論　文

ZrCoの不均化における同位体効果

原　　正憲[1]・小林　孝広[2]・小林　幸司[3]
岡部　俊夫[2]・森　　克徳[3]・渡辺　国昭[1]

[1]富山大学水素同位体機能研究センター
[2]富山大学理学部
[3]富山大学工学部
　〒930 富山市五福3190

Isotope Effect on Disproportionation of ZrCo

Masanori HARA[1], Takahiro KOBAYASHI[2], Koji KOBAYASHI[3]
Toshio OKABE[2], Katsunori MORI[3], Kuniaki WATANABE[1]

[1]Hydrogen Isotope Research Center, Toyama University
[2]Faculty of Science, Toyama University
[3]Faculty of Engineering, Toyama University
　Gofuku 3190, Toyama 930, Japan
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Abstract

To understand hydrogen induced disproportionation of ZrCo, the kinetics and isotope effect were studiesd in isothermal and in heating-cooling cycle modes. Crystallographic change owing to the disproportionation was also examined with powder X-ray diffraction. The rate of disproportionation increased with a temperature up to 873 K, but decreased at higher temperatures. Similar temperature dependence was observed in the heating-cooling mode. The kinetics was analyzed following the method of Sharp et al. The analyses indicated that the reaction mechanism changed from R2 to F1 around 823 K. The Arrhenius plots of the disproportionation rate gave activation energies of 154 and 159 kJ／mol for hydrogen and deuterium, respectively, and the frequency factor as 1.07 and 1.34×10^{10}／s below 823 K. However, the plots showed a negative activation energy for both hydrogens in the high temperature region, where a larger activation energy was suggested for deuterium than for hydrogen. Those characteristics were discussed by assuming the presence of an intermediate between the reactant and product.

1. Introduction

Attention has been paid to hydrogen storage materials not only for developing hydrogen energy systems but also for safe handling of a large amount of tritium used as fuel of thermonuclear fusion reactors[1]. One of the problems of their practical applications is deactivation due to the poisoning of these materials by a small quantity of impurity gases[2]. The poisoning will be reduced to a considerable extent by keeping the working gas free from impurities. Besides the poisoning, however, the activity of these materials is lost by the other mechanism, namely, by the disproportionation of metallic compounds[2-7]. In this phenomenon, a metallic compound decomposes to an hydride of a hydride-forming element of the original metallic compound and a new metallic compound deficient in this element. Consequently, the material loses its activity to absorb and desorb hydrogen reversibly.

This is a serious problem especially for the application to tritium handling. In order to solve this problem, it is indispensable to make clear the conditions causing disproportionation and its mechanisms. From this view point, the present authors have investigated the kinetics and mechanisms of disproportionation of ZrNi and ZrCo[3, 4], which are expected to be candidate materials for tritium storage, recovery and supply. In our previous work[3-5], it was found that ZrCo disproportionates rather fast, whereas ZrNi takes a longer time to complete the disproportionation under almost the same conditions[3]. Accordingly, ZrCo is a good model to investigate in detail the kinetics and mechanisms of the reaction. It is also interesting to examine isotope effects on this reaction. The present paper describes preliminary observations of isotope effect on the disproportionation of ZrCo.

2. Experimental

The sample used was prepared with arc-melting of Zr and Co powders, whose purities were guaranteed as 99.8% and 99.5%, respectively. A block of metallic compound prepared was crushed to granules and crumbled into powder of less than 100 mesh by hydride formation. The crystallography was examined with an X-ray diffractometer before use. Hydrogen and deuterium were purchased from Nihon Sanso Co. Their purities were guaranteed as 99.99995% and 99.6%, respectively. They were used without further purification.

The experimental apparatus used was the same as the previous work[3-5]. It was a high vacuum system equipped with two capacitance manometers, an ionization gauge

and a mass spectrometer. The capacitance manometers were used to measure hydrogen pressure at the reaction system. The apparatus was also installed with a sputter-ion pump and a turbo-molecular pump backed with an oil-sealed rotary pump. Its residual pressure was routinely below 1×10^{-6} Pa. The sample tube made of quartz glass could be heated up to 1200 K with an electric furnace, where the temperature was measured with an alumel-chromel thermocouple fixed to the outer surface of sample tube.

