Development of High-Performance Electric Strain Gage for High-Pressure Hydrogen Gas Use

Takashi Matsuo[1, a], Hiroaki Furukawa[2, b], Katsuo Seki[2, c], Kiyoaki Shimizu[2, d], Shogo Watanabe[1, e] and Saburo Matsuoka[3, 4 f]

[1] Hydrogen Energy Test and Research Center (HyTReC),
915-1, Tomi, Itoshima-shi, Fukuoka, 819-1133 Japan

[2] KYOWA ELECTRONIC INSTRUMENTS CO., LTD.,
3-5-1, Chofugaoka, Chofu-shi, Tokyo, 182-8520 Japan

[3] The Research Center for Hydrogen Industrial Use and Storage (HYDROGENIUS),
National Institute of Advanced Industrial Science and Technology (AIST),
744, Moto-oka, Nishi-ku, Fukuoka-shi, Fukuoka, 819-0395 Japan

[4] International Institute for Carbon Neutral Energy Research (WPI-I^{2}CNER), Kyushu University,
744, Moto-oka, Nishi-ku, Fukuoka-shi, Fukuoka, 819-0395 Japan

[a] tmatsu@hytrec.jp, [b] furukawa@kyowa-ei.co.jp, [c] seki-k@kyowa-ei.co.jp,
[d] shimizu-ki@kyowa-ei.co.jp, [e] swata@hytrec.jp, [f] saburo.matsuoka.121@m.kyushu-u.ac.jp

Keywords: Strain gage, High-pressure hydrogen gas, Electrical resistance, Hydrogen invasion, hydrogen content, hydrogen diffusion.

Abstract The changes in output of Cu-Ni, Ni-Cr and Fe-Cr-Al strain gages in 90 MPa hydrogen gas and 90 MPa nitrogen gas were investigated to reveal the basic principles of electrical resistance strain gages for high-pressure hydrogen gas use. In addition, the relationships between the electrical resistance and the hydrogen content of metallic specimens exposed to 100 MPa hydrogen gas at 270°C for 40 h were investigated to clarify the effects of hydrogen on the electrical resistance of metal foils (Cu-Ni, Ni-Cr and Fe-Cr-Al), gage lead (pure copper: Cu), and solder (lead-free solder: Sn-Ag-Cu) used in the strain gages. The output changes of the Cu-Ni gage and the Ni-Cr gage in 90 MPa hydrogen gas were much larger than those in 90 MPa nitrogen gas. On the other hand, the Fe-Cr-Al gages showed almost the same output changes in 90 MPa hydrogen gas and 90 MPa nitrogen gas. These results suggested that the strain gage output was affected by both of the pressure of the gas and the invasion of hydrogen for Cu-Ni and Ni-Cr gages, while the output was affected only by the pressure of the gas for Fe-Cr-Al gage. This suggestion was supported by the hydrogen content measurement and electrical resistance measurement of the specimens exposed to 100 MPa hydrogen gas. The electrical resistance of Cu-Ni and Ni-Cr specimens was changed by exposure to hydrogen gas, because the large amount of hydrogen invaded into the specimens. On the other hand, the resistance of Fe-Cr-Al specimen was not changed by exposure to hydrogen gas, because almost no hydrogen invaded into the specimen. In addition, almost no hydrogen invaded into the copper and lead-free solder specimens, when they were exposed to hydrogen gas. It was concluded from these results that Fe-Cr-Al metal foil sensor, pure copper gage lead and solder joint are effective for the strain gage for high-pressure hydrogen gas use.

Introduction

The development of fuel-cell vehicles and hydrogen stations is demanded to solve global warming and other energy issues. The easiest way of transporting and storing hydrogen is to keep it in the form of high-pressure gas. Therefore, the strength evaluation of parts and components of hydrogen energy systems is essential for ensuring the safety of the systems. The Research Center for Hydrogen Industrial Use and Storage in Japan (HYDROGENIUS) has 1 MPa to 120 MPa hydrogen fatigue-testing machines. Electrical resistance strain gages are used in load cells and clip-on gages of the machines. Hydrogen Test and Research Center in Japan (HyTReC) is an experimental facility for the strength evaluation of parts and components of hydrogen energy systems. In HyTReC, strain gages are being used to measure the strains of parts and components in high-pressure hydrogen gas of up to 99 MPa.

