Reaction Process in the Combustion Synthesis of ZrNi*

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The combustion synthesis was applied to preparing ZrNi using elemental powder mixtures in a vacuum of 10^{-4} Pa and at initial temperatures of 298–673 K. The combustion synthesis at initial temperatures not exceeding 373 K yielded porous products, whereas the combustion synthesis at the initial temperature of 673 K yielded an ingot type product. The propagation rate of the combustion wave was 9.9 mm/s, the maximum combustion temperature was 1483 K and the maximum heating rate was 1730 K/s in the case of the initial temperature of 373 K. No change in the oxygen content of the sample was observed before and after the combustion synthesis. Products of the combustion synthesis contained ZrNi, $\text{Ni}_{11}\text{Zr}_9$, and Zr_2Ni in all the conditions investigated. The difference in nickel particle size caused no conspicuous differences in the amount of the phases in the products. The conversion ratios of the powder mixtures to ZrNi were approximately 0.75 and 0.88 in the case of initial temperatures of 373 and 673 K, respectively. It is considered in the combustion synthesis of ZrNi that the zirconium-rich liquid phase with 76 at.% of zirconium and the nickel-rich liquid phase with 36 at.% of zirconium were produced in the initial stage of the process and then the two liquid phases reacted each other to form ZrNi.

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I. Introduction

Combustion synthesis, or self propagating high temperature synthesis is a method to prepare compounds using the exothermic reaction, which was developed by Merzhanov and Borovinskaya⁽¹⁾ in 1967. The typical process of the combustion synthesis is as follows. Once the reaction is initiated on one end of a reactant powder mixture by an electrically heated coil, it becomes self-sustaining and propagates through the powder mixture forming a compound without a further supply of the external heat. This method has been reported to be able to produce high purity compounds in a short time without a high temperature furnace and other complex processing equipments, and has been mainly applied to the production of refractory compounds⁽¹⁾⁽²⁾. Some inter-metallic compounds, e.g. $\text{TiNi}^{(3)-(5)}$, $\text{NiAl}^{(6)(7)}$ and $\text{TiAl}^{(8)}$ have been also synthesized so far by combustion synthesis. However, this method seems to be applicable to more systems.

ZrNi, which is well known as a hydrogen storage material⁽⁹⁾, is one of the compounds of Ni and a IV-a group metal, same as TiNi which has already been produced by combustion synthesis. Its heat of formation has been calculated by Watson and Bennett⁽¹⁰⁾ to be -96.4 kJ/mol by means of an electron band theory. This value is higher than that of TiNi (-67.8 kJ/mol) which was determined by an experiment. Therefore, the combustion synthesis of ZrNi was expected, and indeed, it was confirmed experimentally in the present work.

In this paper, the effects of Ni particle size and initial temperature of the powder mixtures on the amount of the phases in the products were investigated, and reaction characteristics and processes of the combustion synthesis of ZrNi are presented.

II. Experimental

One kind of pulverized zirconium powder (CERAC Inc., $10\text{--}50\text{ }\mu\text{m}$, 99.7 mass% pure) and two kinds of carbonyl nickel powders different in particle size (INCO Inc., $1\text{--}5\text{ }\mu\text{m}$ and $5\text{--}15\text{ }\mu\text{m}$, 99.7 mass% pure) were used. Mixed in an agate mortar into equiatomic composition, two kinds of powder mixtures were obtained. The one containing smaller Ni powder was termed Mixture I and the one containing larger Ni powder was termed Mixture II.

About 20 g of a powder mixture was tapped into a quartz crucible (18 mm in diameter and 40 mm in height) to the relative density of about 40%. Then the crucible with the powder mixture was placed in a vacuum vessel with a cylindrical furnace for preheating.

The ignition was carried out using a tungsten filament from above the powder mixture in a vacuum of 1×10^{-4} Pa attained by a diffusion pump over an initial temperature range of 298–673 K. After completion of the reaction, the furnace was immediately turned off. The product was taken out from the vessel after it was sufficiently cooled in the furnace. In some samples, two Pt-(13%) Rh·Pt thermocouples (0.3 mm in diameter) were inserted 10 mm vertically apart to determine the reaction temperature and the wave propagation rate.

