

## **Effect of Hydride Reorientation on Delayed Hydride Cracking In Zr-2.5Nb Tubes**

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### **Abstract**

The objective of this study is to investigate the reorientation of hydrides with applied stress intensity factor, the peak temperature and the time when to apply the stress intensity factor in a Zr-2.5Nb pressure tube during its thermal cycle treatment. Cantilever beam (CB) specimens with a notch of 0.5 mm in depth made from the Zr-2.5Nb tube were subjected to electrolytic hydrogen charging to contain 60 ppm H and then to a thermal cycle involving heating to the peak temperature of either 310 or 380°C, holding there for 50 h and then cooling to the test temperature of 250°C. The stress intensity factor of either 6.13 or 18.4 MPa $\sqrt{m}$  was applied at the beginning of the thermal cycle, at the end of the hold at the peak temperatures and after cooling to the test temperature, respectively. The reorientation of hydrides in the Zr-2.5Nb tube was enhanced with the increased peak temperature and applied stress intensity factor. Furthermore, when the CB specimens were subjected to 18.4 MPa $\sqrt{m}$  from the beginning of the thermal cycle, the reoriented hydrides occurred almost all over the Zr-2.5Nb tube, surprisingly suppressing the growth of a DHC crack. In contrast, when the CB specimens were subjected to the stress intensity factor at the test temperature, little reorientation of hydrides was observed except the notch region, leading the Zr-2.5Nb to grow a large DHC crack. Based on the correlation between the reorientation of hydrides and the DHC crack growth, a governing factor for DHC is discussed along with the feasibility of the Kim's DHC model.

**Key Words** : Zr-2.5Nb, reorientation, hydrides, delayed hydride cracking (DHC), supersaturation, hydrogen

### **1. Introduction**

A necessary condition to induce delayed hydride cracking in zirconium alloys is the precipitation of hydrides at the crack tips that are reoriented with

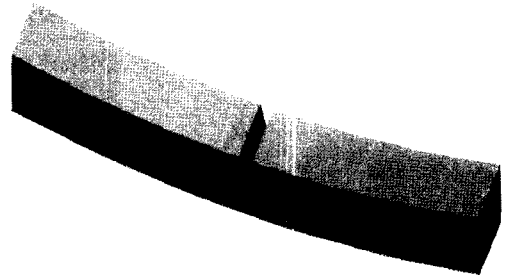
their normals parallel to applied tensile stress [1]. For a Zr-2.5Nb tube with a strong circumferential texture where most of the basal poles are oriented toward the circumferential direction of the tube, hydrides are easy to reorient with their normals

almost parallel to the applied tensile direction corresponding to the circumferential direction. It is because the hydrides are nucleated and grown only on the  $\{10\bar{1}7\}$  habit planes, which determines the growth pattern of the DHC cracks [2]. Since the reorientation of hydrides occurs through the nucleation and growth of hydrides, it would be governed by the supersaturated hydrogen concentration in the zirconium matrix of the Zr-2.5Nb tube, applied tensile stress, texture and the size of the precipitated hydrides [2-5]. The effect of the reorientation of hydrides on the DHC velocity would be that the easier the reorientation of hydrides is, the higher the DHC velocity. Thus, the study has focused on the relationship between the reorientation of hydrides and the DHC velocity in the Zr-2.5Nb tube. To this end, we introduced a change in the amount of reoriented hydrides in the Zr-2.5Nb tube by changing the applied stress intensity from 6.13 to 18.4 MPa $\sqrt{m}$ , and the peak temperature from 310 to 380°C during the DHC tests where the cantilever beam (CB) specimens containing a notch and 60 ppm of hydrogen are subjected to a thermal cycle involving heating to the peak temperature, holding there for 50 h and then cooling to the test temperature. Besides, the time when the stress intensity factor is applied also changed from the beginning of the thermal cycle through the end of holding at the peak temperature to when the CB specimens reach the test temperature.