Figure 1 [1] is a schematic illustration of an electrical resistance strain gage. Metals are used for the foil (sensor), joint and lead. As a part is deformed, the strain gage attached to the part is deformed, causing the change in the electrical resistance of the metallic foil. Strain is calculated from the change in resistance as:

$$\varepsilon=(1/K\mathrm{s})\cdot(\Delta R/R) \tag{1}$$

where ε is strain, Ks is gage factor determined by the foil metal, and R is electrical resistance. Therefore, to ensure the accuracy of strain measurement in high-pressure hydrogen gas, it is necessary to understand the effects of high-pressure hydrogen gas on the electrical resistances of not only the foil, but also joint and lead. Mechanical pressure is known to decrease the electrical resistance of thin metal wires [2, 3]. The change in electrical resistance of thin metallic wires in high-pressure gas has also been measured [4-6]. For example, the electrical resistance of Pt wire decreased as the gas pressure increased in high-pressure hydrogen, nitrogen and helium gases [4]. On the other hand, it was reported that the electrical resistance of vapor-deposit film of pure iron decreased by adsorbing hydrogen on the surface of the film [7]. Y. Manabe et al. reported that the outputs of Cu-Ni and Fe-Cr-Al foil gages under unloading condition decreased in 98 MPa hydrogen gas [8]. These findings suggest that both the pressure of the gas and the invasion of hydrogen affect the electrical resistance of metals in high-pressure hydrogen gas.

In this study, to establish the basic principles of the electrical resistance strain gage for high-pressure hydrogen gas use, the outputs of Cu-Ni, Ni-Cr and Fe-Cr-Al gages under the unloading condition (zero point changes) in 90 MPa hydrogen gas and 90 MPa nitrogen gas were measured. In these gages, metal foils are Cu-Ni, Ni-Cr and Fe-Cr-Al, the joints are lead-free solder (Sn-Ag-Cu), and the gage leads are copper wire (0.12 to 0.16 mm in diameter). In 90 MPa hydrogen gas, both the pressure of the gas and the hydrogen invasion should affect the gage output, that is, the electrical resistance of the metals in the gage. On the other hand, in 90 MPa nitrogen gas, the electrical resistance should be affected only by the pressure of the gas. Then, the effects of hydrogen invasion on electrical resistance of the metals were investigated by exposing Cu-Ni, Ni-Cr and Fe-Cr-Al plates and pure copper wire to 100 MPa hydrogen gas at 270°C for 40 h and measuring their electrical resistance. For these metals and lead-free solder, in addition, the analysis of microstructures and the measurements of hydrogen content and hydrogen diffusion coefficient were conducted.

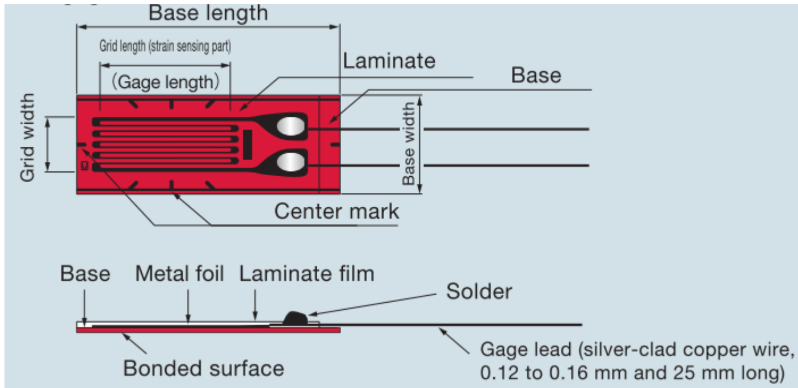


Fig.1 Schematic illustration of strain gage [1].