X-ray (Cu- $K\alpha$) diffraction analysis, electron probe micro analysis (EPMA), optical microscopy and scanning electron microscopy (SEM) were carried out for the products. Oxygen analysis in the powder mixtures and

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the products was also carried out using the inert gas melting carrier-infrared absorptiometric method.

III. Results

1. Combustion synthesis of ZrNi

The combustion synthesis reaction occurred for both powder mixtures over the examined initial temperature range of 298–673 K. However, in some cases at the initial temperature of 298 K, interruption of the combustion wave propagation was observed. Therefore, 373 K was selected for the representative condition of the low initial temperatures in the following observations and analyses. Figure 1 shows photographs of the products of the combustion synthesis. In case a reactant was ignited at the initial temperature not exceeding 373 K, the reaction spread over the upper surface of a reactant and then started to propagate downward through the reactant. Porous products consisting of 0.5–1 mm particles were obtained from Mixture I as shown in Fig. 1(a), and those consisting of 3–5 mm particles were obtained from Mixture II as shown in Fig. 1(b). In case a reactant was ignited at the initial temperature of 673 K, the reaction was explosive enough to blow out a part of the product, and completed instantly. The product was melted down and resulted in an ingot type product which solidified on the inner wall of the crucible.

2. Propagation rate of combustion wave and reaction temperature

The measurement was carried out at the initial temperature of 373 K for Mixture I, which was considered to be the most stable condition for the measurement. Throughout the measurement, the two thermocouples inserted in the sample showed the identical temperature-time curves except for the time lag. The propagation rate

Fig. 1 Photographs of the product of the combustion synthesis: (a) preheated to 373 K from Mixture I; (b) preheated to 373 K from Mixture II; (c) preheated to 673 K from Mixture II.

Fig. 2 Temperature change in the combustion synthesis process of Mixture I preheated to 373 K.

of the combustion wave was 9.9 mm/s, which was calculated using the time lag of temperature rise between the two thermocouples.

Figure 2 shows the temperature change exhibited by one of the thermocouples during the combustion synthesis. As shown in Fig. 2, the abrupt temperature rise was observed to be in two stages, which were from $t=0$ to point A and from point A to point B. The first stage was considered to be caused by the passage of heating zone⁽¹⁾ which precedes the combustion wave front, and the second stage was considered to be caused by the passage of synthesizing zone⁽¹⁾. Taking account of the fact that the temperature rise of the thermocouple is due to the heat conducted from the sample, the former was considered to be the result of the heat conducted through a limited contact area between the thermocouple junction and particles, whereas the latter was considered to be the result of the heat conducted from a liquid which was produced during the reaction. Therefore, the second stage showed a more abrupt temperature rise. In the ranges from $t=0$ to point A and from point A to point B, the observed average heating rates were 730 and 980 K/s, and the observed initial heating rates were 1170 and 1730 K/s, respectively. The temperature decrease observed subsequent to point B was attributed to the heat loss of a small amount of the porous product which was in contact with the thermocouple junction.

As shown in Fig. 2, the maximum temperature observed during the combustion synthesis was 1483 K at point C. From the phase diagram, which is shown later in Fig. 9, it is clear that a solid-liquid coexistent state occurred in the process of the combustion synthesis reaction. The sum of the heat capacity of two thermocouples was only 0.5% of the whole sample, so its effect on the combustion synthesis reaction was negligibly small.

3. X-ray diffraction and EPMA results

Figure 3 shows the X-ray diffraction spectra of the products of the combustion synthesis in comparison with the spectrum of ZrNi which was prepared by arc-melting in

Fig. 3 X-ray diffraction spectra of the product of the combustion synthesis: (a) preheated to 373 K from Mixture I; (b) preheated to 373 K from Mixture II; (c) preheated to 673 K from Mixture II and the spectrum of ZrNi arc-melted in argon (d).

argon. Figure 3(a) shows the spectrum of the product from Mixture I preheated to 373 K. Figure 3(b) and (c) show the spectra of the products from Mixture II preheated to 373 K and 673 K, respectively. Figure 3(d) shows the spectrum of the arc-melted ZrNi. In the spectra of the products of the combustion synthesis, major reflections from $\text{Ni}_{11}\text{Zr}_9$, i.e., (132) and (420), were observed around $2\theta=40^\circ$ in addition to reflections from ZrNi. And the major peak in the spectra consisting of the mixed reflections from (040) and (111) of ZrNi, were recognized to be broadened. Since the grain size of ZrNi in the products was larger than $10\text{ }\mu\text{m}$, the broadening of the peak was not attributed to the effect of the grain size but to the effect of heterogeneous distortion of ZrNi lattices as a result of rapid cooling and/or coexistence of other phases. As shown in Fig. 3(c), the degree of broadening of the peak was small for the product preheated to 673 K. Unidentified peaks recognized in the spectra were considered to be caused by oxides.

