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In-situ high temperature X-ray diffraction study of Ni/SiC interface reactions

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In-situ experiments on the Ni/SiC interface reaction were carried out with a high temperature X-ray diffractometer capable of measuring the X-ray diffraction pattern in 1–2 s using an imaging plate. The kinetic formation processes of the interface reaction layer were measured in short-period exposure experiments with the apparatus. The time-temperature phase diagram of Ni/SiC in N_2 was determined. δ-Ni_2Si and θ-Ni_2Si (high temperature phase of δ-Ni_2Si) were formed at the Ni/SiC interface between 1072 K and 1418 K in N_2. The formation of δ-Ni_2Si obeyed the parabolic rate law. The value of the activation energy suggests that the diffusion of Ni through δ-Ni_2Si controls the rate of formation. The results of thermal expansion coefficient measurements suggest that when a sample is cooled to room temperature, compression caused by δ-Ni_2Si occurs on SiC.

1. Introduction

SiC has been interested in the applications, such as an electronic device and high strength metal composite [1, 2]. Therefore, it is important that the elementary processes of metal/SiC interface reactions are investigated. In this study, we focused our attention on interface reactions of Ni and SiC, because it is thought that Ni may make good high temperature contacts, essential for exploiting the properties of SiC [2]. The interface reactions of Ni/SiC have been investigated by several researchers [1–8]. All of them concentrated on carrying out measurements after the reaction, but *in-situ* experiments are necessary to reveal the elementary reaction processes in detail. In these experiments, X-ray diffraction methods have an advantage for observation of crystal structure changes during the interface reaction.

In this paper, we describe *in-situ* experiments on the Ni/SiC interface reaction, which were carried out with a high temperature X-ray diffractometer [9, 10], capable of measuring the X-ray diffraction pattern in 1–2 s using an imaging plate to elucidate the elementary formation processes of the reaction layer, the relationship between time and temperature in the phase transformation, the reaction control factor from the activation energy of the reaction layer, and the thermal stress relationship between the reaction layer and the substrate (SiC).

2. Experimental procedure

Polycrystalline α-SiC (6H) (sintering additives; B, C: Toshiba Corporation) was cut into pieces measuring 20 mm × 10 mm × 0.5 mm. These were polished with a diamond whetstone and cleaned in acetone for use as substrates. A Ni (purity 99.995%) thin film was deposited on the substrate by means of vacuum deposition at 1×10^{-3} Pa. The thickness of the thin film was 0.5 μm.

Fig. 1 shows a schematic of the high temperature X-ray diffractometer [9, 10] which consists of a Seemann-Bohlin camera [11] and an imaging plate (IP) [12]. Because the Seemann-Bohlin camera is a parafocusing camera which produces high intensity diffraction lines and the two-dimensional IP has good X-ray sensitivity, this high temperature system can record complete diffraction patterns in 1–2 s. Using Cu X-rays at 54 kV and 260 mA filtered by a Ni filter, a peak intensity of approximately 8000 counts is obtained from the (1 1 0) reflection of α-Fe using a 2 s exposure [9, 10]. Further, in this study, the penetration depths of Ni and α-SiC using CuK_α X-rays are about 10 μm and 30 μm, respectively. Therefore, we can observe the interface reactions of sample.

The samples were heated from room temperature to between 1072 K and 1418 K at a rate of 60 K/min, held there for 6 min, and cooled to room temperature. This temperature process was performed in N_2. The *in-situ* measurements were carried out with repeated exposures (exposure time: 2 s) during the heating process.

3. Results and discussion

3.1. Formation of reaction layer

When Ni/SiC was held at 1072 K for about 4 min in N_2, δ-Ni_2Si was formed at the interface of Ni/SiC. In this place, $Ni_{31}Si_{12}$ and Ni_5Si_2, which other researchers reported [4, 5, 7, 8], were not observed. δ-Ni_2Si was distinguished from $Ni_{31}Si_{12}$ and Ni_5Si_2, because there are the differences of the interplanar spacings in them. Pai *et al.* [4] reported that there was only δ-Ni_2Si phase between 973 K and 1173 K. Therefore, it is thought