Experimental Procedures

Strain Gage Output Measurements in 90 MPa Hydrogen Gas and 90 MPa Nitrogen Gas The strain output measurements in 90 MPa hydrogen and 90 MPa nitrogen gases were conducted, using a Cu-Ni gage (foil thickness: 6 μm), a Ni-Cr gage (5 μm) and Fe-Cr-Al gages (5 and 15 μm). The temperature of the gases was maintained constant at 25°C. In three kinds of gages, metal foils are Cu-Ni, Ni-Cr and Fe-Cr-Al, gage leads are pure copper (Cu), and joints are lead-free solder (Sn-Ag-Cu). Table 1 shows the electric resistivity ρ (specific resistance) and temperature coefficient λ of electrical resistance of the materials. Microstructure analysis using EBSD (Electron Back Scatter Diffraction) showed that Cu-Ni and Ni-Cr were face centered cubic (FCC) and Fe-Cr-Al was body centered cubic (BCC). Cu is face centered cubic. It was reported that Sn-Ag-Cu solder consisted of Sn and intermetallic compound of Sn, Ag and Cu [9]. Sn is cubical crystal.

Table 1 Electric resistivity (Ωm) and temperature coefficient (K^{-1}).

	Electric resistivity, ρ	Temperature coefficient, λ
Cu-Ni	4.90×10^{-7}	4.8×10^{-5}
Ni-Cr	1.33×10^{-6}	6.0×10^{-5}
Fe-Cr-Al	1.45×10^{-6}	-2.8×10^{-5}
Cu	1.67×10^{-8}	-
Sn-Ag-Cu	-	-

Electrical Resistance and Hydrogen Content Measurements of Specimens Exposed to 100 MPa Hydrogen Gas To clarify the change in strain gage output in 90 MPa hydrogen gas, Cu-Ni and Fe-Cr-Al thin plates (250 μm thickness, 1 mm width and 100 mm length), Ni-Cr thin plate (50 μm thickness, 1 mm width and 100 mm length) and copper wire with a purity of 99.999 % (250 μm diameter and 100 mm length) were exposed to 100 MPa hydrogen gas at 270°C for 40 h. Under this hydrogen gas exposure condition, the hydrogen content invaded into the specimens was saturated. The electrical resistance of the specimens exposed to hydrogen gas was measured in an ambient atmosphere at room temperature by using the 4-wire resistance measurement method.

To assess the amount of hydrogen that remained in the specimens during electrical resistance measurement, specimens for residual hydrogen content measurement were exposed to 100 MPa hydrogen gas together with the specimen for electrical resistance measurement. The specimens for residual hydrogen content measurement were left in an ambient atmosphere at room temperature near the specimen for electrical resistance measurement. At arbitrary time points during resistance measurement, the specimens for residual hydrogen content measurement were subjected to residual hydrogen content measurement. The residual hydrogen content was measured using thermal desorption spectroscopy (TDS). The rate of temperature rise was 0.33°C/s. The dimensions and shapes of the specimens were thin square plates of 7 mm × 7mm × 250 μm for Cu-Ni and Fe-Cr-Al, thin square plates of 7 mm × 7 mm × 50 μm for Ni-Cr, and thin copper wire of 250 μm diameter and 157 mm length.

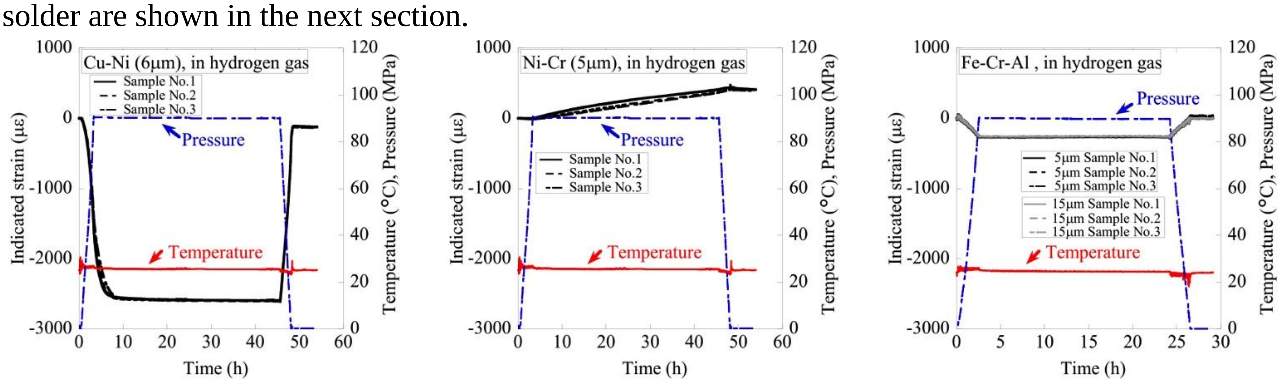
The hydrogen content and hydrogen diffusion coefficient were also measured for Cu-Ni, Ni-Cr, Fe-Cr-Al and pure copper specimens exposed to 100 MPa hydrogen gas. The conditions of exposure, the methods of measuring hydrogen content, and the shapes and dimensions of the specimens were the same as those for residual hydrogen content measurement. Only the hydrogen content measurement was conducted for the lead-free solder. The solder wire (1mm diameter) was exposed to 100 MPa hydrogen gas at 85°C for 40 h.

