Title	Hydrogen-induced Internal Friction of Duplex Stainless Steels
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Citation	Transactions of JWRI. 2007, 36(2), p. 61-66
Version Type	VoR
URL	https://doi.org/10.18910/9299
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Transactions of JWRI, Vol. 36 (2007), No. 2

Hydrogen-induced Internal Friction of Duplex Stainless Steels†

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Abstract

Hydrogen behavior in duplex stainless steel and its weld metals was investigated by means of internal friction measurement. The internal friction measurements were conducted over a temperature range from 77 K to 373 K by using an inverted torsion pendulum for a frequency of 1.5 Hz. A significant peak appeared at 245K after hydrogen charging of the base metal and the weld metals. The peak height increased with increasing hydrogen concentration. The peak was associated with hydrogen in austenite. As the specimens were heated at 1023 K for various times, sigma phase consisting of Fe-Cr compound precipitated in the ferrite at the ferrite/austenite interface. The broadening of the internal friction peak at 245 K and scattering of internal friction value took place after hydrogen charging for the sigma phase precipitation. Overlapped two peaks of the peak associated with hydrogen in austenite and the peak associated with hydrogen in sigma phase were observed. The precipitation of sigma phase suppressed the diffusion of hydrogen in duplex stainless steel and the weld metal. It is considered that hydrogen was dissolved in the sigma phase on the basis of the hydrogen measurement and internal friction measurement.

KEY WORDS: (Duplex stainless Steel) (Internal Friction) (Hydrogen) (Weld Metal) (Austenite) (Snoek Peak) (Sigma Phase)

1. Introduction

Duplex stainless steels having a ferritic-austenitic mixed microstructure combines the toughness, pitting corrosion resistance and stress corrosion cracking resistance of ferrite and in addition, have an order of double the yield strength as compared with common austenitic stainless steels, and are thus being used extensively in the oil, gas, and petrochemical applications, particularly where chlorides are present [1-5].

However, it has been reported that hydrogen embrittlement occurs in the ferrite phase at low hydrogen concentrations [6, 7] in both base metals and weld metals of the duplex stainless steels.

Furthermore, the precipitation of the sigma phase consisting of Fe-Cr compound occurs very quickly at temperatures between 923 K and 1323 K [1-5]. Although these two kinds of phenomenon will occur simultaneously in duplex stainless steels, the effects of sigma . phase on hydrogen behavior have not been reported. Consequently, it is important to clarify the effect of the sigma phase on hydrogen behavior.

The internal friction technique generally provides valuable information about hydrogen mobility and concentration in austenitic steels. Peterson et al [8] first observed the internal friction peak of type 310 austenitic stainless steel containing hydrogen. Asano et al [9] observed an internal friction peak located at about 300K for frequencies of 500 Hz. This peak was interpreted in terms of the reorientation of paired hydrogen atoms in the applied stress field.

Internal friction effects due to hydrogen of fcc systems have been reviewed [9-11], but the effect of sigma phase on hydrogen behavior in the case of duplex stainless steel base metal and the weld metal [1, 2].has not been clarified.Therefore, the purpose of this research is to investigate the effect of sigma phase on hydrogen behavior in duplex stainless steel and the weld metals by using internal friction measurement.

2. Experimental

The base metal used in this investigation is SUS329J1 duplex stainless steel with chemical composition as shown in **Table 1**. For the weld metals, the SMAW 329J4L (DP3) welding rod and SMAW 329J3L (DP8) welding rod with diameter of 3.2 mm were employed. The chemical compositions of the welding

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† Received on December 14, 2007

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

Table 1 Chemical composition of duplex stainless steel (mass %).

Material	C	Si	Mn	P	S	Ni	Cr	Mo	N
SUS329J1	0.014	0.52	0.31	0.030	0.006	4.64	24.92	1.81	0.14

Table 2 Chemical compositions of SMAW electrodes (mass %)

Grade	C	Si	Mn	P	S	Ni	Cr	Mo	N	Cu	W
329J4L(DP3)	0.035	0.42	0.80	0.021	0.005	8.8	25.4	2.98	0.15	0.49	0.28
329J3L(DP8)	0.027	0.83	0.87	0.024	0.006	8.5	22.2	3.21	0.12	0.10	——

rods are shown in **Table 2**. The welding pad was made using sealed metal arc welding (SMAW). Welding current was 120 A, Arc voltage was 20 V, and Heat Input was 9000 J/cm. The internal friction specimens of weld metals were taken from the weld pads.

