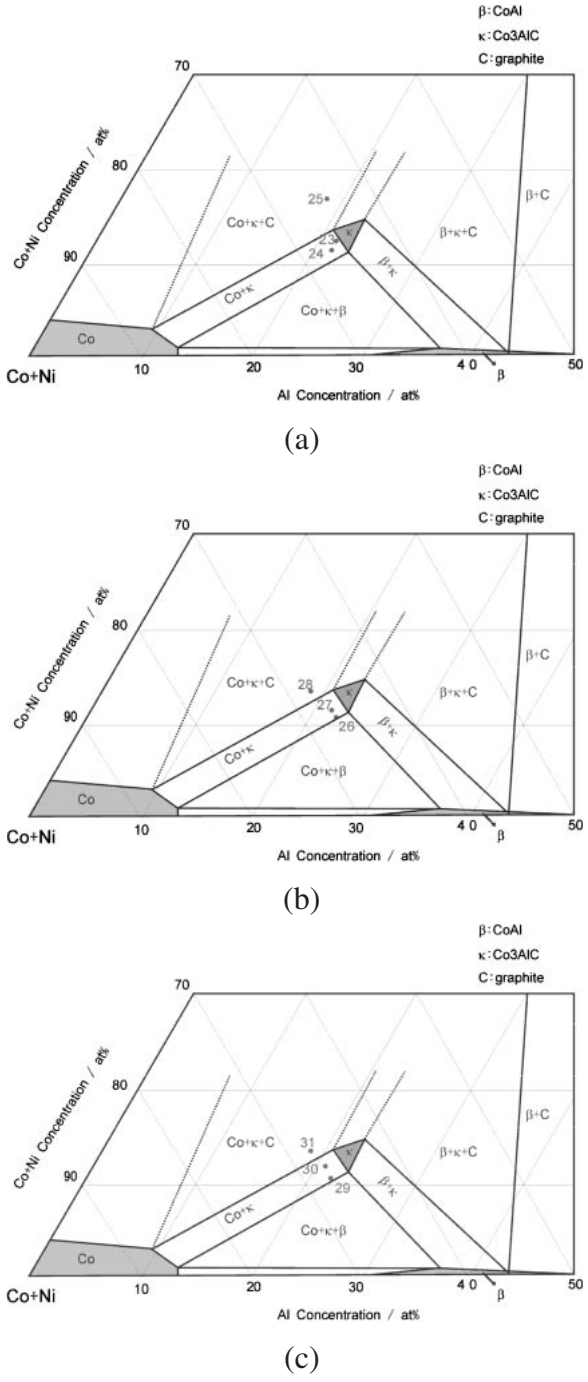

Fig. 8 Phase equilibria in the vicinity of the κ phase in the Co-Ni-Al-C quaternary system. (a) 0.5 mol% Ni addition, (b) 1.0 mol% Ni addition and (c) 3.0 mol% Ni addition.

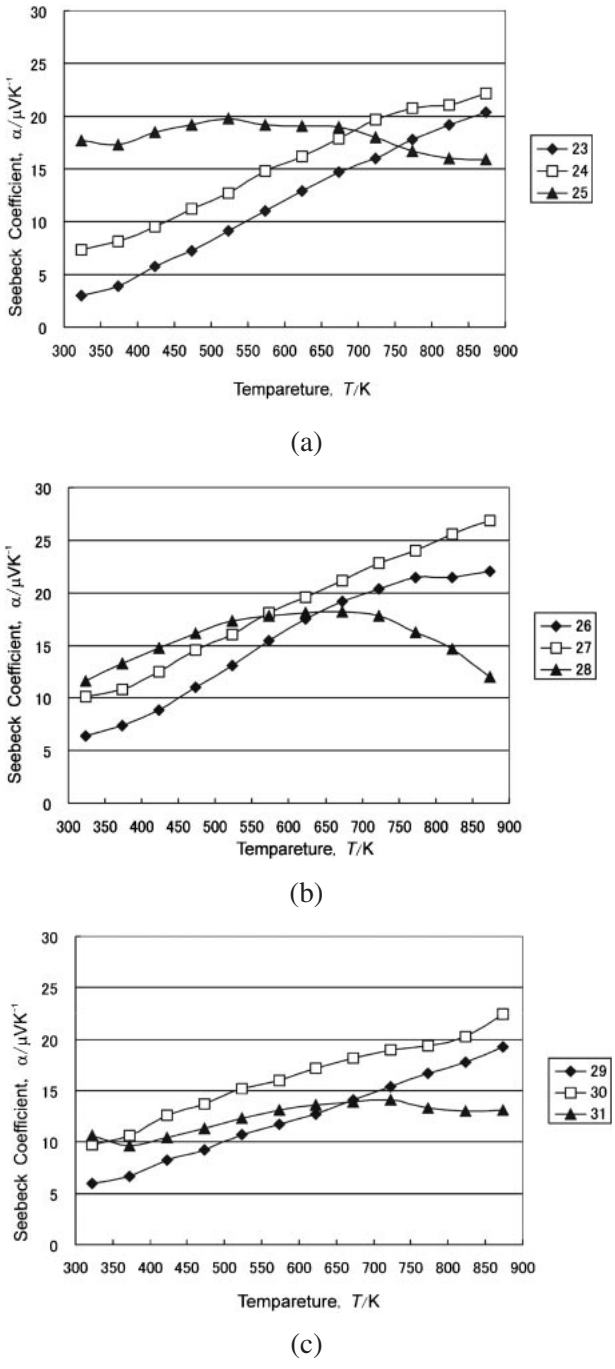

Fig. 9 Seebeck coefficient for the samples in which a part of the Co was replaced by 0.5 mol% Ni (a), 1.0 mol% Ni (b), and 3.0 mol% Ni (c).