Results and Discussion

Strain Gage Output Changes in 90 MPa Hydrogen Gas and 90 MPa Nitrogen Gas The changes in strain gage outputs in 90 MPa hydrogen gas are shown in Fig. 2. In the Cu-Ni gage, the output levels decreased with increasing hydrogen gas pressure. About 8 h after the test started, the output saturated at around -2600 με. When the pressure of hydrogen gas was decreased, the output increased and returned to the zero level. On the other hand, the Ni-Cr gage showed that the output gradually increased in 90 MPa hydrogen gas for about 43 h. When the pressure of hydrogen gas was decreased, the output started to decrease. The change in output of the Fe-Cr-Al gages was similar to that of the Cu-Ni gage. However, the change in output of the Fe-Cr-Al gages between zero point and the saturated strain ε_S was much smaller than that of the Cu-Ni gage: ε_S = -300 με for the Fe-Cr-Al gage and ε_S = -2600 με for the Cu-Ni gage. Two Fe-Cr-Al gages with the different thicknesses (5 μm and 15 μm) were tested. No difference between two gages was observed. Manabe et al. have reported similar results for Cu-Ni and Fe-Cr-Al gages [8].

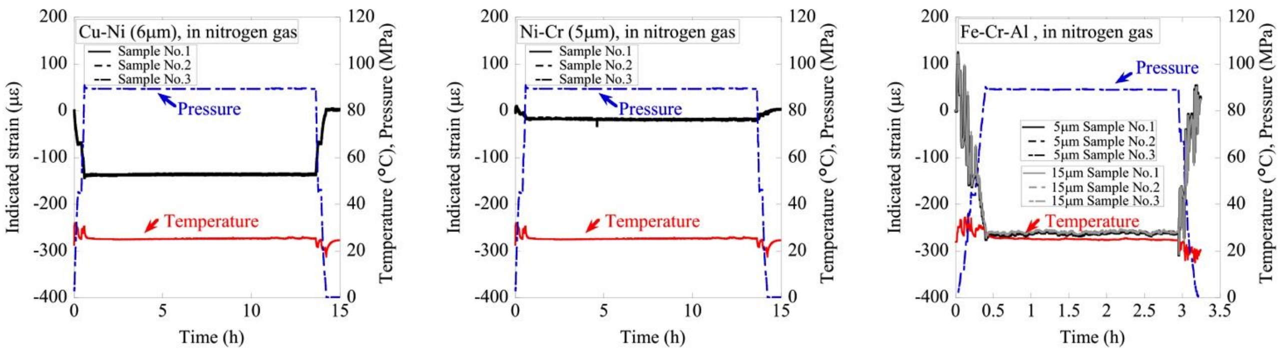
Figure 3 shows the changes in the outputs of the strain gages in 90 MPa nitrogen gas. In all gages, the output was decreased with increasing nitrogen gas pressure, reached saturation after the pressure reached 90 MPa. Then, the outputs returned to the zero level after decompression. The saturated strain ε_S in 90 MPa nitrogen gas depended on the gage. The saturated strain ε_S was -150, -10, and -270 με for the Cu-Ni, Ni-Cr and Fe-Cr-Al gages, respectively.

Comparing the changes in strain gage outputs between Fig.2 and Fig.3, the changes in outputs between zero point and saturated strain of the Cu-Ni and Ni-Cr gages in 90 MPa hydrogen gas were larger than those in 90 MPa nitrogen gas. This suggests that both the pressure of the gas and invasion of hydrogen affected the outputs of the Cu-Ni and Ni-Cr gages. On the other hand, the saturated strains of the Fe-Cr-Al gages were almost the same in hydrogen and nitrogen gases. This suggests that hydrogen had almost no effect on the outputs of the Fe-Cr-Al gages. Therefore, the hydrogen invasion properties of Cu-Ni, Ni-Cr and Fe-Cr-Al foils, Cu gage lead, and Sn-Ag-Cu solder are shown in the next section.