Microstructure observation was performed using electrolytic etching in 10 kmol/m^3 KOH solution. This etching technique colored sigma phase brown, colored ferrite blue and colored austenite white (in case of monochrome photography, the etching technique colored sigma phase black, colored ferrite gray and colored austenite white).

The size of the internal friction specimen was 115.0 mm long, 4.8 mm wide and 0.8 mm thick. The internal friction specimens and X-ray specimens were cathodically charged at room temperature in a 5% sulphuric acid solution containing sodium arsenate as a catalytic agent promoting hydrogen entry. The current density was 200 A/m^2.

The measurement of total hydrogen content in the charged specimens was performed at 1973 K by using a high sensitive hydrogen analyzer. The specimen size for this was the same as the internal friction specimen. X-ray diffraction was employed to confirm precipitation of sigma phase with Kα radiation of copper target.

The internal friction measurement was conducted over a temperature range from 77 K to 373 K by using an inverted torsion pendulum at a frequency of about 1.5Hz. The schematic illustration of the internal friction apparatus is shown in **Fig. 1**. The amplitude of free damping is A_0 in the early period and An in the nth cycle. Internal friction value Q^{-1} was calculated by the following equation.

$$Q^{-1} = [-1/(n\pi)] \ln (A_n/A_0) \qquad (1)$$

3. Results and Discussion

Duplex stainless steel has a microstructure consisting of elongated austenite along the rolling direction in the ferrite matrix. The volume fraction of the ferrite was approximately 55%, and the austenite was approximately 45%. Hydrogen can diffuse easily through the continuous ferrite when hydrogen charging is carried out[12, 13]. The internal friction values (Q^{-1}) obtained for SUS329J1 base metal were plotted against absolute temperature in **Fig. 2**.

Without hydrogen charging, an internal friction peak was hardly observed. The internal friction peak appeared at 245 K after hydrogen charging. The peak height increased with increasing hydrogen charging time. The symmetrical peak is considered to be due to hydrogen in the austenite.

The temperature range of internal friction curves plotted was between 150 K and 350 K, because no peak

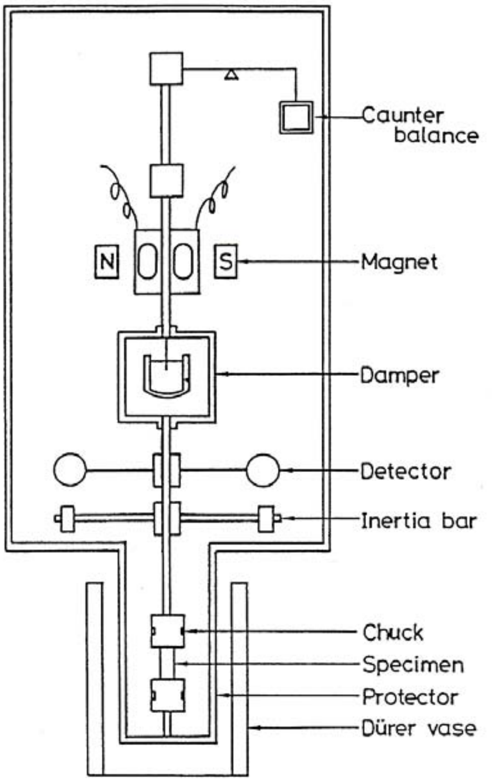

Fig.1 Schematic illustration of apparatus for internal friction measurement.

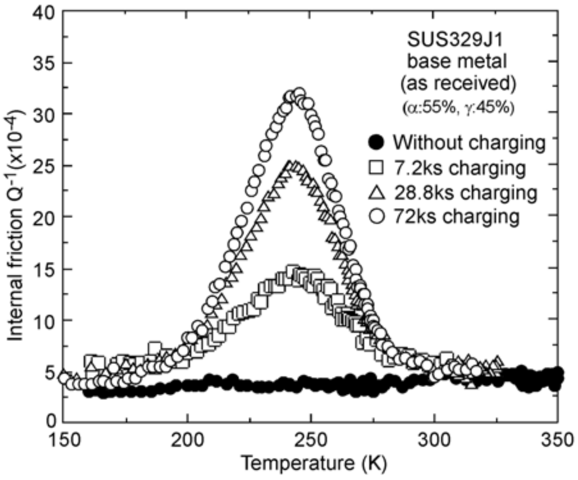

Fig. 2 Internal friction versus temperature curves SUS329J1 base metal.

