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Development of Ceramic Humidity Sensor for the Korean Next Generation Reactor

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Abstract

For the Korean Next Generation Reactor(KNGR) development, LBB is considered for the Main Steam Line(MSL) piping inside its containment to achieve cost and safety improvement. To apply LBB concept to MSL, leak sensors highly sensitive to humidity is required. In this paper, a ceramic material, $MgCr_2O_4$-TiO_2 has been developed as a humidity sensor for MSL applications. Experiments performed to characterize the electrical conductivity shows that the conductivity of $MgCr_2O_4$-TiO_2 responds sensitively to both temperature and humidity changes. At a constant temperature below 100℃, the conductivity increases as the relative humidity increases, which makes the sensor favorable for application to the outside of MSL insulation layer. But as temperature increases beyond 100℃, the sensor composition should be adjusted for the application to KNGR is to be made at temperature above 100℃.

I. Introduction

U.S. N.R.C. regulations require the postulation of instantaneous double-ended guillotine breaks (DEGB) in the large pipes For this, all nuclear power plants designed prior to 1983 were required to take into account the dynamic effects of circumferential and/or longitudinal ruptures in main coolant loop(MCL) and branch line piping(BLP)[2]. As results, these piping systems were required to be installed with various protective measures such as pipe whip restraints, snubbers, jet deflectors, jet impingement shields, and oversized component supporters[2]. But these devices may develop the potential for unintended thermoelastic restraint to piping, the accessibility problems associated during in-service inspection and maintenance, the increased radiation exposure to workers, and the loss of plant thermal output. Furthermore, the protection structures involve components and space are costly to install and maintain.

In early 1980's, the U.S. N.R.C. performed studies on the possibility of a double-ended guillotine break(DEGB) or equivalent of the primary reactor coolant piping systems[3]. Analyses showed that the likelihood of detectable leaks is significantly greater than a large pipe break demonstrated and that the overall safety of a nuclear facility is not jeopardized and indeed can be increased by the elimination of large structural elements previously required for dynamic protection against large breaks[3]. In addition to the significant cost savings, there is a net benefit in terms of reduced man-rem exposure during maintenance and in-service inspection because of the greater accessibility of piping and equipment. The U.S. N.R.C. formulated the LBB approaches and acceptance criteria by issuing NUREG-1061 Volume 3[3]. From this, LBB applications were made by utilities as the request for exemption from the DEGB requirement on a case by case basis.

II. Leak detection system requirement for the main steam line

According to NUREG-1061, the following criteria must be satisfied in the piping systems to qualify for LBB application[2,3] ;

(1) Three independent leak detection systems are required and each with three

redundancy should be capable of detecting leakage less than 1.0 gallon per minute for the primary system.

(2) Throughwall leak size cracks(LSC) which are large enough to leak 10 gpm(NUREG-1061 applies a safety factor of 10) must be stable for the postulated load equal to $\sqrt{2}$ times the sum of the normal operation and safe shutdown earthquake(SSE) loads.

(3) Throughwall cracks twice as long the LSC must be stable under the sum of normal operation and SSE loads.

It is clear that leak detection capability is a critical factor in order to apply the LBB concept successfully to a plant. To date, LBB has not been applied to MSL of nuclear power plants that are in operation or under construction. Hence there is no established leak sensors for MSL, which is operated at 73 atm. and 290℃ in KSNPP. After reviewing various leak detection systems which are applicable to MSL within a containment of nuclear power plants, a ceramic humidity sensor has been developed as described herein.

The tentative requirements of the leak sensors for MSL are established in accordance with NUREG-1061[3] as follows;

(1) Leak detection system should be able to detect 1 gpm in the identified leak, and 0.1 gpm in the unidentified leak.

(2) The leak detection systems must have three diversity, each with three redundancy.