(a) Cu-Ni (b) Ni-Cr (c) Fe-Cr-Al

Fig.2 Output of strain gage in 90 MPa hydrogen gas.



(a) Cu-Ni (b) Ni-Cr (c) Fe-Cr-Al

Fig. 3 Output of strain gage in 90 MPa nitrogen gas.

Hydrogen Invasion Properties The hydrogen desorption profiles of specimens exposed to 100 MPa hydrogen gas at 270°C for 40 h are shown in Fig. 4. A much larger amount of hydrogen invaded into Cu-Ni (about 120 mass ppm) and Ni-Cr (about 150 mass ppm) compared to Fe-Cr-Al (about 2 mass ppm). Cu-Ni and Ni-Cr are FCC metals, and Fe-Cr-Al is BCC metal. Cu is FCC metal. However, only about 0.25 mass ppm of hydrogen invaded into the Cu. In addition, almost no hydrogen invaded into the solder. The amount of hydrogen that invaded into the solder after 40 h exposure to 100 MPa hydrogen gas at 85°C was only about 0.07 mass ppm.

Figure 5 is Arrhenius plot of hydrogen diffusion coefficient. As shown in the figure, the hydrogen diffusion coefficient was the largest in Fe-Cr-Al, followed by Cu-Ni, Ni-Cr, and Cu.

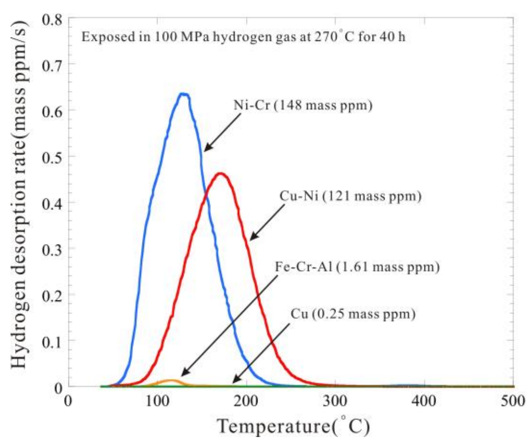


Fig. 4 Hydrogen desorption profiles of Cu-Ni, Ni-Cr, Fe-Cr-Al and Cu exposed in 100 MPa hydrogen gas at 270 °C for 40 h

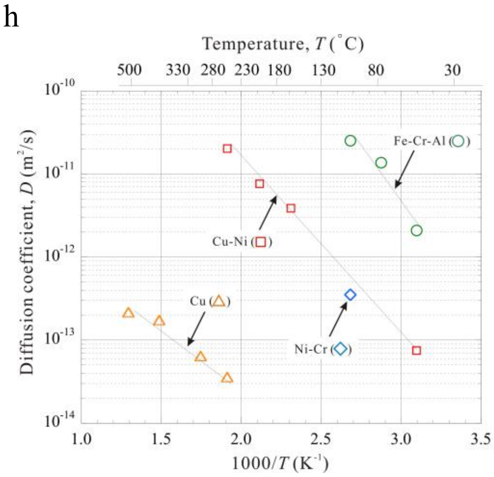
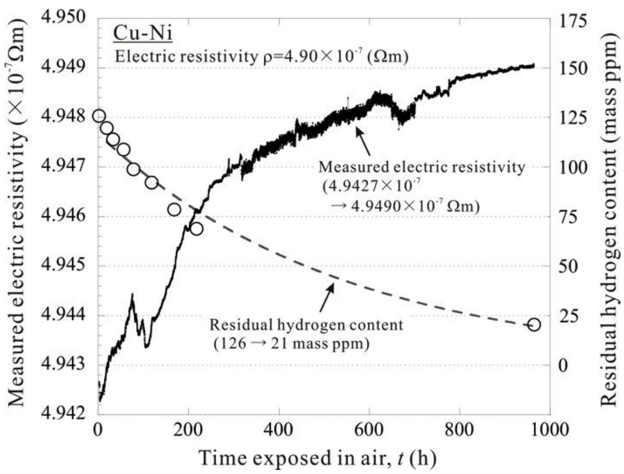