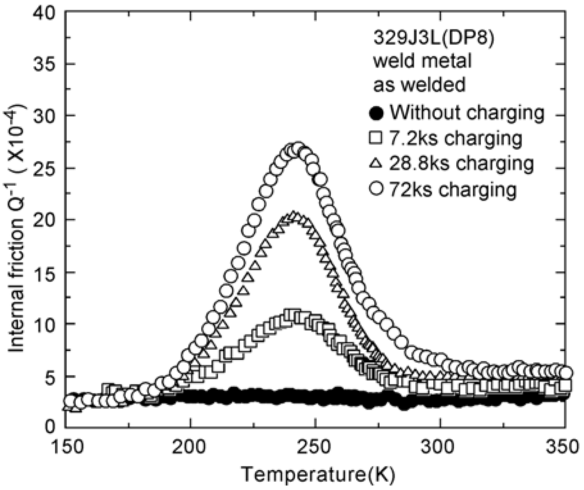

Fig. 3 Internal friction versus temperature curves of 329J3l (DP8) weld metal.

was observed below 150 K. In the as-received condition without hydrogen-charging, no peak was present. It is considered that hydrogen diffuses to the ferrite and diffuses to the austenite as a result hydrogen charging. Therefore, the sigma phase precipitated in the ferrite suppressed the fast hydrogen diffusion. Gibara et al [8]) found the hydrogen Snoek peak occurred at 48 K at 80 kHz in bcc iron containing hydrogen, furthermore Gibara et al [10]) and Asano et al [11]) reported that there was a cold-work peak caused by hydrogen-dislocation interaction in cold-worked ferrite steel over the temperature range from 77 K to room temperature. However a Snoek peak due to hydrogen in ferrite was not observed above 77 K in this research, and a cold worked peak did not occur because the specimens were not cold-worked. Therefore, it was concluded that this observed peak was due to hydrogen in the austenite of the duplex stainless steel. The peak height increased as the hydrogen charging time increased up to 72 ks.

Figure 3 shows internal friction versus temperature curves of 329J3L(DP8) weld metal. No internal friction peak was observed without hydrogen charging. By hydrogen charging, a peak due to hydrogen was also found at 245 K similar to the base metal shown in Fig.2. The peak height increased as the hydrogen charging time increased up to 72 ks. The microstructure of weld metal consisted of widmanstätten, primary austenite, secondary austenite and ferrite, and fine secondary austenite was observed in ferrite matrix after multipass welding. The volume fraction of ferrite was approximately 30%, and austenite was approximately 70%.

Figure 4 shows internal friction curves of 329J3L (DP8) weld metal reheated at 1023 K for 72 ks after welding. After the same time charging, the peak height was decreased as compared to the as-welded weld metal. For the charging time of 72 ks, the peak height Q^{-1} by hydrogen in as-welded DP8 weld metal is 28×10^{-4} as shown in Fig. 4, otherwise in case of the reheated DP8 weld metal, as shown in Fig.5, the peak height Q^{-1} is 12×10^{-4}. Consequently, it can be concluded that hydrogen concentration in the austenite is much lower in the specimen containing sigma phase. The beginning of sigma phase precipitation was observed at ferrite/widmanstätten primary austenite boundaries, and then the sigma phase continuously precipitated and the ferrite almost decomposed the sigma phase and the secondary austenite after reheating at 1023 K for 72 ks. The low peak height has been attributed to the reduction of hydrogen concentration in the austenite (or secondary

