Catalytic Properties of Cold-Rolled $\text{Ni}_3(\text{Si,Ti})$ Intermetallic Foils for Methanol Decomposition

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Methanol decomposition tests were carried out for the first time on cold-rolled $\text{Ni}_3(\text{Si,Ti})$ foils in a temperature range of 513–793 K to investigate their potential catalytic properties for hydrogen production. The catalytic activity was observed at temperatures above 713 K. At 793 K, the catalytic activity changed with the reaction time in three stages: low-activity incubation, rapid spontaneous activation and high-activity state. Surface analysis revealed an intensive formation of fine Ni particles on the foil surfaces after the second stage where rapid spontaneous activation was observed. The formation of the fine Ni particles was considered to be induced by the selective oxidation of Si in $\text{Ni}_3(\text{Si,Ti})$. The catalytic activity in the second and third stages was due to the fine Ni particles formed by the spontaneous activation.

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1. Introduction

Hydrogen is attracting increasing attention as a clean energy source for fuel cell technologies.^{1–3)} Presently, hydrogen is produced mainly by carrying out reforming or decomposition reactions of hydrocarbon and alcohol on heterogeneous catalysts. Hitherto, considerable effort has gone into developing high-performance catalysts for efficient and low-cost hydrogen production. For example, Cu-, Ni-, Pt-, and Ru-base catalysts are typical of these.^{4–6)} Especially, catalysts based on noble metals have been intensively studied.^{7–10)} However, their performance is not yet satisfactory. In addition, noble metals should be avoided from the view points of lacking in resource and high cost. Therefore, there is a continuing demand for developing high-performance, noble-metal-free catalysts.

Recently, we discovered that Ni_3Al intermetallic compound has a high catalytic activity for methanol decomposition into H_2 and CO .^{11–13)} Owing to its excellent high-temperature strength and oxidization/corrosion resistance, Ni_3Al with an L1_2 ordered structure is a well-known high-temperature structural material;¹⁴⁾ however, it has never been regarded as a potential catalyst. The catalytic activity of Ni_3Al was first detected in an alkali-leached powder similar to the case of Raney Ni catalysts,¹³⁾ and then in flat cold-rolled foils without any pretreatment.^{11,12)} Such a high catalytic activity over flat metallic foils is unusual because the foils have a small surface area. Interestingly, the catalytic activity of the foils was found to increase rapidly with an increase in the reaction time during the early stage of reaction for methanol decomposition. In other words, the foils were spontaneously activated during the reaction. The spontaneous activation was attributed to the formation of active, fine Ni particles that were induced by the selective oxidation of Al in Ni_3Al . This discovery suggests a high potential for other Ni-base intermetallic compounds to be used as catalysts.

$\text{Ni}_3(\text{Si,Ti})$ with the same L1_2 ordered structure as Ni_3Al is one of such compounds. Regarding the $\text{Ni}_3(\text{Si,Ti})$ intermetallic compound, we improved the mechanical strength and ductility in a wide temperature range by Ti addition.¹⁵⁾ Making use of good plastic deformability of the polycrystalline ingots, we recently succeeded in fabricating thin foils of $\text{Ni}_3(\text{Si,Ti})$ by cold rolling.¹⁶⁾ The chemical properties of the constituent elements of $\text{Ni}_3(\text{Si,Ti})$ are similar to those of Ni_3Al . The primary constituent element is a catalytically active Ni. The secondary and tertiary elements, Si and Ti, have a strong affinity for oxygen, similarly to Al in Ni_3Al , and thus they are considered to be selectively oxidized, which may make active Ni particles formed. $\text{Ni}_3(\text{Si,Ti})$ foils are thus expected to exhibit high catalytic activity. Since they have never been studied before, we investigated their catalytic properties for methanol decomposition in this study.