The granules were weighted to 0.86 g and put into the sample tube. After the system being evacuated below 2×10^{-5} Pa at room temperature, the sample was activated by vacuum heating at 873 K for 2 hours. Subsequently, the system was filled with hydrogen or deuterium amounting to [Q]／[ZrCo]≒3.1 (Q denotes H or D) to observe clearly the effects of disproportionation on hydrogen or deuterium overpressure. After stoichiometric ZrCo hydride was formed at room temperature in the closed system, the sample was heated to a given temperature with a given temperature ramp. Accordingly, the hydrogen or deuterium overpressure increased with time to reach a given equilibrium pressure at a given temperature, and then decreased with time during the sample being held at this temperature owing to disproportionation. The pressure decrease was measured as function of time at different temperatures.

3. Results and discussion

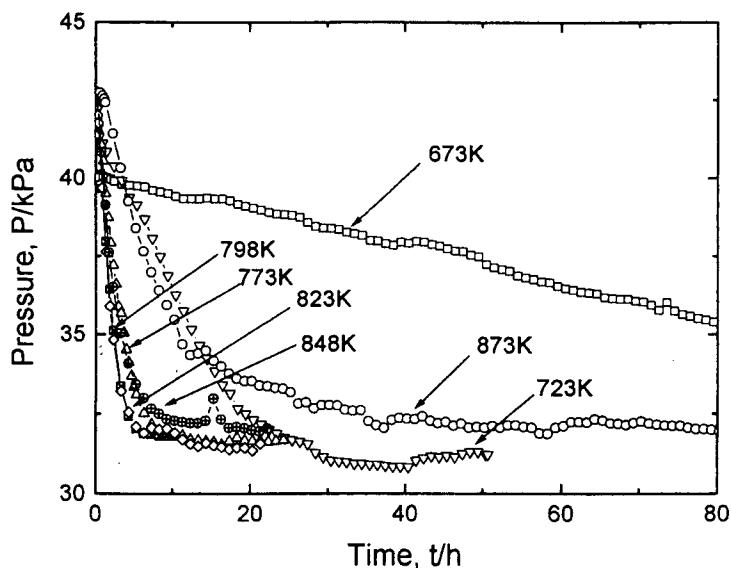Figure 1 shows the time course of the disproportionation reaction by hydrogen at

Fig.1. Change in hydrogen pressure with time on holding ZrCoH₃
at different tenperatures.

different temperatures. The overpressures at the starting point $(t=0)$ correspond to the equilibrium pressures determined by temperature and mass balance between the amounts of ZrCo and of hydrogen in the system, and hence differed each other. As seen in the figure, the hydrogen overpressure decreased with time irrespective of the holding temperature, suggesting the formation of a hydride more stable than $ZrCoH_3$, because the overpressure should be kept constant if there is no change in solid phase. Most probably, the new hydride is ZrH_2, for which the equilibrium pressure is about 133 Pa at 873 K[8], and then acts as hydrogen trap in this system. The X-ray diffraction analyses after these measurements confirmed the formation of ZrH_2 and $ZrCo_2$. Accordingly, the pressure decrease observed in this figure should be attributed to the following disproportionation reaction as[3-7]

$$2\,ZrCo + H_2 \rightarrow ZrCo_2 + ZrH_2. \tag{1}$$

It is noteworthy that the rate of disproportionation increased with temperature from 673 to 798 K, whereas the reaction was decelerated by further increase in temperature above 823 K. Similar reaction time courses and temperature dependence were observed for deuterium[5].