## 2. Experimental Procedures

### 2.1. Specimen Preparation

The cantilever beam specimens, 38mm long x 3.2mm wide, with a 0.5mm deep notch were used for the DHC tests as shown in Fig.1. The notch with a root radius of 0.05mm was made in the radial direction from the circumferential direction



**Fig.1. Schematic Diagram of Cantilever Beam Specimens used for DHC Tests that are taken from a Zr-2.5Nb Tube where R, T and L are Representing the Radial, Transverse and Longitudinal Directions of the Tube**



**Fig. 2. Fine Hydrides Precipitated in the Water-Quenched CB Specimens**

of a CANDU pressure tube, using an electric discharge machine. The CB specimens were electrolytically charged with hydrogen in a H<sub>2</sub>SO<sub>4</sub> solution to form a surface hydride of about 20μm in thickness followed by a homogenization treatment at 305°C for 30 h. The more detailed procedures for hydrogen charging have already been reported elsewhere [6]. The hydrogen content in the CB specimens was analyzed to be 60±5 ppm. After the homogenization treatment, all the CB specimens described herein were water-quenched to have very fine hydrides precipitated as shown in Fig. 2.

## 2.2. DHC Tests

DHC tests were conducted using a cantilever beam tester where a constant load is applied with a step-motor as shown in Fig. 3. All the CB specimens were subjected to the thermal cycle during the DHC tests to consistently induce the crack growth by DHC as shown in Fig. 4. they were heated to the peak temperature of either 310 or 380°C at a rate of 2°C/min, held there for 50 h and then cooled to the test temperature of 250°C at almost the same rate as the heat-up rate.

Applied stress intensity factor changed from 6.13 MPa√m to 18.4 MPa√m and furthermore the time to apply the stress intensity factor to the

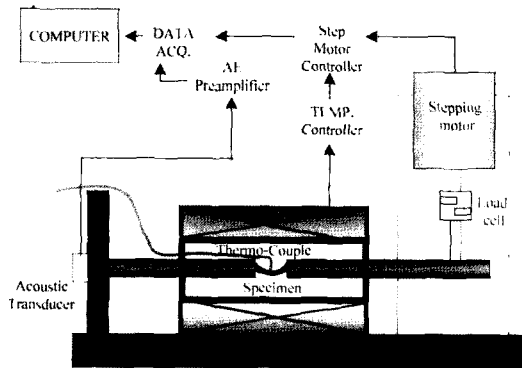


Fig.3. Schematic Diagram of the Cantilever Beam Testing Tester used for DHC Tests

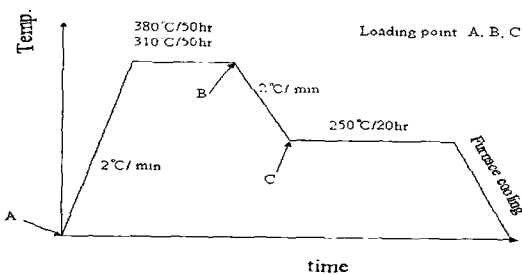


Fig. 4. Thermal Cycle Treatment Applied on the CB Specimens Taken from the Zr-2.5Nb Tube Along with Points of Time when the Stress Intensity Factor is Applied

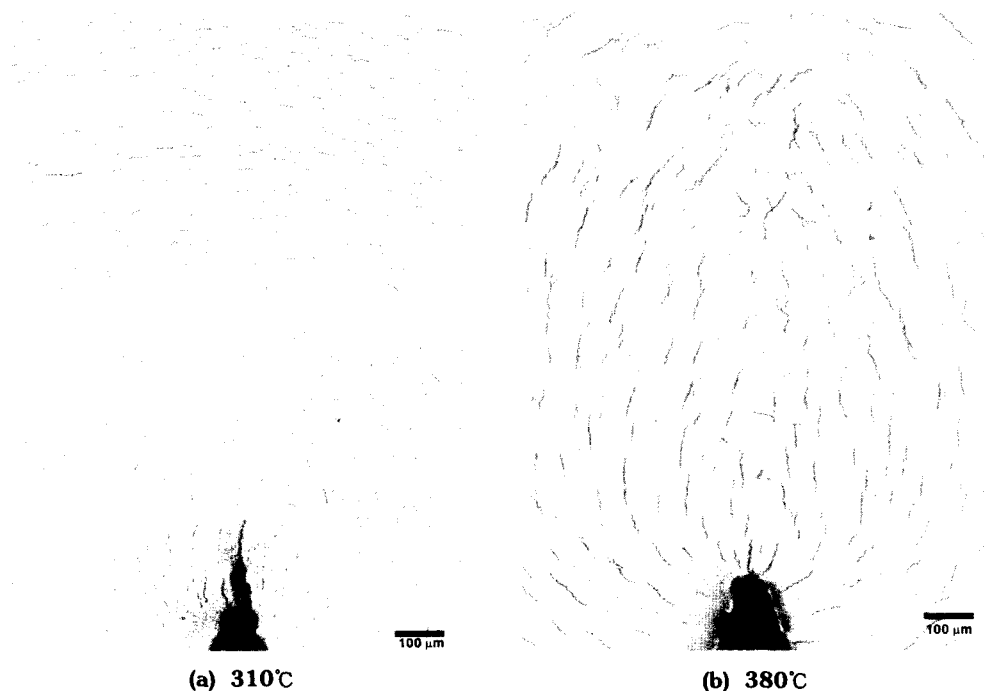
CB specimen was changed during DHC tests: firstly, at the beginning of the thermal cycle corresponding to the A in Fig. 4, secondly, at the end of the hold at the peak temperature corresponding to the B in Fig. 4 and thirdly after the test temperature is reached, corresponding to C in Fig. 4, respectively. After the DHC tests, the distribution of the hydrides were observed on the CB specimens with an optical microscope and a scanning electron microscope after chemical polishing in a mixture of 10 volume percent HF, 30 volume percent HNO<sub>3</sub>, 30 volume percent H<sub>2</sub>SO<sub>4</sub> and 30 volume percent H<sub>2</sub>O.