2. Experimental

2.1 Sample preparation

Foil samples were fabricated by a metallurgical process. Arc-cast button ingots with nominal composition of $\text{Ni}_{79.5}\text{Si}_{11}\text{Ti}_{9.5}$ (expressed by at%) doped with 50 mass ppm boron were homogenized at 1323 K for 48 h and cut into 10-mm-thick plates. The plates were rolled at 573 K and then annealed at 1273 K for 5 h. This process was repeated several times until the plates were 2 mm in thickness. Then, the plates were cold-rolled to 0.2-mm-thick sheets with 90% reduction in thickness, without any intermediate annealing. The sheets were annealed at 1273 K for 1 h, and then cold-rolled to 40- μm -thick foils with 80% reduction in thickness. Microstructure analysis of the foils confirmed a single phase L1_2 $\text{Ni}_3(\text{Si,Ti})$.¹⁶⁾ The detailed procedure for the foil preparation has been described in another paper.¹⁶⁾

2.2 Catalytic reaction

Cold-rolled foils with a geometrical surface area of $7.6 \times 10^{-4} \text{ m}^2$ were used for catalytic tests. The catalytic

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Fig. 1 Changes in (a) methanol conversion and (b) production rates of gaseous products for the Ni₃(Si,Ti) foil as a function of reaction temperature.

tests were carried out in a conventional fixed-bed flow reactor composed of a quartz tube chamber and an electric furnace. The procedure was almost similar to that conducted for the Ni₃Al foils.^{11,12)} Before measurement, the samples were reduced at 773 K for 1 h in a mixture of flowing hydrogen (flow rate of 30 mL·min⁻¹) and flowing nitrogen (flow rate of 5 mL·min⁻¹). After flushing out the quartz tube chamber with nitrogen, methanol was introduced in it at a liquid hourly space velocity (LHSV) of 4.0×10^{-3} m³·h⁻¹·m⁻² with nitrogen carrier gas (flow rate of 30 mL·min⁻¹). Before the introduction, methanol was fully evaporated in a thermal evaporator at a temperature of 423 K. The catalytic properties of the foils were evaluated in a temperature range of 513–793 K by measuring the outlet composition of the gaseous products using a gas chromatograph and the total flow rate of outlet gases using a soap bubble meter. Since the samples were in a foil form, production rate of each gaseous product was expressed in mol·h⁻¹·m⁻².

Two types of reaction tests—isochronal and isothermal tests—were performed. The isochronal test was conducted to investigate the temperature dependence of the catalytic reactions. In this test, we performed methanol decomposition by increasing the reaction temperature from 513 to 793 K at regular intervals of 40 K. After the samples were held at each temperature for 20 min, the composition and the flow rate of the gaseous products were measured. In order to investigate the time dependence of the catalytic properties, isothermal tests were conducted at two temperatures—713 K and 793 K.

2.3 Surface characterization

The surface of the foil sample was characterized after isothermal tests. The surface morphologies were observed by scanning electron microscopy (SEM; HITACHI, S4800) with a field emission gun. The composition of the surface products was analyzed by energy dispersive X-ray spectroscopy (EDS) and SEM. The crystal structures of the surface products were identified by X-ray diffraction (XRD; Rigaku, RINT2500HK) using CuK α radiation and transmission electron microscopy (TEM; JEOL, JEM-2000FX and JEM-2100F). The X-ray profile data were analyzed by a peak-stripping method using a WinFit 1.2.1 program. The powder samples were collected by scraping off the surface products

for TEM observation; the powder was suspended in ethanol and then loaded into a pure copper mesh grid. After the isothermal test conducted at 793 K, the chemical states of the foil surfaces were measured using X-ray photoelectron spectroscopy (XPS; ULVAC-PHI Quantera SXM) with a twin anode AlK α X-ray source and hemispherical energy analyzer. Following the isothermal tests, the Brunauer-Emmett-Teller (BET) surface areas of the foils was measured with a surface area analyzer using Kr as the adsorbent.

3. Results

3.1 Isochronal test

Figure 1 shows the methanol conversion and production rates of gaseous products as a function of the reaction temperature. The methanol conversion was low below 713 K; however, it increased significantly as the temperature rose above 713 K (Fig. 1(a)). As shown in Fig. 1(b), the main products of the catalytic reaction were H₂ and CO. The production rate of H₂ was almost twice that of CO; this indicated the occurrence of the following methanol decomposition.

Thus, as with the Ni₃Al foils,^{11,12)} the Ni₃(Si,Ti) foils were found to be catalytically active for methanol decomposition above 713 K.

3.2 Isothermal tests

Figure 2 shows the methanol conversion and internal pressure of the reaction chamber as a function of reaction time. Methanol conversion was low at the beginning of the reaction; however, it increased with increasing reaction time. This indicates that the cold-rolled Ni₃(Si,Ti) foils were spontaneously activated during the reaction. The activation manner indicates a strong dependence on the reaction temperature. At 793 K, methanol conversion with reaction time was observed to have changed in three stages, while this phenomenon was not observed in the case of the Ni₃Al foils.^{11,12)} The three stages are as follows. After an initial sharp increase, methanol conversion remained approximately 10% for the first 7 h. This first stage is an incubation period

Fig. 2 Changes in (a) methanol conversion and (b) internal pressure of chamber for the $\text{Ni}_3(\text{Si,Ti})$ foils as a function of reaction time.