Figure 4 shows a typical result of EPMA for the product preheated to 373 K from Mixture I. The phases shown in Fig. 4 were identified by means of the X-ray intensities of Zr- $L\alpha$ and Ni- $K\alpha$. As shown in Fig. 4, Zr_2Ni and $\text{Ni}_{11}\text{Zr}_9$ were observed in addition to the dominant phase ZrNi. The same phases were also observed in the products preheated to 673 K.

Fig. 4 EPMA result for the product of the combustion synthesis preheated to 373 K from Mixture I.

4. Structure of products of the combustion synthesis

Figure 5 shows the optical micrographs of the product: (a) preheated to 373 K; (b) preheated to 673 K. Figure 6 shows the scanning electron micrographs of them. Figure 7 shows a scanning electron micrograph of the surface of the product preheated to 373 K. These figures were only for the products from Mixture I, but it should be noted that the difference in Ni particle size caused no con-

Fig. 5 Optical micrographs of the product of the combustion synthesis from Mixture I: (a) preheated to 373 K; (b) preheated to 673 K.

spicuous differences in the structure of the products.

The product preheated to 373 K consisted of two regions as shown in Fig. 5(a). One is the equiaxial structure region of ZrNi of 10–40 μm grains, and the other is $\text{Ni}_{11}\text{Zr}_9$ region where the equiaxial ZrNi grains of 10–40 μm or columnar ZrNi grains of 5–10 μm in diameter and 50–150 μm in length were scattered. Zr_2Ni was 0.1–5 μm and most of them were observed at grain boundaries of ZrNi in the equiaxial structure region. Zr_2Ni was also observed at the surface of the product as shown in Fig. 7. Figures 6(a) and 7 reveal the existence of the primary crystals of Zr_2Ni .

In the product preheated to 673 K, columnar ZrNi grains of 5–10 μm in diameter and 50–150 μm in length, which were surrounded by a thin $\text{Ni}_{11}\text{Zr}_9$ layer, were observed as shown in the whole field of Figs. 5(b) and 6(b). In Fig. 6, white polyhedra are Zr_2Ni and white spheres are oxides. Since the oxides were smaller than 1 μm , it was difficult to determine their composition precisely, but the composition ratio estimated from the X-ray intensity in EPMA was in the range of $\text{Zr}:\text{Ni}:\text{O}=10:4\text{--}8:1\text{--}4$, which revealed the zirconium-rich nature of the oxides. The oxides were observed in the $\text{Ni}_{11}\text{Zr}_9$ region or the boundaries between ZrNi and $\text{Ni}_{11}\text{Zr}_9$ in all of the products.

Small amounts of eutectic of ZrNi and Zr_2Ni were observed between the primary crystals of each phase in the products preheated to 373 K, and observed in the columnar crystals, which were termed ZrNi for simplicity,

Fig. 6 Scanning electron micrographs of the product of the combustion synthesis from Mixture I: (a) preheated to 373 K; (b) preheated to 673 K.

Fig. 7 Scanning electron micrograph of the surface of the product of the combustion synthesis from Mixture I preheated to 373 K.

Table 1 Oxygen contents of the powder mixtures and the products of the combustion synthesis.

Mixture No.	Oxygen content (mass%)				
	Reactant	C.S.* at 298 K	C.S. at 373 K	C.S. at 473 K	C.S. at 673 K
I	0.33	0.31	0.30	—	0.32
II	0.27	0.26	0.26	0.26	0.29

*C.S.=combustion synthesis.

shown in Figs. 5(b) and 6(b) in the product preheated to 673 K, respectively.