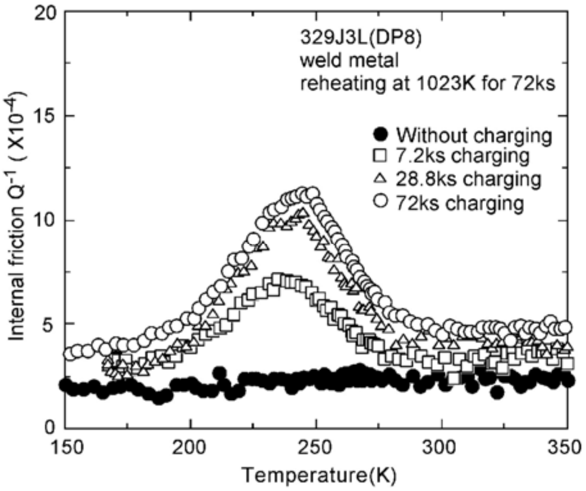

Fig. 4 Internal friction versus temperature curves of DP8 weld metal reheating at 1023 K for 72 ks.

austenite) owing to the precipitation of the sigma phase and the secondary austenite. This tendency was also the same as the 329J3L (DP8) weld metal reheated at 1123 K. T. Kuroda et al [12, 13] reported that the peak height was mainly affected by hydrogen concentration (H_γ) and volume fraction of austenite (V_γ). Peak height $Q^{-1}_\gamma = V_\gamma \times H_\gamma$, but the volume fraction of austenite hardly changed after reheating at 1023 K for 72 ks, therefore the lowering of peak height is mainly due to the decrease of hydrogen concentration in austenite. The broadening of the peak and scattering of the internal friction value occurred by sigma phase precipitation. This suggests that hydrogen-sigma phase interaction may be occurring, and it implies hydrogen present in the sigma phase lattice or trapped hydrogen or trapped molecular hydrogen at sigma/austenite interfaces.

Figure 5 shows the internal friction curves of 329J4L (DP3) weld metal reheated at 1023 K for 72 ks. After hydrogen charging, the peak height was substantially lower than that of as-welded metal shown in Fig.4. This has been attributed to the reduction of hydrogen concentration in the austenite owing to the precipitation of the sigma phase. This would be supported if total hydrogen concentration was substantially smaller in the material with precipitated sigma phase, in which the ferrite decomposition caused lower ability of hydrogen diffusion inside of the sample. If this peak is only due to hydrogen in austenite, it should show an internal friction spectrum with single relaxation time, as a symmetric curve with respect to the peak position.

However the sigma phase precipitation caused not only suppression of the internal friction peak height but also the broadening the peak at 245 K and scattering of the internal friction value. Since this phenomenon occurred in the duplex stainless steel weld metal containing sigma phase, another internal friction peak due to hydrogen-sigma phase interaction may occur at lower temperatures than 245 K as shown in **Fig.6**. This implies small amounts of hydrogen exist in the sigma phase lattice or as trapped hydrogen at sigma/austenite phase boundaries. The trapped hydrogen at the interfaces of sigma/austenite, and the hydrogen atom (H) at sigma/austenite phase boundaries implies weakly trapped hydrogen in the interfaces of sigma/austenite.

The internal friction peak height due to hydrogen in austenite was significant higher in as-welded weld metal, because the diffusivity of hydrogen in ferrite was much faster. The lower peak height indicates hydrogen diffusivity in sigma phase or sigma/austenite phase boundaries was substantially lower than that of the ferrite. The sigma phase has several interstitial sites such as tetrahedral sites. It is assumed that the hydrogen atom can enter into the sigma phase if the space of the interstitial sites is bigger than that of hydrogen atom.

Discussion of only two sites was performed here although there are four tetrahedral sites in lattice of sigma phase. If the hydrogen atom enters into a tetrahedral A site (0.04 nm in radius), four neighbor substitution atoms will distort symmetry at 0.006 nm. Hydrogen atom can enter with strained 0.002 nm in case of tetrahedral B site. This strain is the same phenomena as the moment of tetrahedral A site.