Fig. 3 Production rates of gaseous products in methanol decomposition reaction at (a) 713 K and (b) 793 K for the $\text{Ni}_3(\text{Si,Ti})$ foil as a function of reaction time.

for the next rapid activation. The second stage began after 7 h. Methanol conversion rapidly increased with increasing reaction time, and reached to 70%. The third stage showed a high-activity- and steady-state conversion of methanol until 50 h. However, the methanol conversion increased again after 50 h. This increase is considered to be due to the increase of the internal pressure of the reaction chamber. As shown in Fig. 2(b), the internal pressure of the reaction chamber started to increase after 30 h; this indicated a plugging of the reaction chamber. The plugging is due to carbon deposition which will be described in the following sections. At the onset temperature of 713 K, the methanol conversion showed a monotonously increasing trend with increasing time. Moreover, the conversion value was very low. The internal pressure remained unchanged during the entire reaction time, indicating no significant plugging of the reaction chamber.

Figure 3 shows the production rates of the gaseous products as a function of reaction time. At 793 K, the production rates of the main products— H_2 and CO —varied with increasing reaction time as seen in the case of the first and second stages of the methanol conversion. The production rates reached a maximum at the end of the second stage. The production rates of the main products monotonously decreased with increasing reaction time during the third

stage, in contrast to the relatively stable methanol conversion. The production rates of the rest of the products such as CO_2 , CH_4 , and H_2O remained very low during the entire reaction. In comparison with those of the main products at 793 K, the production rates at the onset temperature of 713 K were much lower. They varied with reaction time in the same way as the methanol conversion.

Figure 4 shows the selectivities of the main and minor products as a function of the reaction time. The values were calculated according to the method followed in the studies cited in references.^{12,17)} From the beginning of the first stage at 713 and 793 K, the selectivities of the main products (H_2 and CO) increased sharply to greater than 80% with increasing reaction time. The high values of the main products remained almost constant in the following second stage, and even at the end of the third stage during which the plugging of the reaction chamber had occurred. The selectivities of the minor products (CH_4 , H_2O , and CO_2) were very low—below 10%—except at the beginning of the first stage. In the third stage, a slight increase in the selectivities of CH_4 and CO_2 was observed with reaction time. The results show that during the entire reaction, the methanol decomposition as depicted by eq. (1) is the main reaction.

Fig. 4 Selectivities of (a) H_2 , (b) CO, (c) CH_4 , (d) H_2O , (e) CO_2 , and (f) C during methanol decomposition for the $\text{Ni}_3(\text{Si,Ti})$ foil at 713 K and 793 K as a function of reaction time, respectively.

Fig. 5 XPS Ti 2p (a) and Si 2p (b) spectra for $\text{Ni}_3(\text{Si,Ti})$ foils at different states of reaction at 793 K. #1: after reduction treatment, #2: 1 min after reaction, #3: 3 min after reaction, and #4: 20 min after reaction.

3.3 Surface characterization after isothermal tests

In order to understand the spontaneous activation mechanism, we examined the structure evolution on the foil surface during the reaction. In this paper, we focus on the results at 793 K where the methanol conversion was high.

We performed an XPS analysis as shown in Figs. 5 and 6. Figure 5 shows the Ti 2p and Si 2p spectra after the hydrogen reduction treatment (i.e., before reaction), and after 1, 3 and 20 min of reaction. After the reduction treatment, the spectra show the presence of SiO_2 and TiO_2 . Carbides such as SiC and TiC were not found in the samples although Si and Ti are strong carbide forming elements. Both Ti 2p and Si 2p spectra showed negligible change in the beginning of the first stage. Figure 6 shows the Ni 2p_{3/2} spectrum after the hydrogen reduction treatment, and after 1, 3 and 20 min of reaction. The Ni 2p_{3/2} spectrum can be