## 3. Results and Discussion

### 3.1. Effects of the Peak Temperature and Stress Intensity Factor on the Hydride Reorientation

When the stress intensity factor of 18.4 MPa√m is applied to the CB specimens from the beginning of the thermal cycle (corresponding to the A point in Fig. 4), the reorientation of hydrides strongly depends on the peak temperature. Fig. 5 shows the reorientation of the hydrides in the CB specimens with the peak temperature changing from 310 to 380°C. At the lower peak temperature of 310°C, the CB specimens had a reorientation of the fine hydrides in the radial direction occurring locally near the notch (or approximately within 0.8 mm from the notch), not in the regions far from it and a DHC crack had grown. However, when the peak temperature increased to 380°C, the CB specimens had coarse hydrides nucleated and reoriented in the radial direction not only near the notch region but in their overall cross section but surprisingly they had no growth of the DHC crack.

These results shown in Fig. 5 are not consistent with what we expected. In other words, the pre-

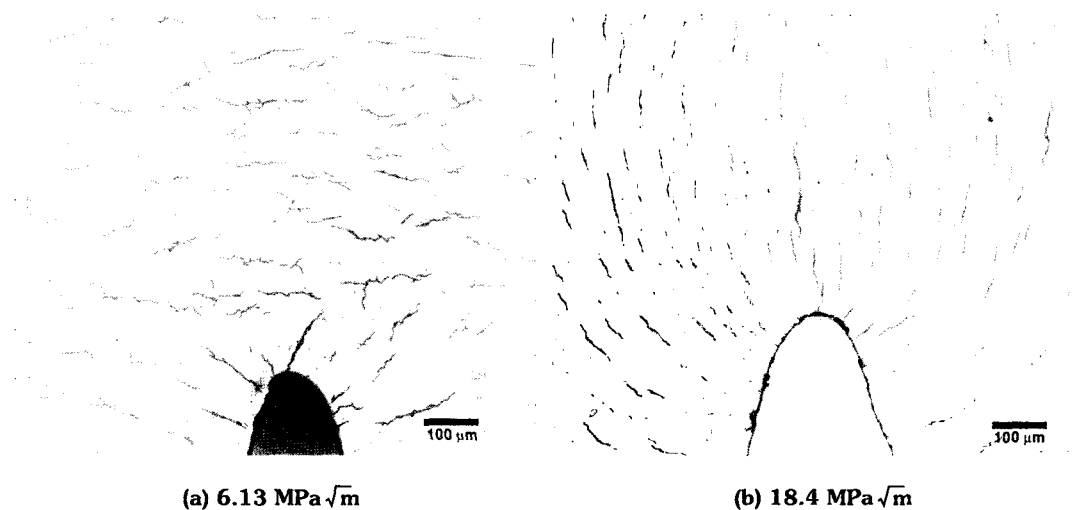


**Fig. 5. Distribution of Reoriented Hydrides in the Zr-2.5Nb Tube with the Peak Temperature when the Stress Intensity Factor of  $18.4\text{MPa}\sqrt{\text{m}}$  is Applied from the Beginning of the Thermal Cycle**

existence of reoriented hydrides at the notch should have facilitated the growth of the DHC crack under an applied stress intensity factor that is large enough to fracture the hydrides. This fact points out that something else other than the reorientation of the hydrides may govern delayed hydride cracking in zirconium alloys, like the supersaturated concentration of hydrogen as suggested by Kim's DHC model [5].