However hydrogen must transport across a saddle point before a hydrogen atom present in a tetrahedral A site moves to a tetrahedral B site. The diffusion of a hydrogen atom will not take place easily, because hydrogen must distort three neighbor substitution atoms when hydrogen atoms are present in the saddle point. It is

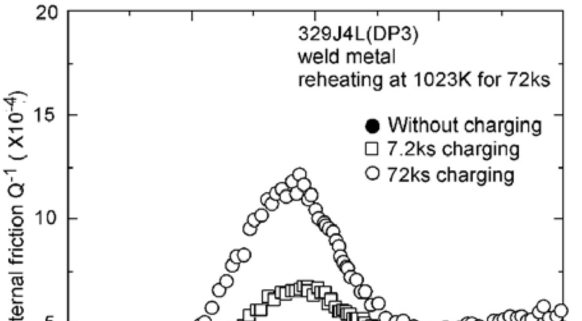

Fig. 5 Internal friction versus temperature curves of DP3 weld metal reheating at 1023 K for 72 ks.

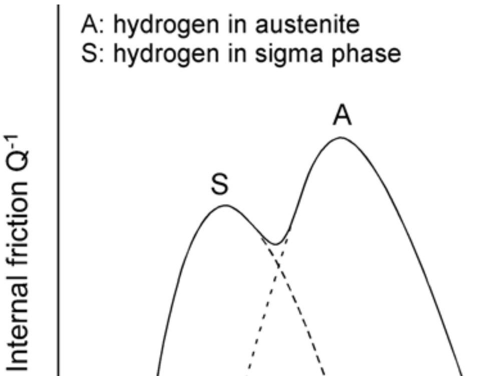

Fig. 6 Schematic illustration of separation of two peaks.

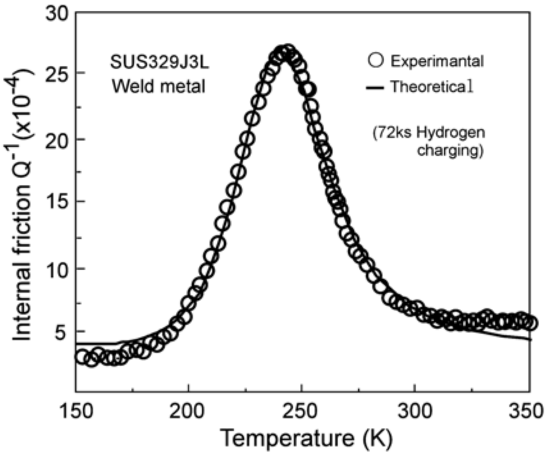

Fig.7 Comparison of experimental data and theoretical calculation for the internal friction curves after hydrogen charging in duplex stainless steel weld metal.

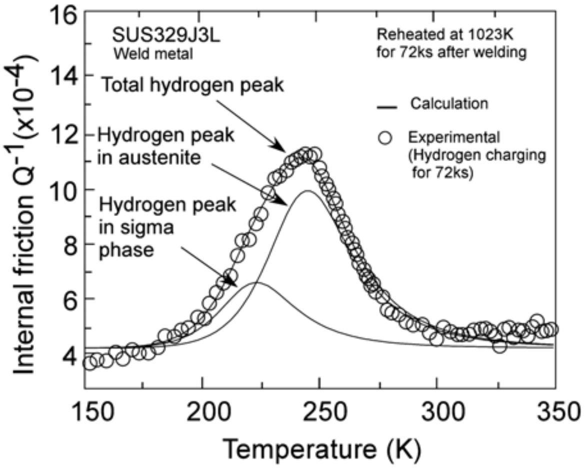

Fig.8 Comparison of experimental data and theoretical calculation for internal friction curves after hydrogen charging in the reheated duplex stainless steel weld metal.

assumed that it's impossible to confine hydrogen in these interstitial sites because the size of interstitial sites is a little smaller than that of a hydrogen atom, and this implies that the solubility of hydrogen in sigma phase will be substantially smaller than that in fcc crystal by geometrical consideration.

Figure 7 indicates the internal friction versus temperature curves of the weld metal with experimental data and theoretical curve. An activation energy for hydrogen diffusion in austenite was measured for super duplex stainless steels. A Snoek relaxation peak is generally observed in bcc materials. The internal friction value Q^{-1} is theoretically described as follows.

$$Q^{-1} = sec\,[\,H / R\,(\,1/T - 1/Tp\,)\,] \qquad (2)$$

H is activation energy, Tp is peak temperature and R is the gas constant. Experimental data are described as open circles. Calculation curve is described as solid line. The activation energy of hydrogen is calculated from the half width of the peak. H_γ is 30kJ/mol. The data obtained in the present research is smaller than another report such as 52 kJ/mol. In case of the duplex stainless steel, the activation energy was 30 kJ/mol.