5. Result of oxygen analysis

Table 1 shows the oxygen content of the powder mixtures and of the products of the combustion synthesis. It should be noted that there was almost no change in oxygen content before and after the combustion synthesis. This is attributed to the oxygen dissociation pressure of the oxides in the products being much lower than the partial pressure of oxygen (approximately 10^{-5} Pa) in the vessel even at the melting point of ZrNi. The oxygen which existed at the surface or the inside of the powder particles were considered to form oxides or to be dissolved in the product after the combustion synthesis.

The above result suggests that it is difficult to reduce the oxygen content in the combustion synthesis of intermetallic compounds in which the reaction proceeds at relatively low temperatures. Therefore, powders with low oxygen content must be used in order to obtain products with low oxygen content.

IV. Discussion

In combustion synthesis, it is essential for the reaction to become self-sustaining that the rate of heat accumulation in the sample caused by the exothermic reaction should exceed the rate of heat loss caused by the conduction and radiation. But it is difficult to treat the balance of heat accumulation and loss in the sample, because of the complicated nature of the reaction between the

powder particles. However, we can predict the possibility of the self-propagation and the characteristics of the synthesis reaction to some extent by introducing the concept of adiabatic combustion temperature (T_{ad})⁽²⁾. The adiabatic combustion temperature (T_{ad}) is defined as a temperature that will be attained by the product if all of the heat of formation is consumed for heating the product. T_{ad} can be calculated using the data on the heat of formation, heat capacity and heat of transformation of the product. If T_{ad} is lower than the melting point of the product, the reaction is rate-determined by diffusion in solid phases and is difficult to form a combustion wave which propagates spontaneously. Whereas, if T_{ad} is equal to or higher than the melting point of the product, a liquid phase is produced during the reaction. The reaction is accelerated by a rapid diffusion in the liquid phase, consequently the condition for self-sustaining of the reaction is likely to be established.

Figure 8 shows the temperature-enthalpy relations for equiatomic Zr-Ni system. T_{ad} of ZrNi can be also estimated from Fig. 8. The enthalpy for the reactant denoted by the solid line was obtained by summation of the enthalpies for zirconium and nickel in the thermodynamic data⁽¹¹⁾⁽¹²⁾. As for the heat of formation, -96.4 kJ/mol which was previously described was used. The enthalpy for ZrNi including the latent heat of melting denoted by the dashed line was estimated on the basis of the values for zirconium and nickel. From Fig. 8, when the synthesis reaction completes adiabatically at 298 K, the state of the system changes from point A to point B. It is predicted that T_{ad} will reach the melting point of ZrNi (1533 K) and that about 40% of the product will be

Fig. 8 Temperature-enthalpy relations for equiatomic Zr-Ni system.

Fig. 9 The phase diagram for the Zr-Ni system.

melted. Figure 9 shows the phase diagram for Zr-Ni system⁽¹³⁾. The phase diagram exhibits the eutectic points which are about 200 to 300 K lower than the melting point of ZrNi in both sides of the composition of ZrNi. Therefore, the liquid phase formation is expected at much lower temperatures than 1533 K during the heating up of the powder mixture. From above considerations, in equiatomic Zr-Ni system, the occurrence of combustion synthesis reaction can be explained even at the initial temperature of 298 K.

Because of some heat loss, the observed maximum temperature was 1483 K even at the initial temperature of 373 K. And in some cases of the initial temperature of 298 K, the propagation of the combustion wave was interrupted. Therefore, under the condition employed in this investigation (particle size, atmosphere, relative density...etc.), 298 K is roughly considered to be the critical initial temperature for the propagation of the combustion wave.

As shown in Fig. 9, Zr-Ni system contains eight intermetallic compounds. However, the phases observed in the products of the combustion synthesis were ZrNi, Ni₁₁Zr₉ and Zr₂Ni. The other intermetallic compound phases and unreacted zirconium and nickel were not observed. Therefore, the reaction in the combustion synthesis of ZrNi in this investigation can be expressed in the following equation:

where x denotes the conversion ratio of the powder mixture into ZrNi. For the strict treatment, oxygen and oxide terms must be contained in eq. (1). However, the