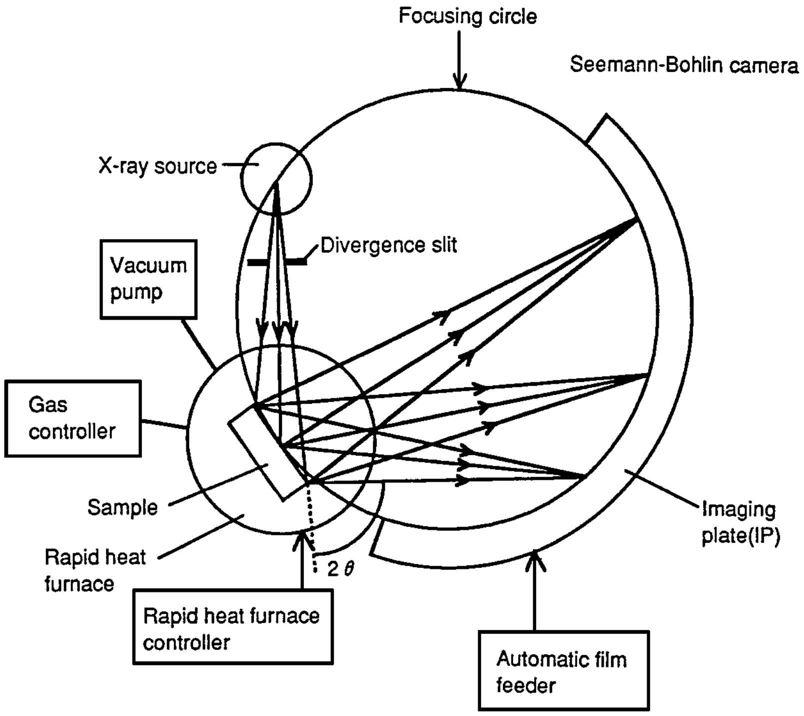

Figure 1 Schematic of the high temperature X-ray diffractometer [9, 10].

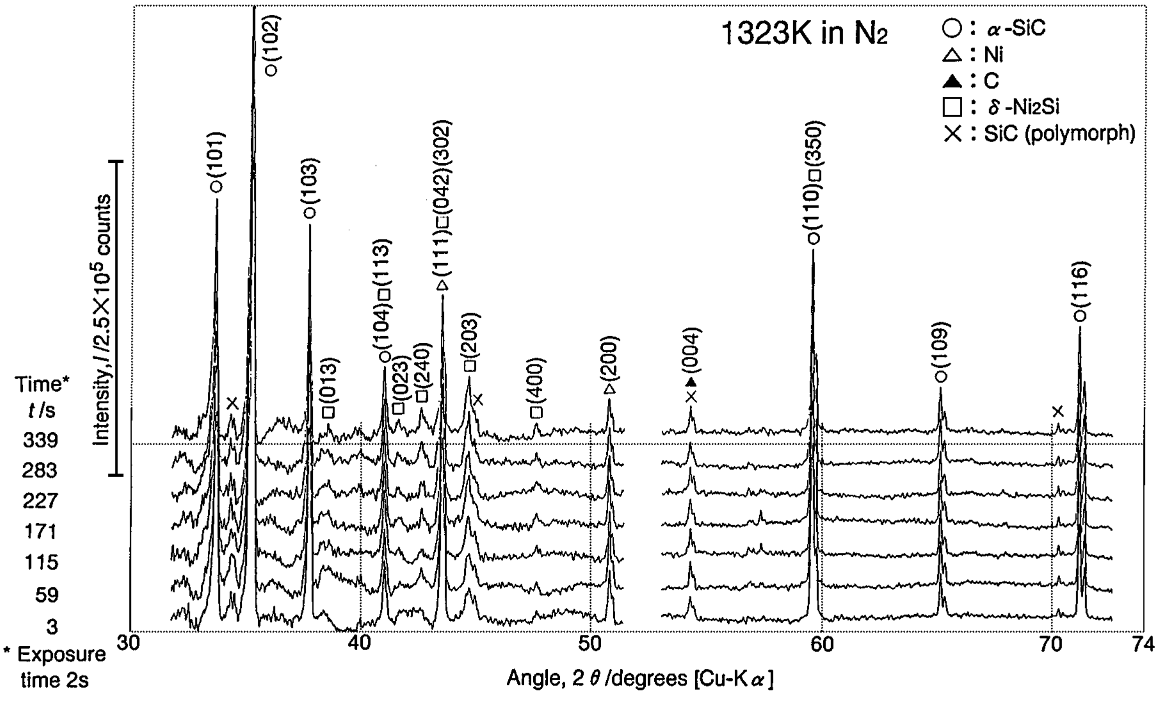

Figure 2 X-ray diffraction patterns of Ni/SiC held at 1323 K in N_2.