well fitted by three components of Ni, NiO and $\text{Ni}(\text{OH})_2$, indicating the coexistence of Ni, NiO and $\text{Ni}(\text{OH})_2$ during the reaction. The oxides and the hydroxide detected after the reduction treatment are considered to be naturally formed on the foils surface in air during the foil fabrication process. The thickness of the oxides and the hydroxide was estimated to be approximately 20 nm by the XPS depth analysis using argon sputtering (not shown here). The coexistence of Ni, NiO and $\text{Ni}(\text{OH})_2$ suggests that NiO and $\text{Ni}(\text{OH})_2$ were partially reduced during the reduction treatment, resulting in formation of the metallic Ni. In comparison to NiO and $\text{Ni}(\text{OH})_2$, SiO_2 and TiO_2 remained unchanged after the reduction treatment because it is more difficult for SiO_2 and TiO_2 to be reduced than NiO and $\text{Ni}(\text{OH})_2$.

Figure 7 shows the FE-SEM images of the foil surface for three stages at 793 K, i.e., after 2.5 h (first stage), 22 h (second

Fig. 6 XPS Ni 2p_{3/2} spectrum (a) after the hydrogen reduction treatment, and after (b) 1 min, (c) 3 min and (d) 20 min of reaction.

Fig. 7 Secondary electron (SE) images (a)–(c) and corresponding back scattered (BE) images (d)–(f) of the surface of Ni₃(Si,Ti) foils for reaction at 793 K after 2.5 h (a), (d), 22 h (b), (e), and 65 h (c), (f), respectively.

stage) and 65 h (third stage). Secondary electron images (SEI) and corresponding backscattered electron images were taken at the identical position of the foil surfaces. After 2.5 h, the SEI revealed small particles accompanied by fibrous products all over the foil surface (Fig. 7(a)). These surface products were analyzed by TEM. Figure 8 shows the bright-field (BF) image and selected area diffraction pattern (SADP) obtained from the region containing a single particle surrounded by fibers. From the SADP, the particle and fibers were identified as a single crystal of nickel with fcc structure and polycrystalline graphite with a hexagonal structure, respectively. Figure 9(a) shows the elemental mapping of the particle and fibers by TEM-EDS; it can be observed that the particle and fibers consist of nickel and carbon, respectively. The TEM-EDS spectrum in Fig. 9(b) revealed that no constituent element of the foil, such as Si and Ti, was included in the particle. In other words, the Ni particles obtained were pure. The C peak in the spectrum arises from the surrounding carbon fibers. The Cu and Cr peaks arise from the grid mesh and sample holder, respectively. Thus, it is evident that pure fcc Ni particles were formed along with carbon fibers on the foil surface in the first stage. Using the backscattered electron (BE) image, the distribution of the Ni particles was confirmed as shown in Fig. 7(d). The Ni particles with bright contrast were almost homogeneously dispersed all over the foil surface. Figures 7(b) and 7(c) show that both the Ni particles and carbon fibers have grown in diameter in the second and third stages. Figure 10 shows the

Fig. 8 TEM bright field image showing a Ni particle on carbon fibers. Observation was conducted using the powders scraped from the surface of the $\text{Ni}_3(\text{Si,Ti})$ foils after reaction at 793 K for 2.5 h. Selected area diffraction pattern (SADP) for the Ni particle and carbon fibers is taken in the condition of incident beam direction parallel to [011] for nickel.

Fig. 9 (a) TEM bright field image and two-dimensional (2D) elemental maps by transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS) for the surface products after the reaction at 793 K for 2.5 h and (b) corresponding (TEM-EDS) spectra.

Fig. 10 X-ray diffraction (XRD) profiles for the $\text{Ni}_3(\text{Si,Ti})$ foils before the reaction (i.e., as cold-rolled) ((a) and (b)), and after reaction at 793 K for 22 h ((c) and (d)), respectively. The detailed analysis was conducted for the XRD profiles around 200 peak of the $\text{Ni}_3(\text{Si,Ti})$ phase as shown in (b) and (d). Result of peak separation between $\text{Ni}_3(\text{Si,Ti})$ and Ni phases is also shown in (d).