III. Development of the ceramic humidity sensor

Conductivity of $MgCr_2O_4$-TiO_2

In dry air condition, the intrinsic conductivity of $MgCr_2O_4$-TiO_2 is dominated by hole[8]. In humid air condition, however, conductivity dan further increase ith the frraction of surface overed by adsorbed water molecule. For this reason, conductivity increases with temperature in dry air. But in humid air, surface adsorption dominate and surface coverage(θ) decreases as T increases, so does the conductivity.

Surface conduction mechanism in humid air

In a solid where bulk ionic conduction dominates, ions can move easily through the lattice upon application of an electric field(migration) or a concentration gradient (diffusion). The mechanism of surface ionic conduction in $MgCr_2O_4-TiO_2$ involves several microprocesses. The migration or diffusion of ions from site to site is usually described by the hopping model as the process of discrete jumps of a particle over an energy barrier. First, a few water vapor molecules chemisorb on the grain surface, as shown in Fig 1, by a dissociative mechanism to form two surface hydroxyl ions; one hydroxyl ion adsorbs on a surface metal ion and the other forms a second hydroxyl with an adjacent surface oxygen ion. The hydroxyl groups, then, dissociate to provide mobile protons. Chromium is believed to be the most active surface metal ion since the Cr^{3+} ion combines with hydroxyl easily providing a mobile proton. The proton can migrate by hopping from site to site on the surface. For H^+ is unstable, if additional water molecule is adsorbed physically on the surface, it forms a H_3O^+ with mobile proton. The hydromium ion in form of H_3O^+ is more stable than H^+. The greater availability of mobile protons can further increase the conductivity. When molecular water is abundant, H_3O^+ ion will be hydrated and stabilized leaving the proton as the dominant charge carrier.[8,9]

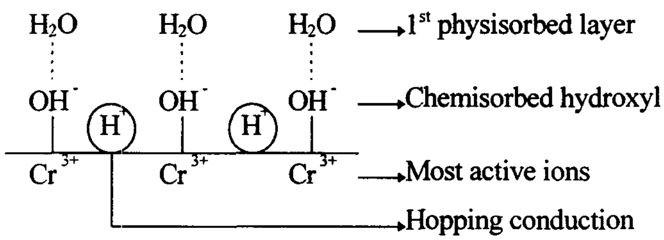

Fig 1. Conduction mechanism in $MgCr_2O_4-TiO_2$

Experimental

Raw materials used in preparing the specimens were MgO, Cr_2O_3, and TiO_2. $MgCr_2O_4$-TiO_2 is composed of 70 mol% $MgCr_2O_4$ and 30 mol% TiO_2. The raw materials were milled with a alumina ball mill in ethanol for 24 hours. After drying, calcination was carried out at 1100℃ for 10 hours. Then, X-ray diffraction(XRD) was performed with model M18XHF22 XRD analyzer to verify that the calcined material has single phase. After the verification, the powder mixture calcined at 1100℃ was sieved. Then the powder mixture was pressed into a rectangular form at a pressure of 32 MPa, and with cold-isostatic pressing(CIP) at a pressure of 100 MPa. Finally, $MgCr_2O_4$-TiO_2 was sintered at 1400℃ for 10 hours in air.

Conductivity measurements

A static 1-liter autoclave was used as an environmental chamber for which temperature and humidity were controlled. Four-probe DC resistance measurement method was chosen with using Ni wires for both current supply and voltage drop measurement.

Keithley model 220 and Keithley model 617 were used as the current source and electrometer for measuring voltage, respectively. The autoclave was evacuated by mechanical vacuum pump to remove possible humidity in atmosphere and the inserted test water. Controlled amount of water waas then inserted through a micrometer in order to achieve the desired humidity. The resistance was measured with time using computerized data acquisition system.