that even though there were $Ni_{31}Si_{12}$ and Ni_5Si_2, the amount of them would be very small and less than the minimum of this measurement. Fig. 2 shows the X-ray diffraction patterns of Ni/SiC held at 1323 K in N_2, but there are dead angles at the center of the diffraction patterns, because the apparatus uses two sheets of IP. The intensity of the δ-Ni_2Si diffraction peaks increased with time, and the intensity of the Ni diffraction peaks decreased with time. There was a diffraction peak of C obtained by the dissolution of SiC. There were diffraction peaks of the polymorph of SiC. This existed from the beginning and was not formed during the heating process. Fig. 3 shows the X-ray diffraction patterns of Ni/SiC held at 1370 K in N_2. The Ni diffraction peaks disappeared at 31 s, and all of the Ni changed to δ-Ni_2Si. When Ni/SiC was held at 1400 K, θ-Ni_2Si was formed. θ-Ni_2Si is the high temperature phase of δ-Ni_2Si. Fig. 4 shows the X-ray diffraction patterns of Ni/SiC held at 1418 K in N_2. The δ-Ni_2Si diffraction peak disappeared at 3 s, and all of the δ-Ni_2Si changed to θ-Ni_2Si. Fig. 5 shows a time-temperature phase diagram of Ni/SiC in N_2 obtained. The details of reaction process of the interface of sample are obtained from this phase diagram. Note that these results were obtained under the experimental conditions in this study. According to the experiments conducted by Jackson *et al.* [3] and