oxygen content in the sample was low (0.3 mass%) as shown in Table 1, and most of the oxygen was considered to be dissolved in $\text{ZrNi}^{(14)}$. Therefore, those terms can be neglected here. It is difficult to determine the molar fraction of the phases in a multi-phase mixture by ordinary analyses. However, it is possible to estimate the value of x in eq. (1) by inspecting the hydrogen pressure-composition isotherms (PCT curves) of the products, because of the conspicuous differences in PCT behaviors of ZrNi , $\text{Ni}_{11}\text{Zr}_9$ and $\text{Zr}_2\text{Ni}^{(14)}$. Table 2 shows the molar fraction of the phases determined by this method. In Table 2, each phase is represented to contain two atoms for the simplicity of the quantitative comparison. $\text{Ni}_{1.1}\text{Zr}_{0.9}$ and $\text{Zr}_{1.33}\text{Ni}_{0.67}$ denote $\text{Ni}_{11}\text{Zr}_9$ and Zr_2Ni , respectively. As shown in the result of the products preheated to 373 K, the difference in conversion ratio between both mixtures was small.

Philpot *et al.*⁽⁶⁾ reported as to the combustion synthesis of nickel aluminides that the synthesis reaction occurred more easily and the amount of the resultant phases was larger when a smaller-sized nickel powder was used. Their investigation was performed at non-equiatom compositions, and the synthesized phases were mainly the resultant of a solid state reaction. Whereas in the combustion synthesis of ZrNi at present work, the liquid phase is produced easily as mentioned previously. Once a liquid phase is produced, the mixing of the both elements occurs in much larger range than the particle size. It is, therefore, considered that the difference in nickel particle size had little influence on the conversion ratio in the examined range. The following discussion will be based on the result of the products from Mixture I.

Figure 10 shows the reaction paths of combustion synthesis in the partial phase diagram of the Zr-Ni system, which are based on the experimental results. In Fig. 10, a pair of dashed lines and a pair of dash-dot-dash lines denote the degree of the progress of the reaction from the powder mixtures for the products preheated to 373 and 673 K, respectively. That is, relations among the amount of the three phases observed in the products preheated to 373 and 673 K, which are listed in Table 2, were equal to those when the equal mole of liquids which had the composition represented by a pair of dashed lines ($\text{Zr}_{0.482}\text{Ni}_{0.518}$ and $\text{Zr}_{0.518}\text{Ni}_{0.482}$) and a pair of dash-dot-dash lines ($\text{Zr}_{0.491}\text{Ni}_{0.509}$ and $\text{Zr}_{0.509}\text{Ni}_{0.491}$) solidified without decomposition of $\text{Ni}_{11}\text{Zr}_9$, respectively. From this result, the reaction process can be discussed in the zirconium-rich region and nickel-rich region individually in the phase diagram.

Table 2 Molar fraction of the phases in the products of the combustion synthesis determined by their PCT behavior.

Products	Molar fraction of the phases		
	ZrNi	$\text{Ni}_{1.1}\text{Zr}_{0.9}$	$\text{Zr}_{1.33}\text{Ni}_{0.67}$
C.S. at 373 K, Mixture I	0.76	0.18	0.06
C.S. at 373 K, Mixture II	0.73	0.21	0.06
C.S. at 673 K, Mixture I	0.88	0.09	0.03

Fig. 10 Schematic representation of the reaction and solidification processes of the combustion synthesis of ZrNi .

In case of the initial temperature of 373 K, the observed temperature rose to 1481 K, which is approximately equal to the observed maximum temperature of 1483 K, at the top of the abrupt temperature rise as shown in Fig. 2. It is, therefore, considered that the compositions of the liquids almost reached points P and Q in Fig. 10 after the passage of the synthesizing zone of the combustion wave. And it is considered that the further reaction occurred between the two liquids. The paths of the reaction are denoted by the dashed arrows ① and ②, along which the composition and the temperature changed, in Fig. 10. Finally, the reaction proceeded to the compositions as shown by a pair of dashed lines in Fig. 10. The constant temperature part of the arrows ① and ② corresponds to the section between points B and C in Fig. 2, which was the stage to form solid ZrNi keeping the compositions of the liquids at points P and Q. In proceeding the reaction in this stage, it is considered that the latent heat for solidification of ZrNi (-38.1 kJ/mol) played an important role as heat source in addition to the heat of formation of ZrNi (-96.4 kJ/mol). In Fig. 10, the arrows ① and ② show the average reaction paths in the whole sample, and various other reaction paths could exist locally. Since primary crystals of Zr_2Ni were observed in the product as shown in Figs. 6(a) and 7, the reaction path such as denoted by the dashed arrow ③ in Fig. 10 existed in the zirconium-rich region evidently. In the nickel-rich region, however, no reaction paths which caused $\text{Ni}_{10}\text{Zr}_7$ or still higher-nickel phases existed even locally.