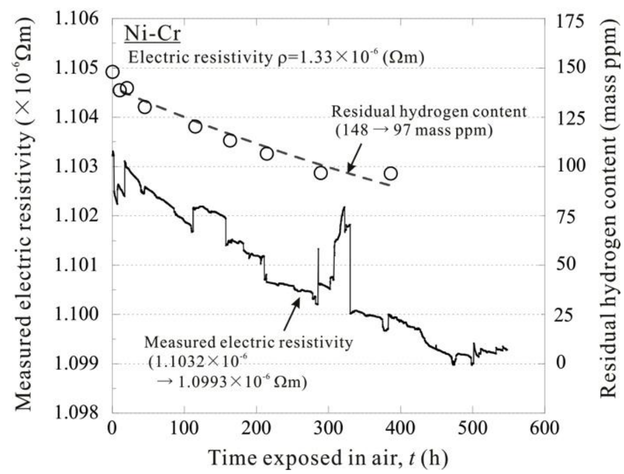
Fig. 5 Arrhenius plot of hydrogen diffusion coefficient of Cu-Ni, Ni-Cr, Fe-Cr-Al and Cu.

Effects of Hydrogen Invasion on Electrical Resistance The effects of hydrogen invasion on electrical resistance were investigated, using the specimens exposed to 100 MPa hydrogen gas. Figure 6 plots the electrical resistance and residual hydrogen content against time during which the specimens were left in air. In Cu-Ni specimen, the electric resistivity increased from 4.9427×10^{-7} Ωm to 4.9490×10^{-7}Ωm, as the residual hydrogen content $C_{H,\,R}$ decreased from 126 mass ppm to 21 mass ppm. That is, the decrease in electrical resistance was caused by hydrogen invasion. In Ni-Cr specimen, the electric resistivity decreased from 1.1032×10^{-6} Ωm to 1.1000×10^{-6} Ωm, as $C_{H,\,R}$ decreased from 148 mass ppm to 97 mass ppm. On the contrary to Cu-Ni, the electric resistance of Ni-Cr increased by hydrogen invasion. The electric resistivity in Cu-Ni and Ni-Cr, which are face centered cubic, changed largely, because a large amount of hydrogen invaded into the metals. The changes in electrical resistance by hydrogen invasion were consistent with the strain gage output changes in 90 MPa hydrogen gas in Fig. 2.

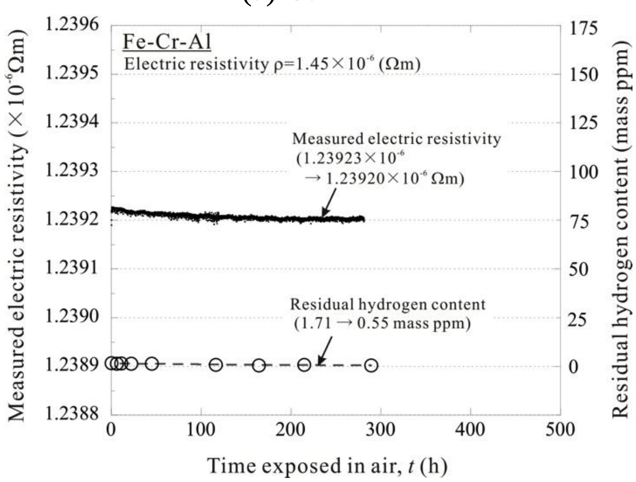
On the other hand, only a small amount of hydrogen invaded into Fe-Cr-Al, which is body centered cubic. Therefore, in Fe-Cr-Al specimen, the electric resistivity was decreased only slightly from 1.23923×10^{-6} Ωm to 1.23920×10^{-6} Ωm, as $C_{H,\,R}$ decreased from 1.71 mass ppm to 0.55 mass ppm. This change in measured electric resistivity of Fe-Cr-Al specimen exposed to 100 MPa hydrogen gas was so small. These results agreed with the changes in outputs of the Fe-Cr-Al gages in 90 MPa hydrogen gas (Fig. 2) and 90 MPa nitrogen gas (Fig. 3). The Fe-Cr-Al gages in 90 MPa hydrogen gas were affected by only the pressure of the gas.