Thus, we have to focus on a correlation between the reorientation of the hydrides and the delayed hydride cracking from the viewpoint of the supersaturated concentration of hydrogen. At the peak temperature of either 310 or 380°C, all the CB specimens will have all the precipitated hydrides dissolved because the temperature for the terminal solid solubility for dissolution of 60 ppm H is 305°C [7,8]. During cooling to the test temperature, the CB specimens become

supersaturated with hydrogen in solution and tend to precipitate the hydrides whose rate depends on the degree of undercooling, applied tensile stress and the peak temperature [8]. The higher tensile stress, higher peak temperature and larger degree of undercooling can lead to a faster nucleation of the hydrides when the CB specimens are cooled from the peak temperature to the test temperature. Thus, under the constantly applied stress intensity factor of  $18.4\text{MPa}\sqrt{\text{m}}$ , the higher peak temperature of 380°C will facilitate the precipitation of the reoriented hydrides in the CB specimens even during its cooling from the peak temperature to the test temperature. It is because annealing at the higher peak temperature will remove most of the dislocations left behind where the previously precipitated hydrides have dissolved during heat-up [9], suppressing the reprecipitation of the hydrides at those sites where they have

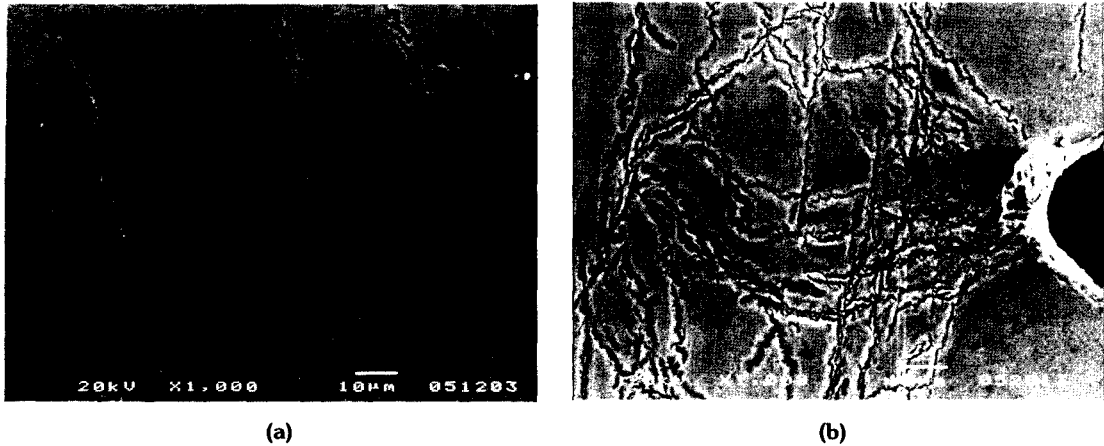


**Fig.6. Reorientation of Hydrides in the Zr-2.5Nb Tube with the Stress Intensity Factor when it is Applied from the Beginning of the Thermal Cycle**

been [10-11] and provide the larger amounts of undercooling during cooling, facilitating the enhanced precipitation of the reoriented hydrides at dislocations in the plastically deformed regions made by the stress intensity factor of  $18.4 \text{ MPa}\sqrt{\text{m}}$ . The reoriented hydrides are observed to occur over most of the whole cross section of the specimens as shown in Fig. 5b, leaving the bulk regions and the notch tip with no supersaturation of hydrogen. At the test temperature, therefore, there will be little difference in hydrogen concentration between the bulk regions and the notch tip, preventing hydrogen from moving to the notch from the bulk regions. This results in no growth of the DHC crack as shown in Fig.5. In contrast, the lower peak temperature such as  $310 \text{ }^\circ\text{C}$ , due to a lesser degree of undercooling, will suppress the precipitation of the reoriented hydrides during the cooling stage such that the reoriented hydrides are precipitated only at the crack tip region (as shown in Fig. 5) subjected to a higher stress intensity factor. It leaves the bulk regions and the notch tip region supersaturated and less supersaturated with hydrogen,

respectively. Hence, at the test temperature, a difference in the hydrogen concentration develops between the notch tip and the bulk regions, driving the hydrogen to diffuse to the notch tip with the less supersaturation of the hydrogen so that a DHC crack grows at the notch.