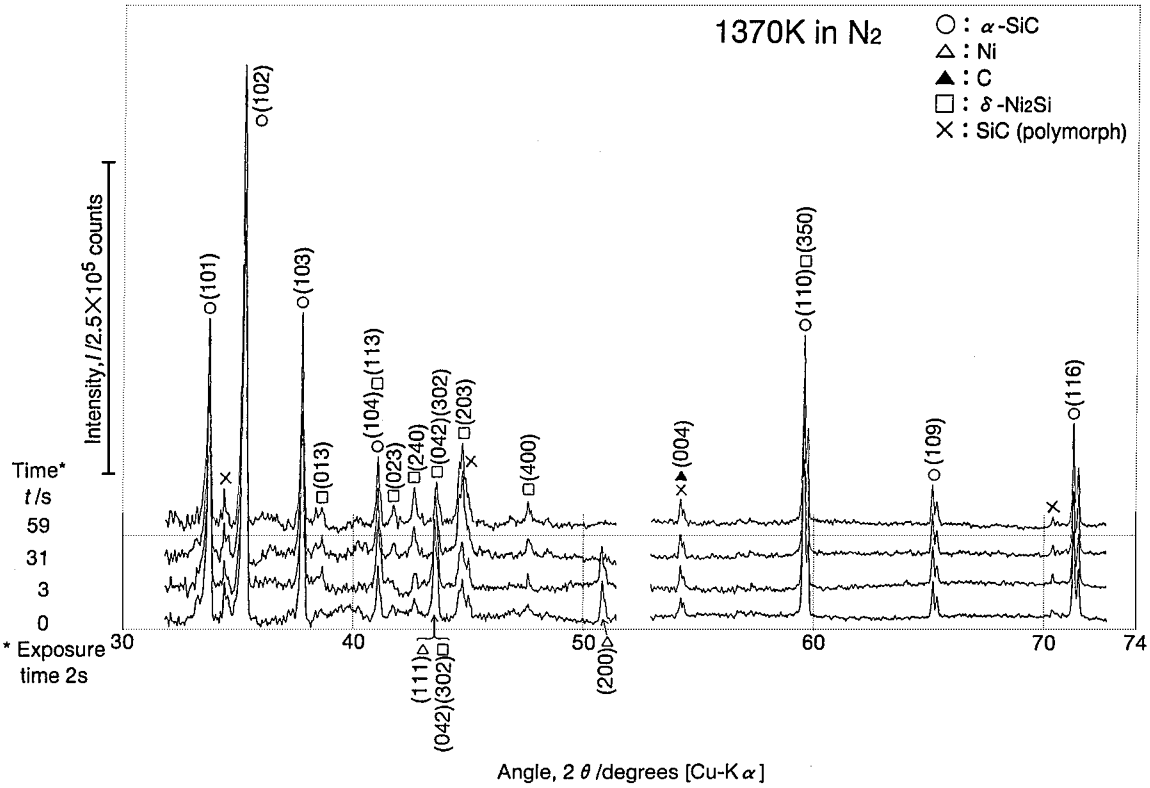

Figure 3 X-ray diffraction patterns of Ni/SiC held at 1370 K in N_2.

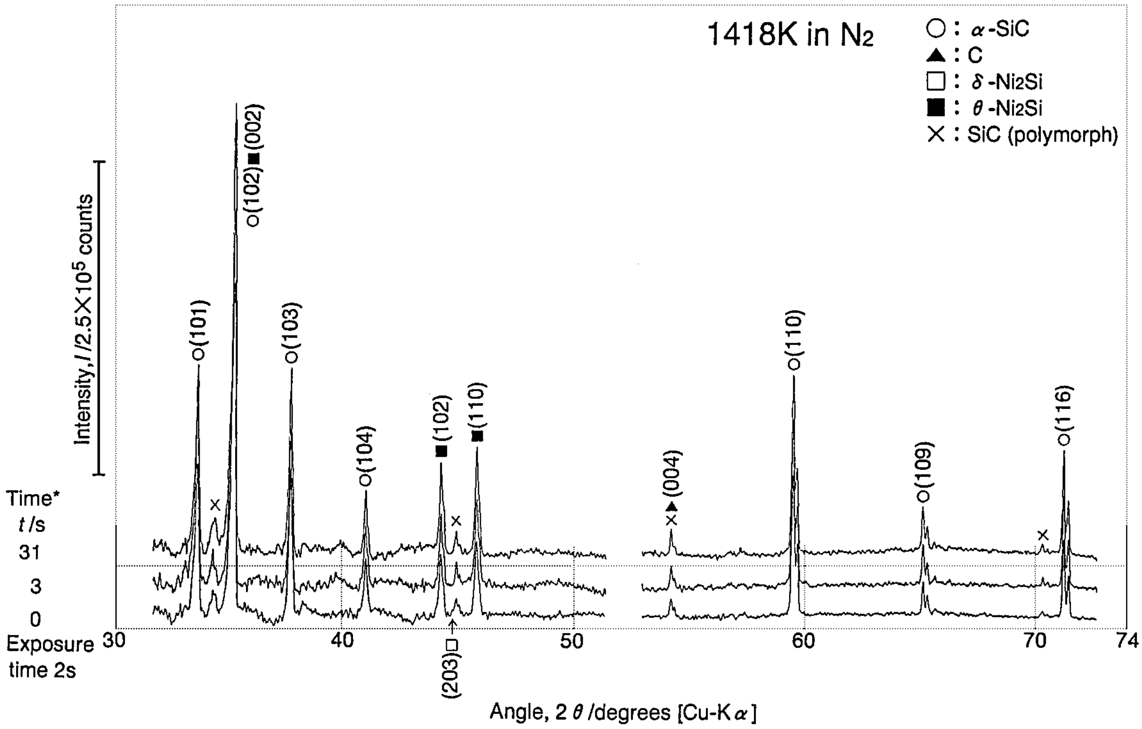

Figure 4 X-ray diffraction patterns of Ni/SiC held at 1418 K in N_2.

Schiepers and co-workers [5, 8], Ni silicide and C coexist. Therefore it is thought that the same phenomenon, i.e., the coexistence of Ni silicide and C, occurred in this study.

The above observations suggest that the reaction formulas are $2Ni + SiC \rightarrow \delta\text{-}Ni_2Si + C$ and $\delta\text{-}Ni_2Si \rightarrow \theta\text{-}Ni_2Si$. A model of these reactions is shown in Fig. 6. The diffusion path from SiC to Ni is thought to be $SiC \rightarrow \delta\text{-}Ni_2Si + C \rightarrow Ni$, on the basis of the phase diagram of Ni-Si-C taken from Jackson *et al.* [3], but δ-Ni_2Si changes to θ-Ni_2Si at a high temperature.