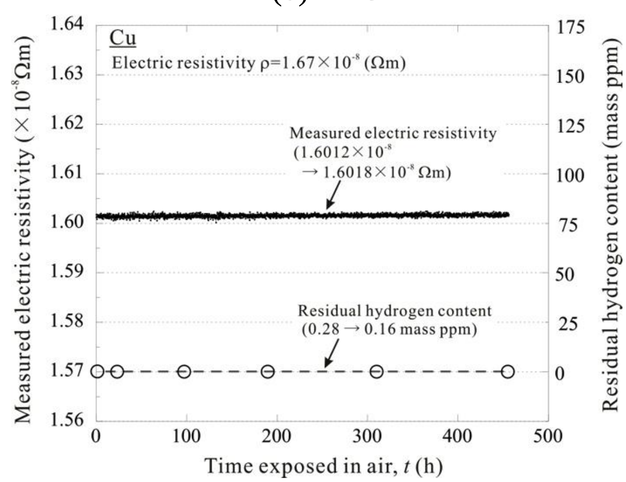
(a) Cu-Ni



(b) Ni-Cr



(c) Fe-Cr-Al



(d) Cu

Fig. 6 Relationship between electric resistivity and residual hydrogen content.

Although, pure copper used for the lead is face centered cubic, the amount of invaded hydrogen was small. Thus, the electric resistivity increased very slightly from 1.6012×10^{-8} Ωm to 1.6018×10^{-8} Ωm, as $C_{H, R}$ changed only slightly from 0.28 mass ppm to 0.16 mass ppm. Almost no hydrogen invaded into the solder, and therefore, the change in electrical resistance in the solder is considered to be almost zero.

Electric Resistance Strain Gage for High-Pressure Hydrogen Gas Use Metals that are implementable for the foil (sensor), lead and joint of an electric resistance strain gage for use in high-pressure hydrogen gas are summarized below.

(1) Foil Metals to be used for the foil of an electric resistance strain gage for use in high-pressure hydrogen gas should (a) not allow a large amount of hydrogen to invade in high-pressure hydrogen gas, (b) have a large hydrogen diffusion coefficient, and (c) undergo small changes in electrical resistance by high pressure of the gas. The properties (a) and (b) are related to the changes in electrical resistance by the hydrogen invasion. In terms of (a), a large amount of hydrogen invaded into Cu-Ni and Ni-Cr (Fig. 4). As a result, electrical resistance changed remarkably by the hydrogen invasion in Cu-Ni and Ni-Cr (Fig. 6). On the other hand, only a small amount of hydrogen invaded into Fe-Cr-Al and thus change in electrical resistance of Fe-Cr-Al was much smaller than that of Cu-Ni and Ni-Cr. Therefore, Fe-Cr-Al is a superior foil metal for an electric strain gage for high-pressure hydrogen gas use compared to Cu-Ni and Ni-Cr. In terms of (b), Ni-Cr has a small hydrogen diffusion coefficient. Electrical resistance of Ni-Cr specimen changed gradually when Ni-Cr specimen was left in an ambient atmosphere (Fig. 6). Reflecting the change in electrical resistance of Ni-Cr specimen, the output of the Ni-Cr gage changed over a long period of time in 90 MPa hydrogen gas (Fig. 2). These results suggest that Ni-Cr has inferior properties compared to Cu-Ni and Fe-Cr-Al, which have large hydrogen diffusion coefficients. In terms of changes in electrical resistance by the gas pressure in (c), Fe-Cr-Al showed the largest changes in strain gage output in 90 MPa nitrogen gas (Fig. 3). However, considering the changes in output of three gages in Fig. 2, Fe-Cr-Al was concluded to be superior to Cu-Ni and Ni-Cr as the foil for strain gages for high-pressure hydrogen gas use. Foil metals superior to Fe-Cr-Al will be found by searching for foil metals of strain gages for high-pressure hydrogen gas use from the viewpoints of (a), (b) and (c). The crystal structure of metal may be a key point in the search for foil metals for strain gages to be used in high-pressure hydrogen gas. Cu-Ni and Ni-Cr are face centered cubic, and Fe-Cr-Al is body centered cubic. Needless to say, the electric resistivity (specific resistance) and temperature coefficient of electrical resistance shown in Table 1 are also the important properties for foil metals of strain gages for high-pressure hydrogen gas use.