IV. Results and discussion

Results

Tests were performed both in the dry air and in the humid condition. Resistivity measured in the dry air shows that resistivity decreases as

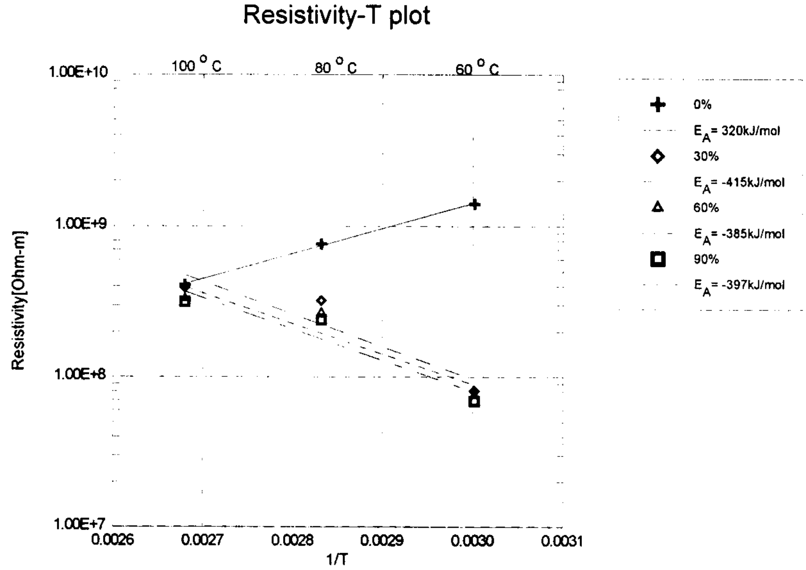

Fig. 2 Resistivity change with changing humidity and 1/T

temperature increases. Resistivity versus 1/T plot is represented in Fig 2, for both varying temperature and humidity condition. Since the conductivity is the reciprocal of the relative humidity, each curve has the opposite sign of slopes which is proportional to ΔE_A as described below.

$$\sigma = \frac{1}{\rho} = \sigma_0 \exp(-\frac{\Delta E_A}{RT}) = \frac{1}{\rho_0 \exp(\frac{\Delta E_A}{RT})}$$

The activation energy is determined by the least square fittings for each measurement conditions from data in Fig. 2. Each value is as follows,

Table 1. Activation energy for each conditions

condition	0% (dry air)	30%	60%	90%
ΔE_A (kJ/mole)	31.8	-41.4	-38.7	-39.7

Discussion on sensor behavior

Ceramics, if it were in the dry air, the conductivity would increase as temperature increases, as shown below.

$$\sigma \propto \exp(-\frac{\Delta E_A}{RT})$$

Temperature dependency of conductivity appears to be the characteristics of intrinsic conduction behavior. When MgO is added to $MgCr_2O_4$, conductivity would increase which can be explained by controlled-valency theory. The increased hole concentrations resulting from incorporation of MgO are responsible for the increased conductivity of $MgCr_2O_4$. This indicates that $MgCr_2O_4$ is a p-type semiconductor[8]. In the humid condition, the conductivity of the ceramic would increase as relative humidity increases at a given temperature. But as temperature increases, surface coverage θ decreases, then the conductivity also decreases at the fixed humidity. That is, in the same temperature, as relative humidity increases, the conductivity of the ceramic increases. The conductivity decreases as temperature increases, as shown below[14];

$\theta = \frac{bP}{1+bP}$; fraction of surface coverage

where $b = \frac{k_a}{k_d} \exp(\frac{\Delta H_{phys}}{RT})$

V. Conclusion

For LBB application to MSL of KNGR, ceramic-based humidity sensors are suggested as a leak detection system with adequate properties. Main steam line at KNGR is operated at 290℃ with insulation sheath filled with glassfiber. Developed ceramic humidity sensor has a operation range below 100℃. Therefore we can apply it where temperature is below 100℃. Temperature of the insulation sheath is about 50℃. Therefore, as the first option, we should apply sensor to the position below 100℃ inside the insulation tube. Second option is to decrease intrinsic conductivity or increase conductivity when there are adsorbed water molecules. For this reason, further development of the sensor above 100℃ is underway.

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