When a lower stress intensity factor of  $6.13 \text{ MPa}\sqrt{\text{m}}$  was applied from the beginning of the thermal cycle to the CB specimens, the precipitation of the reoriented hydrides occurred only near the notch tip as shown in Figs. 5a and 6. Comparison of the amount of the reoriented hydrides under  $6.13$  and  $18.4 \text{ MPa}\sqrt{\text{m}}$  as shown in Fig. 6 leads to the conclusion that the higher stress intensity factor facilitates the reorientation of hydrides in the radial direction from the circumferential direction of the tube, or in other words, accelerates the precipitation of the reoriented hydrides during cooling from the peak temperature to the test temperature. Even under  $6.13 \text{ MPa}\sqrt{\text{m}}$  after one cycle, the reorientation of some hydrides precipitated ahead of the notch tip as shown in Fig. 7a but unfractured hydrides did not let the DHC crack grow ahead of the notch,



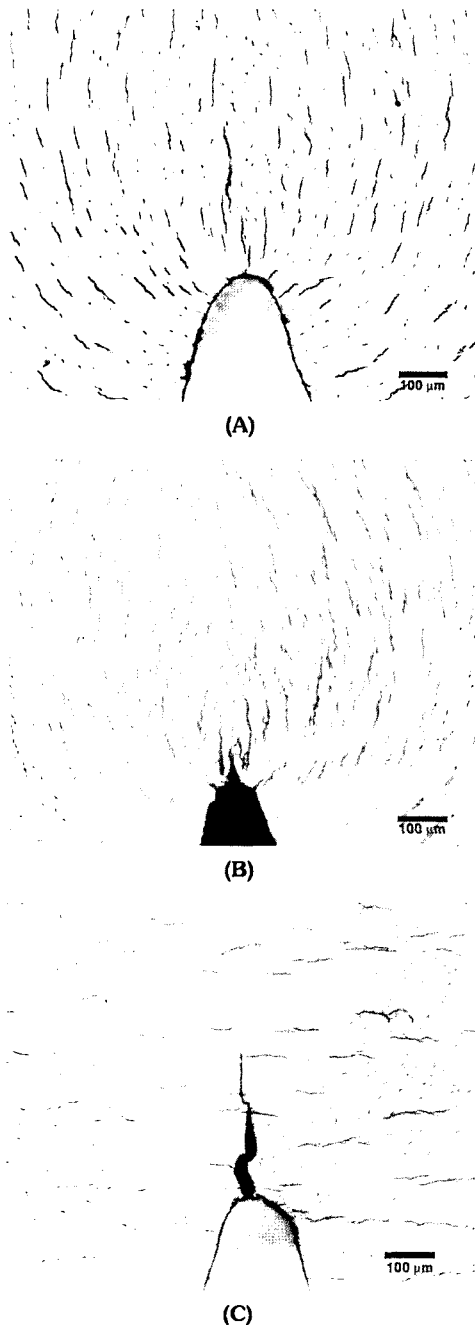
**Fig.7. Reorientation of Hydrides Ahead of the Notch Tip in the Zr-2.5Nb Tube with the Number of the Thermal Cycle when  $6.13 \text{ MPa}\sqrt{\text{m}}$  is Applied from the Beginning of the Thermal Cycle:(a) After 1 Cycle and (b) after 5 Cycles**

which was confirmed after 5 runs of the thermal cycle as shown in Fig. 7b. It is because the little gradient of hydrogen concentration between the notch tip and the bulk regions results from a gradual stress gradient ahead of the notch. Thus, a necessary condition to grow the DHC crack is expected to be the fracture of the reoriented hydrides at the notch tip, developing a steep stress gradient and thereby the hydrogen concentration gradient between the notch tip and the bulk regions.