Figure 2 summarized the observations for H_2 and D_2. To compare data with slightly different initial conditions, the pressure decrease was normalized as $[Q]/[ZrCo]$, where $[Q]$ represents the number of moles of Q [H, D] atoms absorbed, and [ZrCo]
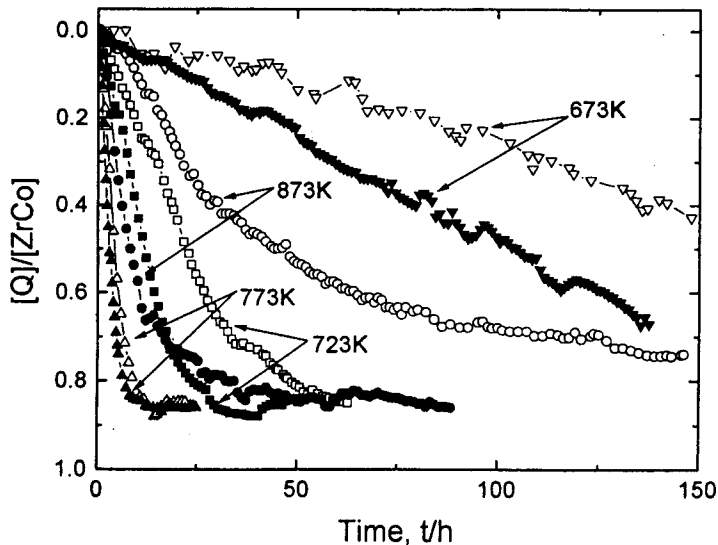

Fig.2. Isotope dependence of the time course of disproportionation at different temperatures.
Open marks:ZrCo-D system .Close marks:ZrCo-H system

is that of ZrCo in formula unit. The [Q]/[ZrCo] ratio corresponds to the extent of the reaction and becomes unity at the completion of the reaction. The open and close marks denote deuterium and hydrogen data, respectively. As seen in this figure, [Q] /[ZrCo] increased almost linearly with time up to about 0.7 at any temperature except [D]/[ZrCo] at 873 K, and then the reaction proceeded very slowly afterward. Finally, the value of [Q]/[ZrCo] reached 0.9, suggesting that the composition of Zr hydride was $ZrQ_{1.8}$. The rate of disproportionation was faster for hydrogen than for deuterium at any temperature. The isotope effect was appreciable at 673 K, but decreased with temperature increase up to 773 K; for example, the time attaining to the 50% reaction extent ([Q]/[ZrCo]=0.5) was 100 and 160 hours for hydrogen and deuterium, respectively, whereas there was only a slight difference between them at 773 K, where the reaction rates were substantially faster than at 673 K. Contrary to this tendency, the isotope effect became greater again at the higher temperature of 873 K, in accordance with the slowing down of the reaction rate.

The temperature dependence of the disproportionation rate is rearranged to Arrhenius plots for both hydrogen and deuterium in Fig 3, by taking account of the half-life (τ) being inversely proportional to rate constants, as discussed below. It can be seen in this figure that the rate constant of disproportionation increased with temperature
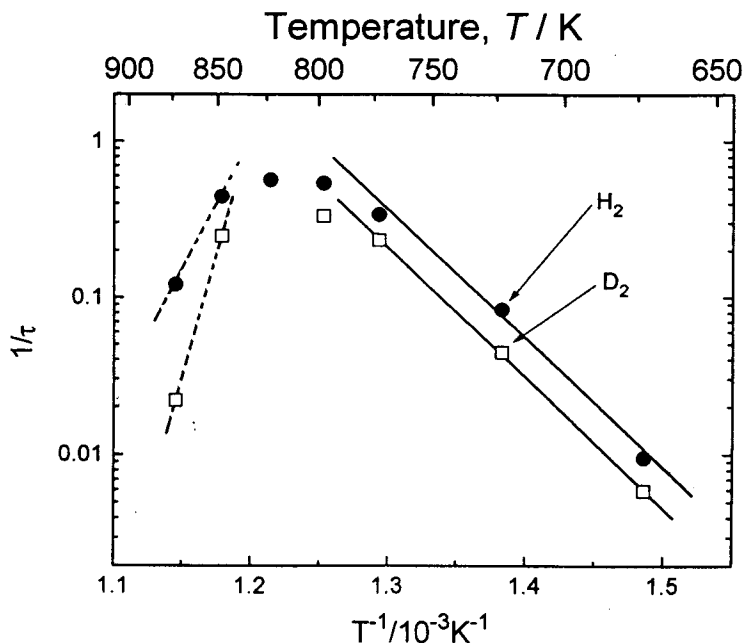

Fig.3. Arrhenius plots of disproportionation rate.

below 798 K, but decreased at higher temperatures for both of the isotopes. In the lower temperature region, straight lines could be drawn. From the slopes, the activation energies were determined as 154 and 159 kJ/mol, respectively. The difference between the activation energies was very small. On the other hand, the frequency factors were 1.07 and 1.34×10^{10} s^{-1} for hydrogen and deuterium, respectively. Namely, the ratio of the frequency factors amounts to 1/1.25. Accordingly, the difference in the disproportionate rates is predominantly determined by the difference between the frequency factors.