(2) Lead and joint Cu-Ni and Ni-Cr gages are commercial strain gages to be used in an ambient atmosphere at room temperature. These gages have leads consisting of pure copper and joints consisting of lead-free solder. Almost no hydrogen invaded into pure copper (Fig. 4). As a result, no changes in electrical resistivity occurred in pure copper (Fig. 6). The lead-free solder also showed almost no hydrogen invasion, therefore, it is concluded that pure copper and lead-free solder are implementable for the lead and joints in the strain gage for high-pressure hydrogen gas use.

Conclusions

In this study, the changes in outputs of Cu-Ni, Ni-Cr and Fe-Cr-Al strain gages in 90 MPa hydrogen gas and 90 MPa nitrogen gas were investigated to establish the basic principles of strain gages for use in high-pressure hydrogen gas. The effects of hydrogen on the electrical resistance of foil metals (Cu-Ni, Ni-Cr, Fe-Cr-Al), lead (pure copper: Cu), and joint (lead-free solder: Sn-Ag-Cu) were investigated using specimens exposed to 100 MPa hydrogen gas at 270°C for 40 h. The conclusions are summarized below.

(1) Cu-Ni and Ni-Cr gages showed different output changes between 90 MPa hydrogen gas and 90 MPa nitrogen gas. In 90 MPa hydrogen gas, the gages were affected by both the pressure of the gas and the hydrogen invasion. Fe-Cr-Al gages showed no difference in output changes in nitrogen and hydrogen gases. The outputs of the Fe-Cr-Al gages were affected only by the pressure of the gas.
(2) Cu-Ni and Ni-Cr are face centered cubic, and a large amount of hydrogen invaded into the specimens when they were exposed to 100 MPa hydrogen gas. On the other hand, Fe-Cr-Al is body centered cubic, and only a small amount of hydrogen invaded into the specimen. Almost no hydrogen invaded into pure copper and lead-free solder specimens. The hydrogen diffusion coefficient was the largest in Fe-Cr-Al specimen, followed by Cu-Ni, Ni-Cr, and pure copper specimens.
(3) In Cu-Ni specimen, electrical resistance decreased by hydrogen invasion. That is, the electrical resistance increased as residual hydrogen content decreased. In Ni-Cr specimen, the electrical resistance increased by hydrogen invasion. In Fe-Cr-Al and pure copper specimens, into which almost no hydrogen invaded, almost no changes in electrical resistance were occurred by hydrogen invasion.
(4) The above results suggest that Fe-Cr-Al, pure copper and lead-free solder are appropriate metals for the foil (sensor), lead and joint, respectively, of strain gages for high-pressure hydrogen gas use.

Acknowledgments
This research is supported by the NEDO Fundamental Research Project on Advanced Hydrogen Science (2006 to 2012). The authors gratefully acknowledge the support of the International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), sponsored by the Japanese Ministry of Education, Culture, Sport, Science and Technology. The authors acknowledge KYOWA ELECTRONIC INSTRUMENTS CO., LTD. for preparing the specimens and discussions.

References

[1] Information on http://www.kyowa-ei.co.jp/eng/support/technical/tecnical_info/strain_gages/gages/principle_of_strain-gages.html
[2] P. W. Bridgman: Proceedings of the American Academy of Arts and Science Vol.52, No.9 (1917), pp. 573 – 646.
[3] H. D. Stromberg and D. R. Stephens: J. Phys. Chem. Solids Vol.25 (1964), pp. 1015 – 1022.
[4] S. Moroe: Doctoral Dissertation (2011), p. 72.
[5] S. Moroe, P. L. Woodfield, K. Kimura, M. Kohno, J. Fukai, M. Fujii, K. Shinzato and Y. Takata: Int. J. Thermophys. Vol.32, No.9 (2011), pp. 1887 – 1917.
[6] H. M. Roder and R. A. Perkins: Journal of Research of the National Institute of Standards and Technology Vol.94, No.2 (1989), pp. 113 – 116.
[7] M. Aramaki and Y. Hayashi: J. Japan Inst. Metals Vol.50, No.3 (1986), pp. 298 – 303.
[8] Y. Manabe and Y. Miyashita: KOBE STEEL ENGINEERING REPORTS Vol.58, No.2 (2008), pp. 19 – 23.
[9] H. Takao, A. Yamada and H. Hasegawa: R&D Review of TOYOTA CRDL Vol.35, No.2 (2000), pp. 39 – 46.