### **3.2. Effect of the Plastic Deformation on the Hydride Reorientation and DHC During the Thermal Cycle**

To understand the effect of prior plastic deformation on the reorientation of hydrides in the Zr-2.5Nb tube, we applied the stress intensity factor of  $18.4 \text{ MPa}\sqrt{\text{m}}$  to the CB specimens at different points of time during the thermal cycle: firstly, at the beginning of the thermal cycle, or RT, secondly, at the end of the hold at the peak

temperature and thirdly, at the beginning of the test temperature (Fig. 4). When the CB specimens were subjected to  $18.4 \text{ MPa}\sqrt{\text{m}}$  from the beginning of the thermal cycle, the precipitation of the reoriented hydrides occurred over almost the whole cross section as shown in Fig. 8a. When the CB specimens were subjected to  $18.4 \text{ MPa}\sqrt{\text{m}}$  at the end of the hold time at the peak temperature, a small region near the notch rather than the bulk regions far from it showed the reoriented hydrides as shown in Fig. 8b. When the CB specimens were subjected to  $18.4 \text{ MPa}\sqrt{\text{m}}$  after cooling to the test temperature, no noticeable reorientation of hydrides was observed (Fig. 8c). An important thing to note is that the DHC crack grows only in the CB specimens with a little reoriented hydrides, not in those with a significant precipitation of the reoriented hydrides. To suppress the growth of the DHC crack, therefore, it is necessary to have reoriented hydrides precipitated onto the CB specimens before they reach the test temperature. In summary, these results demonstrate that the precipitation of reoriented hydrides suppresses the



**Fig. 8. Reorientation of Hydrides in the Zr-2.5Nb Tube with when to Apply Stress Intensity Factor on the CB Specimens Subjected to the Thermal Cycle: (a) at the Beginning of the Thermal Cycle, (b) at the End of the Hold at the Peak Temperature and (c) at the Test Temperature of 250°C**

growth of the DHC crack.

The results shown in Figs. 8a and 8b demonstrate that the reoriented hydrides are precipitated during cooling from the peak temperature to the test temperature, which is enhanced due to the prior plastic deformation by the applied stress intensity factor of  $18.4 \text{ MPa}\sqrt{\text{m}}$ . Therefore, we suggest that the dislocations introduced by the plastic deformation during the hold time at the peak temperature likely provide hetero-nucleation sites for the precipitation of hydrides [9-11], featuring the enhanced precipitation of the reoriented hydrides there. That is why the CB specimens subjected to the stress intensity factor from the beginning of the thermal cycle had many reoriented hydrides appearing over most of the whole cross section area. In contrast, when the stress intensity factor is applied at the end of the hold time at the peak temperature, only a limited region near the notch will be subjected to plastic deformation, causing the reoriented hydrides to appear there only, not in the bulk regions far from it as shown in Fig. 8b. The precipitation of the reoriented hydrides, however, will decrease the extent of the supersaturation of hydrogen in the zirconium matrix, which is a driving force for DHC according to the Kim's DHC model [5]. This can explain why a small DHC crack appears in the CB specimen with a lesser amount of reoriented hydrides precipitated (Fig. 8b), not in the CB with a full precipitation of the reoriented hydrides (Fig. 8a). Further evidence is provided from the experimental fact that the CB specimen with a little precipitation of the reoriented hydrides has a very large DHC crack as shown in Fig. 8c. From these results, we conclude that the supersaturation of hydrogen is governing the diffusion of the hydrogen from the bulk regions to the notch tip. Furthermore, these results validate the feasibility of the Kim's DHC model [5].

#### 4. Conclusions

The reorientation of hydrides in the Zr-2.5Nb tube was enhanced with an increased peak temperature and applied stress intensity factor, and under a larger stress intensity factor applied at the beginning of the thermal cycle treatment when the cantilever beam specimens with 60 ppm H were subjected to the DHC tests at 250°C. The enhanced precipitation of the reoriented hydrides during cooling from the peak temperature to the test temperature suppressed the DHC crack while the CB specimen with a little precipitation of the reoriented hydrides had a large DHC crack. These results demonstrate that the supersaturation of hydrogen governs DHC in Zr-2.5Nb tubes, providing critical evidence of the feasibility of the Kim's DHC model proposed recently.

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