In the high temperature region, straight relations can be also expected between the log (1/τ) and (1/T) as suggested by the dotted lines for hydrogen and deuterium. The slopes are negative and hence the activation energies are negative. The plots suggest a smaller activation energy and a larger frequency factor for hydrogen than those for deuterium.

Similar temperature dependence of the disproportionation rate and the isotope effect were observed by the heating-cooling cycle experiments; this operation mode which is of more practical importance than the isothermal process, because this kind of materials is used for recovery, storage and supply of hydrogen isotopes and hence heating-cooling operations are required. Figure 4 summarizes the results observed for hydrogen and deuterium at two different heating temperatures, (a) for 773 K and (b) for 873 K. The data are cited from previous papers[3,4] and rearranged to the [Q]/
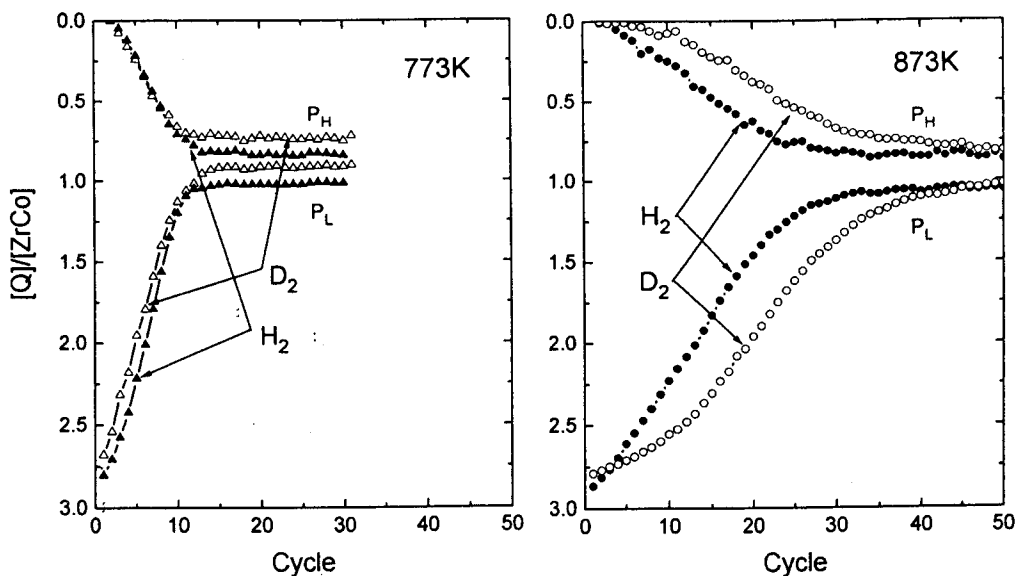

Fig.4. Changes in [D]/[ZrCo] on heating-cooling cycle mode.

[ZrCo] ratio. The lower (P_L) and higher points (P_H) at each cycle number represent the ratios at room temperature and at given heating temperatures, respectively. The ratios for P_L at the starting points were around 2.8, which corresponds to the stoichiometric hydride of $ZrCoQ_{2.8}$. If the ZrCo phase was held up during these heating-cooling cycles, both the P_L and P_H should be kept constant. It can be seen, however, both the ratios changed sigmoidally with the cycle. The P_H ratio increased to about 0.8 and the P_L decreased to about 1.0. The decrease of P_L indicates that the sample became inactive to absorb hydrogens, suggesting the reduction of ZrCo phase in the sample. On the other hand, the increase of P_H is due to the formation of a new trapping site like ZrQ_2. X-ray diffraction analyses after the heating-cooling cycles confirmed the formation of ZrQ_2 and $ZrCo_2$[3, 4]. The difference between P_Hs and P_Ls after reaching constant levels should be due to the absorption and desorption by $ZrCo_2$.

It took only 10 cycles to complete the disproportionation at 773 K, while over 30 cycles were required for the completion at 873 K, namely, the reaction was faster at the lower temperature than at the higher temperature. In addition, only a slight difference was observed at 773 K between hydrogen and deuterium, whereas an appreciable isotopic difference was observed at 873 K. The smaller the reaction rate was, the larger the apparent isotope effect. Those features are quite similar to the isothermal process.