In the case of the initial temperature of 673 K, the maximum temperature was roughly assumed to be about 1520 K from the proportion of the liquid being 90%, which was obtained using Fig. 8, and from the analogy of the relation between the maximum temperature and the amount of the three phases in the product preheated to 373 K. As shown in Fig. 6(b), the product showed a non-equilibrium structure, where ZrNi grains were surrounded by the $\text{Ni}_{11}\text{Zr}_9$ layer which formed through the peritectic reaction. However, since somewhat macroscopic mixing of liquids occurred by melting down of the sample, almost the whole sample solidified along

the paths such as denoted by the arrows ④ and ⑤ in Fig. 10. Consequently, the large areas of $\text{Ni}_{11}\text{Zr}_9$ and the areas where Zr_2Ni particles existed close together were not observed, which were observed in the product preheated to 373 K.

From all the results and the considerations described above, the combustion synthesis investigated in this study can be interpreted to be the process that liquid phases are produced in both sides of ZrNi composition in the initial stage and then they react each other with forming ZrNi. The liquid phases produced in the initial stage should be determined by the nature of the phase diagram and should be independent of the preheating temperatures. The liquid phase with 76at.% Zr is likely to be produced at first because it exhibits the lowest eutectic temperature in the Zr–Ni system as shown in Fig. 9. The liquid phase will change its composition toward the ZrNi composition as temperature rises. Then in nickel-rich region, the liquid phase with 36 at.% Zr is likely to be produced by dissolution of nickel particles into a zirconium-rich liquid which has already formed. This assumption is in good accordance with the experimental results that such phases as Ni_7Zr_2 and $\text{Ni}_{21}\text{Zr}_8$ were not observed in the product.

In the zirconium side of the phase diagram, since there is a stable compound Zr_2Ni between the eutectic point of 76 at.% Zr and the melting point of ZrNi, it is considered that some amount of Zr_2Ni can form during the process toward ZrNi composition. In the case of the initial temperature of 373 K, the maximum temperature of 1483 K observed during the process suggests that the Zr_2Ni melted again. But the composition of all the liquids could not exceed the point R, and a part of the liquid followed the path such as denoted by the dashed arrow ③ in Fig. 10. In this case, from the relations of the liquidus temperatures, primary crystals of ZrNi had already grown to a certain size when Zr_2Ni started to crystallize. Therefore, the Zr_2Ni particles which surround ZrNi grains as seen in the center of Fig. 6(a) are those which formed through the path like this. Some Zr_2Ni particles which are observed in ZrNi grains are considered to remain in the ZrNi grains which grew through the reaction between Zr_2Ni and a nickel-rich liquid. In the case of the initial temperature of 673 K, it is considered that the heat supplied by the preheating was enough to make the composition of almost all of the zirconium-rich liquid exceed the point R in Fig. 10 and proceed to around ZrNi composition.

In the nickel side of the phase diagram, since the liquidus line exists continuously from the eutectic point of

36 at.% Zr to the melting point of ZrNi, it is considered that the reaction proceeded without interruption to around ZrNi composition even at the initial temperature of 373 K.

V. Conclusion

Combustion synthesis was found to be applicable to prepare ZrNi. That is attributed to the high value of the heat of formation and the low eutectic temperatures in the Zr–Ni system. However, the products of the combustion synthesis exhibited a non-equilibrium structure. In the products, some amount of Zr_2Ni and $\text{Ni}_{11}\text{Zr}_9$ were observed which exist in both sides of ZrNi composition in the phase diagram in addition to the dominant phase ZrNi. The combustion synthesis investigated in this study can be interpreted as follows. At first the zirconium-rich liquid phase with 76 at.% Zr and then the nickel-rich liquid phase with 36 at.% Zr were produced in the initial stage, subsequently, they reacted each other with forming ZrNi.

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