XRD patterns after 22 h of the reaction, when the methanol conversion reached a local maximum value. In this figure, the XRD patterns of the Ni particles and the carbon fibers before (a) and (b) and after the reaction (c) and (d) are shown. Note that Figs. 10(a) and 10(b) were obtained using the as cold rolled foils (i.e., before the hydrogen reduction treatment). The comparison of these XRD patterns reveals that Ni, graphitic carbon, and SiO_2 could be detected by XRD after 22 h of the reaction, suggesting that a considerable amount of the Ni particles as well as the carbon fibers were formed on the foil surfaces. These results also indicate that only Si was oxidized to form SiO_2 , i.e., the Si in $\text{Ni}_3(\text{Si,Ti})$ was selectively oxidized in the second stage. The NiO and $\text{Ni}(\text{OH})_2$ observed by XPS in the early part of the first stage (Fig. 6) were not detected; however, metallic Ni was detected. It is assumed that the NiO and $\text{Ni}(\text{OH})_2$ were reduced to metallic Ni. TiO_2 was still not detected. As shown in Figs. 7(c) and 7(f), both the Ni particles and carbon fibers grew further in the third stage. This was clearly confirmed by XRD, as shown in Fig. 11. The sample for this measurement was collected by scraping off the surface products. Evidently, the intensive formation of the carbon fibers caused the plugging of the reaction chamber.

Table 1 gives the BET surface area of the $\text{Ni}_3(\text{Si,Ti})$ foils before and after the reaction. In this table, the surface area is expressed in m^2/m^2 , which is the BET surface area

Fig. 11 X-ray diffraction profile for surface products on the $\text{Ni}_3(\text{Si,Ti})$ foils after the reaction at 793 K for 65 h.

normalized by the geometrical surface area of the foil sample. The value of the surface area before the reaction is also expressed in m^2/g , showing that the surface area of the foil sample is very small compared to that of the common metallic catalysts. The surface area of the $\text{Ni}_3(\text{Si,Ti})$ foils show a considerable increase with increasing reaction time, particularly in the second stage at 793 K. The observed

Table 1 Surface area (m²/m²) of Ni₃(Si,Ti) foils before and after reaction at 713 K and 793 K. The surface area was expressed by normalizing the BET surface area (m²) by the geometrical surface area (m²). Data for Ni₃Al foils are obtained from the literature.¹²⁾

Alloy	Reaction temperature	Before reaction (m ² /m ²)	After reaction (m ² /m ²)		
			2.5 h	22 h	65 h
Ni ₃ (Si,Ti)	793 K	21.3	821.2	12604.3	11934.9
	713 K	(0.1422 m ² /g)	—	—	11496.3
Ni ₃ Al ¹²⁾	793 K	16.6	—	—	1711.3
	713 K	—	—	—	1959.1

increase of the surface area is possibly due to not only the Ni particles but also the carbon fibers. The data of the Ni₃Al foils¹²⁾ are also given in the table for comparison. The surface area of the Ni₃(Si,Ti) foils is much larger than that of the Ni₃Al foils.

4. Discussion

This study proved that as observed in the case of the Ni₃Al foils,^{11,12)} cold-rolled Ni₃(Si,Ti) foils have a high catalytic activity for the methanol decomposition above 713 K (Fig. 1). The catalytic properties are characterized by the three-staged activation above the onset temperature (Fig. 2). In the following sections, we will discuss the activation process and compare the catalytic properties of the cold-rolled Ni₃(Si,Ti) foils with those of the Ni₃Al foils.

4.1 Activation process

The three-staged activation process consists of low-activity incubation, rapid spontaneous activation, and high-activity state (Fig. 2). It is certain that this change of the activation process is attributed to the surface structure evolution during the reaction described in section 3.3. We consider the following mechanism for the activity change.

XPS analysis showed that before the reaction, the foil surface was covered with the mixed substances—pure Ni, NiO, Ni(OH)₂, SiO₂, and TiO₂—as shown in Figs. 5 and 6. In the early part of the first stage, the activation is considered to be mainly caused by the preexistence Ni particles before the reaction (i.e., after the hydrogen reduction treatment) which may be produced by reduction of NiO and Ni(OH)₂ (Fig. 6). Fine Ni particles act as catalysts for methanol conversion as previously reported.^{18–21)} This was confirmed in the first stage (Fig. 2(a)). However, since the methanol conversion was low, the number of fine Ni particles obtained in the first stage is not considered to be large enough.