Both the isothermal and the heating-cooling cycle observations strongly suggest that the disproportionation by tritium is much slower than lighter isotopes and that the reaction mechanism is different between the low and the high temperature regions.

Then, the reaction curves shown in Fig.2 were analyzed following the method by Sharp et al[9]. for heterogeneous reactions between solid and gas. Thus, the heterogeneous reactions can be described by simple integrated formula as

$$F1: \ln(1-\alpha) = -k\ t = 0.693t / \tau \tag{2}$$
$$R2: 1 - (1-\alpha)^{1/2} = (u/r)\ t = 0.293t / \tau \tag{3}$$
$$R3: 1 - (1-\alpha)^{1/3} = (u/r)\ t = 0.206t / \tau \tag{4}$$
$$A2: (-\ln(1-\alpha))^{1/2} = kt = 0.833t / \tau \tag{5}$$
$$A3: (-\ln(1-\alpha))^{1/3} = kt = 0.855t / \tau, \tag{6}$$

where α represents the extent of reaction, τ the half-life period and k the rate constant; u and r in Eqs. 3 and 4 are the moving velocity of boundary and the radius of interface between a reactant and a product, respectively. Eq. 2 stands for the first order reaction. Eq. 3 is valid for the mechanism in which the interface between the

reactant and the product moves from outer to inner areas with reaction, where the interface is assumed to be of circular plate. When the interface is spherical, the kinetics is expressed by Eq. 4. When the reaction rate is determined by nucleation and nucleus growth, the kinetics is described with Avrami-Erofeev equations[10-12]. Eq. 5 stands for plate like growth of the reactant, whereas Eq. 6 is valid for spherical growth.

Figure 5 shows the results analyzed by these equations for hydrogen. The experimental data at 723 and 773 K in the low temperature region agreed fairly well to the R2 mechanism, agreeing to Konishi et al[6]. The data at 673 K could not be examined because the reaction did not complete within the limit of experimental time. On the other hand, the high temperature data at 873 K could be reproduced by the F1 mechanism. The same conclusion was obtained for the disproportionation by deuterium.
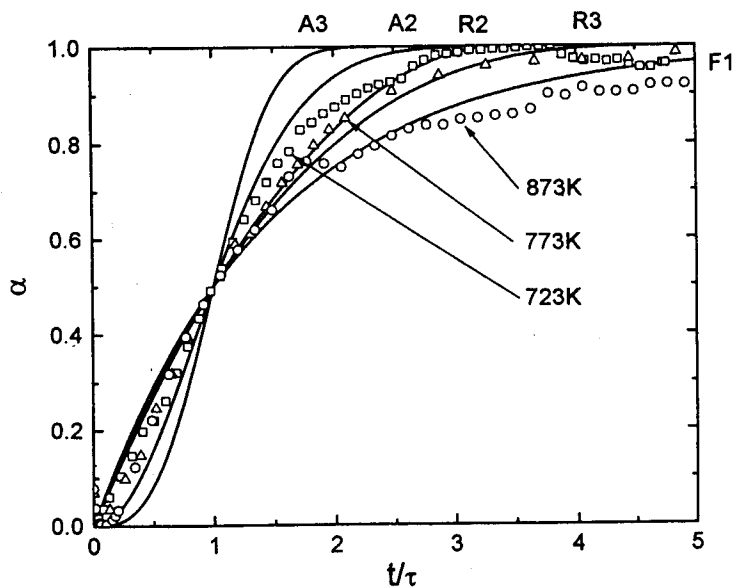

Fig.5. Plots of fraction reacted, α, versus t/τ.

The change in the temperature dependence as seen in Fig. 3 is now understood as a result of the change in the reaction mechanism from R2 to F1 around 823 K. In addition, this kind of volcano type Arrhenius plots can be interpreted by a series reaction like $A \to B \to C$, where A and C represent the reactant and the product, respectively; B is an intermediate. In the present case, the reactant is $Q_2 + ZrCo$ and the product $ZrQ_2 + ZrCo_2$. When the potential well of the intermediate is sufficiently

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deep, one can assume a potential curve as shown schematically in Fig.6. It can be also assumed that the process A→B has an high activation energy with a large frequency factor, whereas the process B→C dose a low activation energy with a low frequency factor.