3.2. Activation energy of δ-Ni_2Si growth

In order to determine the growth rate of the δ-Ni_2Si layer at 1273, 1323 and 1348 K from the time history of the integrated intensity of (240) reflection of δ-Ni_2Si, the time history of the thickness of the δ-Ni_2Si layer at each temperature was calculated. It was assumed that

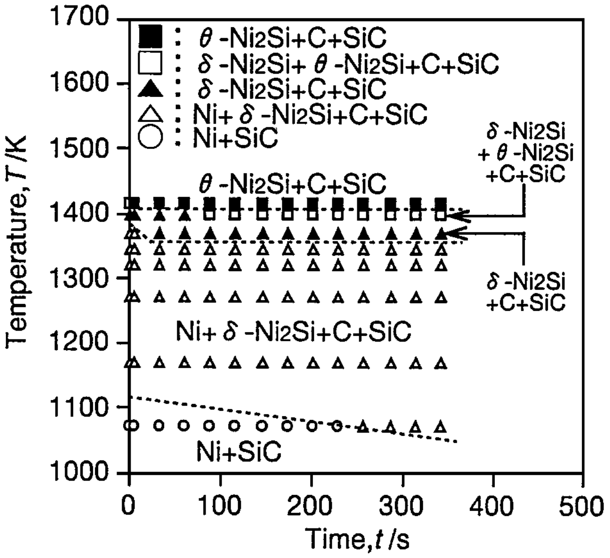

Figure 5 Time–temperature phase diagram of Ni/SiC in N_2.

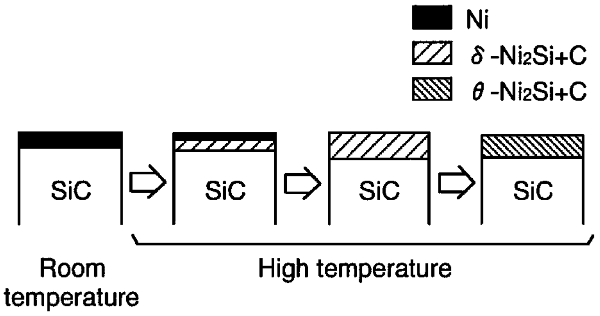

Figure 6 Formation model of the reaction layer at Ni/SiC interface in N_2.

the thickness of the δ-Ni_2Si layer formed from all of the deposited Ni corresponds to the integrated intensity of (240) reflection in δ-Ni_2Si when the reaction layer of δ-Ni_2Si was completely formed. However, in this calculation, the effects of thermal expansion were ignored, since the values were compared with those obtained in thermal treatment experiments performed by other researchers. The relationship between the square of the thickness (x) of δ-Ni_2Si layers at each temperature and time (t) is shown in Fig. 7. It is apparent that the parabolic rate law ($x^2 = Kt$; K: rate constant) [13] is upheld.

Since K is proportional to the diffusion coefficient,

$$\log K = 0.4343(-Q/RT) + A,$$

where 0.4343 is the conversion constant from natural logarithms to common logarithms, Q is the activation energy, R is the gas constant, T is the temperature and A is a constant. Q is obtained from the gradient of log K and $1/T$. Fig. 8 shows the relationship between log K and $1/T$ for the growth of δ-Ni_2Si in our experiments. The value of K was about 9×10^{-16} m^2/s at 1348 K in this work. K value was estimated from the experimental results of δ-Ni_2Si and C layer reported by Schiepers *et al.* [8]. It was about 8×10^{-16} m^2/s. Therefore, K value in this work compared with it. The value of Q was 212 kJ/mol. Q value for Ni diffusion in δ-Ni_2Si and C layer growth in the experiments of 70Ni–20Cr–10Al/SiC (973–1428 K) conducted by Jackson *et al.* [3] was 184 kJ/mol, which is close to our value. It can therefore be inferred that Ni diffusion in δ-Ni_2Si controls the reaction rate when the sample is held at a high temperature.

