Entropy Change and Radiation Induced Deformation in Zr-2.5%Nb Pressure Tube Materials

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1. Introduction

The CANDU pressure tube material surrounds the fuel and is exposed to fast neutron radiation from fission. Zr-2.5%Nb alloy pressure tube materials are known to have a low neutron absorption cross section, high strength, and high corrosion resistance[1-3]. This material undergoes delayed hydride cracking (DHC) damage due to absorption of deuterium formed by irradiation hardening and corrosion by fast neutron irradiation in the operating environment[4].

Fast neutron irradiation of a pressure tube causes a dimensional change in the material. The phenomenon in which deformation occurs when neutron irradiation occurs in a stress-free state is called irradiation growth[3]. In addition, the phenomenon in which deformation occurs under stress is called irradiation creep. These two phenomena are called irradiation-induced transformation.

Recently, a concept has been suggested that if the assumption that an atom is a sphere is abandoned and the assumption is that it is an ellipsoid, it can explain the change in length of a material when the arrangement of fast neutron atoms is disturbed[5-8]. This paper tried to explain the irradiation-induced transformation phenomenon based on the arrangement change of ellipsoidal atoms.

Table 1. Chemical composition of D084 Zr-2.5%Nb (wt %).

elements	Zr	Nb	Fe	Ta	Cr	Ti	W	O	H
composition	Balance	2.6%	980 ppm	100 ppm	<100 ppm	<50 ppm	<50 ppm	1100 ppm	<3 ppm

2. Increase in entropy due to changes in atomic arrangement

In discussing the entropy of materials, two essential points must be considered; (a) whether the atom is a sphere, or (b) whether entropy is formed even in pure metals, not alloys. (a) We have assumed that atoms are spheres, but atoms are not spheres. It is only assumed for convenience. (b) Since an atom is not a sphere, it should be considered that entropy is formed according to the arrangement of atoms.

Until recently, entropy only considered the mixing entropy that occurs when atoms A and B are mixed. This is because the definition of entropy proposed by Boltzmann was defined by the mixing of A and B atoms. However, in reality, atoms are not spheres, so entropy is formed as the arrangement of atoms is disturbed. And regardless of Boltzmann's formula, the entropy remaining in the material can be obtained through thermal analysis. Based on this, entropy change can be measured by the second law of thermodynamics (S=Q/T).

Recent research shows in principle that entropy increases and length increases when the atomic arrangement is disturbed by assuming an elliptical shape[5,6]. The entropy formed in a pure metal or alloy has a mixture component and an arrangement component. However, until now, the field dealing with the regular arrangement of atoms in high-concentration alloys has only considered entropy due to the regularity of mixed atoms. For example, the short-range rules dealing with alloys such as Cu_3Au, CuAu, and $CuAu_3$ consider only the entropy of the mixture. However, configuration entropy is an important and broad concept of entropy that is formed not only in pure metals but also in alloys. Moreover, it should be noted that the arrangement entropy component is much larger than the mixing entropy component.

Figure 1 (a) compares the case where the atoms are elliptical and well-ordered, and (b) shows that the area increases when the entropy increases because the atomic arrangement is disordered[5,6]. When the elliptical atoms are arranged, the area occupied by the same atoms increases, which is an effect of increasing entropy due to the disordered atomic arrangement.

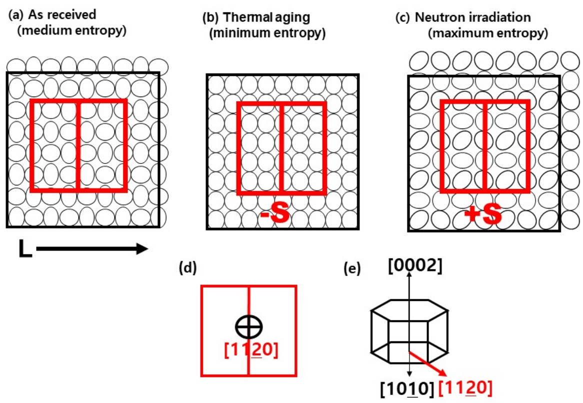

Fig. 1. Schematic illustration of dimensional change in Zr-2.5%Nb pressure tube material with orientation.

3. Length increase due to entropy increase

According to Boltzmann, when A atoms are N_A and N_B atoms are mixed, the entropy in this system is defined by the following equation (1).

$$S = k \text{ in } \omega = k \ln ((N_A+N_B)!/N_A!/N_B!) \quad (1)$$

where S is the entropy, k is the Boltzmann constant, and N_A and N_B are the number of atoms A and B, respectively.

When metal is heated, its temperature rises and absorbs heat energy. When it is cooled, the heat escapes. The heat that escapes at this time is called sensible heat. On the other hand, the form of heat that remains after a phase transformation or requires a diffusion process to escape is called latent heat. If a material in which latent heat remains, such as a cold-processed material, is first thermally analyzed while heating, and the same material is thermally analyzed secondarily, the difference in heat quantity (ΔQ) in these two cases can be known. The definition of entropy, known as the second law of thermodynamics, is expressed as the change in heat before and after a reaction.

$$\Delta S=\Delta Q/T \quad (2)$$

where ΔS is the change in entropy before and after the reaction, ΔQ is the change in heat before and after the reaction, and T is the absolute temperature.

The entropy of a material is important because at least as entropy increases length and volume. Figure 1 shows each of the squares marked with black lines. In the state with the lowest entropy, all atoms are contained within the black line as shown in Figure 1 (b). However, as the entropy increases, the number of atoms outside the square increases, as shown in Figure 1 (a) or Figure 1 (c), which are intermediate states. This explains the physical meaning that volume increases as entropy increases. Atoms are not well explained using the sphere model. To overcome this, an ellipsoidal model was introduced.

Because the CANDU pressure tube contains the nuclear fuel, it is directly exposed to the fast neutron radiation emitted by the fission of the nuclear fuel. When the fast neutrons collide with the atoms in the Zr-2.5%Nb pressure tube, the atoms move and/or rotate. This is the irradiation effect. This process itself increases entropy as it disrupts the atomic arrangement and forms lattice defects. As explained above, an increase in entropy results in an increase in length. This is the cause of irradiation organic transformation. As shown in Figure 1, when the entropy of the pressure tube material increases due to disorganized atoms or lattice defects, the in-reactor deformation phenomenon, in which the length increases, can be understood mechanically.

4. Conclusion

When the fast neutron irradiation of the CANDU pressure tube collides with the atoms of the Zr-2.5%Nb pressure tube, the atoms move and/or rotate. This process itself increases entropy as it disrupts the atomic arrangement and forms lattice defects. This increase in entropy results in an increase in length. This is the cause of the radiation induced deformation, and the radiation induced deformation of the pressure tube can be mechanically explained by using the ellipsoidal atomic model.

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