analyzed compositions of the κ phase and the Co-rich phases in these samples, the phase equilibria were determined, as summarized in Fig. 8 (in reference to Fig. 3). In order to ensure a better understanding of the data, the sum of the molar fractions of Co and Ni, (Co + Ni), was used as the compositional axis.

Samples 23, 26 and 29 consisted of two phases: a Co-rich phase and a κ phase. These compositions would have been in the single-phase area of the κ phase, if the same amount of Fe had been added instead of Ni. The phase combination in these three samples was the same as that in the ternary system. Namely, the compositions of samples 23, 26 and 29 were very close to those of samples 1, 2 and 3, respectively, assuming (Co + Ni). The latter ternary samples consisted of two phases: a Co-rich phase and a κ phase. Especially sample 23 was located almost within the single-phase area of the κ phase, and this situation is similar to that of the ternary sample 1. To sum up, the phase equilibria near the κ phase in the quaternary Co-Ni-Al-C system were nearly the same as those in the ternary Co-Al-C system. Ni addition did not cause the single-phase area of the κ phase to expand.

Figure 9 shows the temperature dependency of the Seebeck coefficient for the samples to which Ni was added. The temperature dependencies of samples 2, 24, 27 and 30

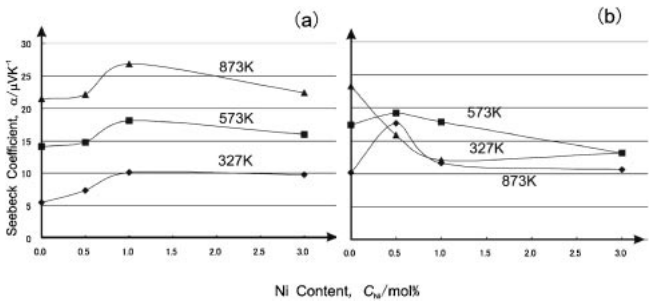

Fig. 10 Dependency of the Seebeck coefficient on Ni addition. (a): (Co + Ni):Al:C = 3.0:1:0.56, (b): (Co + Ni):Al:C = 3.4:1:0.75.

were similar because their compositions were similar. The largest recorded Seebeck coefficient was 26.85 μV/K at 873 K (sample 27). Figures 10(a) and 10(b) show a comparison of the samples with the molar ratios of (Co + Ni):Al:C = 3.0:1:0.56 (samples 2, 24, 27 and 30) and (Co + Ni):Al:C = 3.4:1:0.75 (samples 5, 25, 28 and 31), respectively. The addition of Ni did not significantly change the Seebeck coefficient, as shown in Fig. 10. To sum up, the replacement of Co by Ni was not as effective in changing the Seebeck coefficient as that by Fe.

4. Discussion

This work showed that the single-phase area of the κ phase was located near $Co_3AlC_{0.67}$ (more precisely, at a slightly higher carbon concentration than that of $Co_3AlC_{0.63}$), but that it was completely different from that of the stoichiometric Co_3AlC. Therefore, the energy density of states (DOS) at the κ phase was different from the calculated value at the stoichiometric Co_3AlC.[14] The site occupancy of carbon should affect DOS at E_F, although the details of the contribution were not clear.

The highest Seebeck coefficient in this work was measured for the sample containing 0.5 mol% Fe. This suggests that some electrons and/or holes were transferred between Co and Fe, and that this charge transfer modified the distribution of DOS from that in the ternary κ phase. The addition of Ni did not affect the Seebeck coefficient. This may suggest that the experimental DOS is not sensitive to the possible electron transfer from Ni to Co. We expect that a realistic DOS value of $Co_3AlC_{0.67}$ can be calculated by adjusting for the non-stoichiometry of carbon.

5. Conclusions

The phase equilibria and the Seebeck coefficient of the κ phase, *i.e.*, the Perovskite phase with the nominal chemical formula Co_3AlC, were investigated experimentally. The single-phase area of the κ phase in the ternary Co-Al-C system was located within the narrow off-stoichiometric range, *i.e.*, at Co:Al = 3:1 and between 13.6 and 15.6 mol% carbon. This corresponds to the chemical formula of $Co_3AlC_{0.67}$. The Seebeck coefficient reached its maximum, 23.21 μV/K, in the single-phase area at 873 K (sample 1). When a part of the Co was replaced by Fe, the single-phase area expanded and the maximum Seebeck coefficient was 32.56 μV/K at 873 K for $Co_{3.506}Fe_{0.025}AlC_{0.77}$. However, the addition of Ni did not lead to the expansion of the single-phase area, nor did it improve the Seebeck coefficient.

Acknowledgement

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