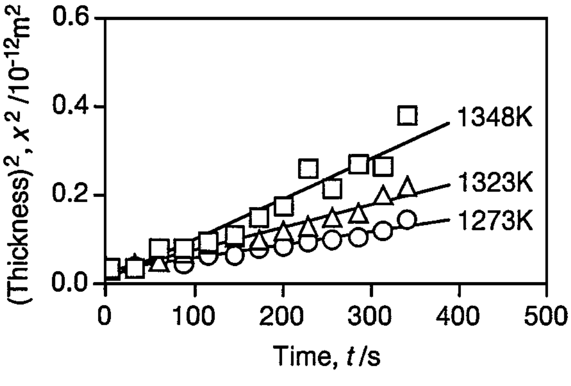

Figure 7 Relationship between the square of thickness (x) of δ-Ni_2Si layers at each temperature and time (t). The parabolic rate law is upheld.

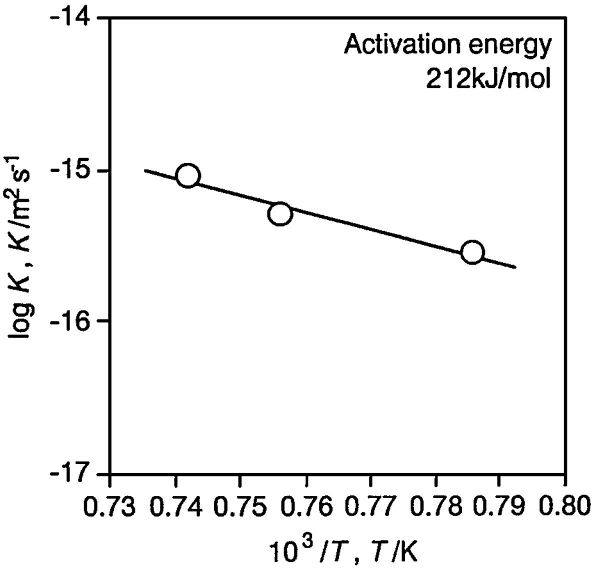

Figure 8 Relationship between log K and $1/T$ for the growth of δ-Ni_2Si. Activation energy was estimated as 212 kJ/mol.

3.3. Stresses at phase interfaces

The stresses around the interfaces were checked, taking into account the reported values of the thermal expansion coefficients. Table I shows the experimental and reference values [14–16] of the thermal expansion coefficients for the lattice constants of SiC, Ni and δ-Ni_2Si. The value for δ-Ni_2Si is near the Ni value and is larger than that for SiC. It is thought that, as a sample cools

TABLE I Experimental and reference values [14–16] of thermal expansion coefficients evaluated from the lattice constants of SiC, Ni and δ-Ni_2Si

Material (System)	Thermal expansion coefficient ($\times 10^{-4}$/K)			
	a	*b*	*c*	Reference
α-SiC (Hexagonal)	0.07	—	0.06	0.05 [14]
Ni (Cubic)	0.20	—	—	*a* : 0.13 [15]
δ-Ni_2Si (Orthorhombic)	0.21	0.17	0.14	0.19 [16]

to room temperature, compression caused by δ-Ni_2Si occurs on SiC.

4. Conclusions

In-situ high temperature X-ray diffraction experiments were carried out on the Ni/SiC interface reaction. The following conclusions were reached.

(1) The kinetic formation processes of the interface reaction layer were measured by short-period exposure experiments with a high temperature X-ray diffractometer.

(2) The time–temperature phase diagram of Ni/SiC in N_2 was determined. δ-Ni_2Si and θ-Ni_2Si (high temperature phase of δ-Ni_2Si) were formed at the Ni/SiC interface between 1072 K and 1418 K in N_2. The elementary reaction processes were $2Ni + SiC \rightarrow \delta\text{-}Ni_2Si + C$ and $\delta\text{-}Ni_2Si \rightarrow \theta\text{-}Ni_2Si$. Note that these results were obtained under the experimental conditions in this study.

(3) The formation of δ-Ni_2Si obeyed the parabolic rate law. The activation energy was 212 kJ/mol. This value suggests that the diffusion of Ni through δ-Ni_2Si controls the rate of formation.

(4) The results of thermal expansion coefficient measurements suggest that when a sample is cooled to room temperature, SiC is compressed by δ-Ni_2Si at the interface.

Acknowledgements

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