In the lower temperature region, it is presumed that the process B→C is comparatively faster than the preceding process, A→B. Consequently, the intermediate will be consumed rapidly to from the product, C. In such a case, the rate determining step should be the process as A→B, and hence the positive activation energy is observed. It can be also assumed that the potential well of the activated complex (AC_L) is not so much different from that of a Q_2 molecule, and hence the isotope effect on the activation energy is small.

As the temperature goes up, all of the relevant rate constants become greater. However, the difference in the rate constants between the forward and reverse direc-
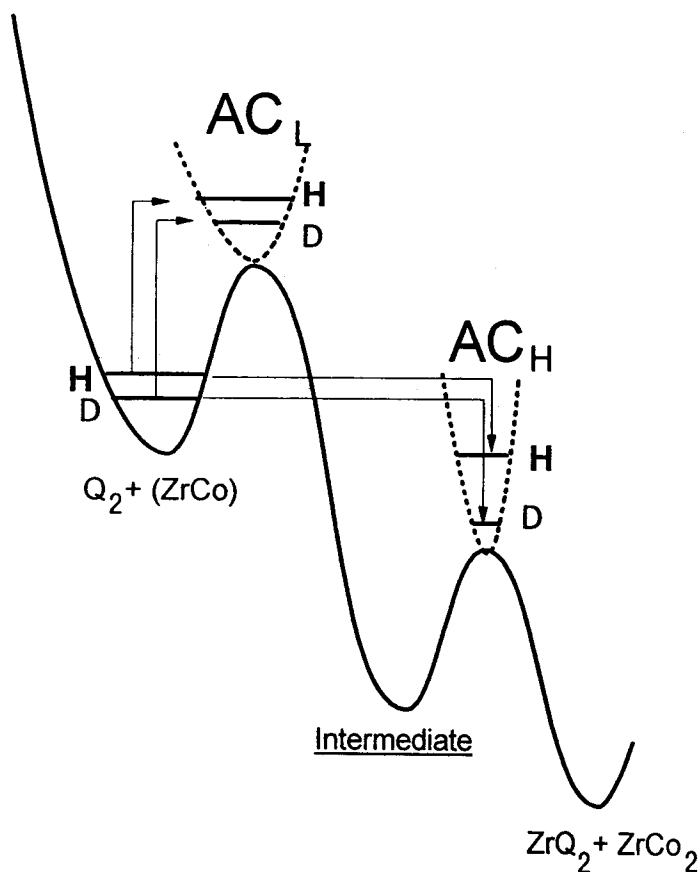
Fig.6. Schematic potential diagram for disproportionation of ZrCo.

tions of A⇄B will become smaller than the rate constant of the forward reaction, B→C, if the temperature dependence is much smaller for this step than those for A⇄B. This results in the slower rate for the B→C process than for the A→B process. Eventually, the rate determining step changes as B→C, while gives a negative apparent activation energy. In the case that the potential well of the related activated complex (AC$_H$) is steeper than that of a Q$_2$ molecule, the apparent activation energy is expected to be large for deuterium than for hydrogen.

4. Conclusions

Hydrogen induced disproportionation of ZrCo was studies in isothermal and in heating-cooling cycle modes in a temperature range from 673 to 873 K. In both the modes, the rate increased with temperature up to 823 K, whereas it decreased with further increased in the temperature. It was revealed that the reaction mechanism changed around 823 K from R2 (interface growth mechanism) in the lower temperature region to F1 (homogeneous first order mechanism) in the higher temperature region. The Arrhenius plots showed a volcano-type curves for both hydrogen and deuterium. The plots gave the activation energies as 154 and 159 kJ／mol for hydrogen and deuterium, respectively, and the frequency factors as 1.07 and 1.34×10^{10}／s below 823 K. On the other hand, the plots suggested the negative activation energies for both hydrogens in the high temperature region, where a larger value was expected for deuterium than for hydrogen. The change in the reaction kinetics and the mechanism as well as the isotope effect was discussed by assuming the presence of a stable intermediate on the reaction path between the reactant (ZrCo + Q$_2$) and products (ZrQ$_2$ + ZrCo$_2$).

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