In the second stage, the number of the fine Ni particles was found to increase until they could be detected in the XRD patterns (Fig. 10). This increase occurs via the selective oxidation of Si, as pointed out in section 3.3. When Si in Ni₃(Si,Ti) is selectively oxidized, Ni atoms are left behind and aggregate to form fine particles, as witnessed in the case of Ni₃Al.^{11,12,22,23)} We assume that the newly produced fine Ni particles contribute to the rapid spontaneous activation, resulting in the large amount of H₂ and CO produced via the methanol decomposition expressed by eq. (1). The selective oxidation of Si is probably yielded by the main products

generated in the second stage—H₂ and CO (Fig. 3). With production of these gases, the reaction atmosphere must be reducing. Even in such reducing atmosphere, Si can be oxidized because the formation energy of SiO₂ is negatively very large. Ti was also expected to be oxidized because the formation energy of TiO₂ is negatively larger than that of SiO₂. However, TiO₂ was not observed in the XRD pattern (Fig. 10). Even though TiO₂ is formed, we can assume that an apparent catalytic property does not take place because of a poor crystallinity and/or limited quantities.

In the third stage, the formation of fine Ni particles may be saturated and/or some of these Ni particles may become deactivated, resulting in the nonincreasing (i.e., steady-state) conversion of methanol (Fig. 2(a)). At the end of the third stage, the methanol conversion increased again, probably due to the intensive carbon deposition as shown in Fig. 7(c). The deposited carbon plugged the reaction chamber, which decreased the methanol flow rate. This in turn led to the *apparent* increase in conversion after 50 h.

4.2 Comparison of catalytic properties between Ni₃(Si,Ti) and Ni₃Al foils

Three characteristic features can be observed in the catalytic properties of Ni₃(Si,Ti) foils. The first one is the spontaneous activation in the second stage of the reaction due to the build up of fine Ni particles, as discussed in section 4.1. This phenomenon is also observed in the case of Ni₃Al foils although the incubation period before the activation was not observed.^{11,12)} The second one is the high selectivities of H₂ and CO during the entire reaction, which indicates that the methanol decomposition (eq. (1)) is the dominant reaction. This feature is also observed in the Ni₃Al foils. Very small amounts of H₂O, CH₄, and CO₂ were produced, indicating the occurrence of side reactions such as methanation (eq. (2)) and water-gas-shift reaction (eq. (3)):

The selectivities of CH₄, H₂O, and CO₂ were very low in the first and second stages except the very beginning of the first stage. The selectivities gradually increased with reaction time in the third stage (Fig. 4), indicating some contribution of the side reactions expressed in eqs. (2) and (3). The low selectivity of CH₄ is in contrast to the common Ni base catalysts, which are known to enhance methanation for methanol decomposition. For example, methane is the main product of methanol decomposition of SiO₂ supported Ni catalysts.¹⁹⁾ The third characteristic feature is the intensive carbon deposition at the end of the third stage (Fig. 7). These carbon fibers are considered to be produced by the Boudouard reaction:

The surface morphology observations showed that carbon grew on the surface of the fine Ni particles. In addition to methanol conversion, the fine Ni particles apparently acted as a catalyst for the carbon deposition. Carbon deposition commonly occurs during the methane decomposition and reforming over Ni catalysts, often causing deactivation of catalysts and plugging of reaction chamber.^{6,24)} However,

carbon deposition is rare in the case of methanol decomposition. To the best of our knowledge, there have been very few reports on carbon deposition over Cu base catalysts.^{25,26)} With the exception of our studies on the Ni₃Al foils,^{11,12)} there have been no report on carbon deposition over common Ni-based catalysts. The Ni₃(Si,Ti) and Ni₃Al foil catalysts can be categorized as Ni base catalysts because the fine Ni particles serve as catalyst in both cases, but their activity for carbon deposition is considerably different from that of the common Ni base catalysts. The details remain unclear at present.

5. Conclusion

The catalytic properties of cold-rolled Ni₃(Si,Ti) intermetallic foils for methanol decomposition were investigated at the temperatures ranging from 513 to 793 K. The main results are as follows:

- (1) The cold-rolled Ni₃(Si,Ti) foils were found to exhibit catalytic activity for methanol decomposition to give H₂ and CO above 713 K.
- (2) At 793 K, the catalytic activity changed with increasing reaction time in three stages: low-activity incubation, rapid spontaneous activation, and high-activity state. At 713 K, the catalytic activity almost monotonously increased with increasing time, showing a considerably lower value than that at 793 K.
- (3) Fine Ni particles dispersed on carbon fibers were formed on the surface of the foil in the second stage of reaction. It was suggested that the observed spontaneous catalytic activation was attributed to the fine Ni particles induced by the selective oxidation of Si in Ni₃(Si,Ti).
- (4) Carbon fibers were deposited intensively over the foils, causing plugging of the reaction chamber.

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