Figure 8 indicates the internal friction curves of the sigma phase precipitation samples with experimental data and theoretical curves. Peak spectrum shows as follows. Asymmetric, Broadening. It is considered to be the overlapping of two peaks. In case of as-received samples, only one spectrum was observed at 245 K for hydrogen in austenite. However, two peaks are observed for the specimens consisting austenite and sigma phase.

The activation energy of hydrogen in the sigma phase was evaluated using mathematical analysis. In case of conventional duplex stainless steel (DP8), two calculation curves were evaluated as hydrogen in austenite, and hydrogen in sigma phase. As the results, the activation energy of hydrogen diffusion in sigma phase was 25 kJ/mol at 220 K. The results are also same for the duplex stainless steel.

Figure 9 shows the relation between peak height at 245 K and hydrogen content for SUS329J1 base metal. When the precipitation of sigma phase occurred, hydrogen content for the same peak height is different as compared to the as-received specimen. The volume fraction of the austenite was almost same because secondary austenite was hardly formed in the case of SUS329J1 base metal after reheating at 1023 K for 72 ks. The peak height should be the same when hydrogen content and volume of austenite was almost same because Peak height Q_γ^{-1} is consisting of V_γ x H_γ. However, the

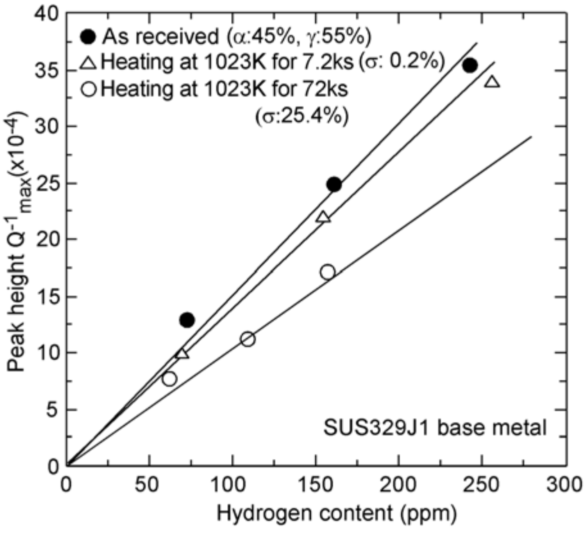

Fig.9 Relation between peak height at 245 K and hydrogen content for the internal friction curves of SUS329J1 base metal.

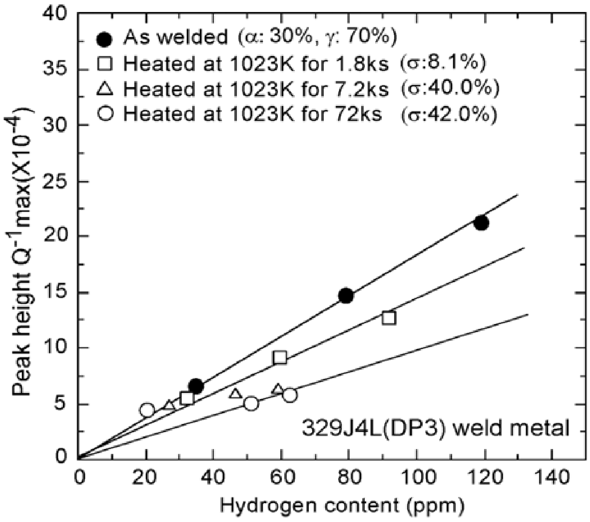

Fig. 10 Relation between peak height at 245 K and hydrogen content for the internal friction curves by hydrogen charging.

sigma phase can accommodate more hydrogen content, this phenomenon also implies that hydrogen exists in sigma phase or hydrogen is trapped at ferrite/sigma phase boundaries.

Figure 10 indicates the relation between peak height at 245 K and hydrogen content for the DP3 weld metal. Hydrogen content to form the same peak height was more necessary as compared to the as-welded condition, and the difference was observed between as-welded condition and the condition of heated at 1023 K for 72 ks.

In the DP3 weld metal, hydrogen at ferrite/austenite phase boundaries was deeply trapped, and the hydrogen atom was also deeply trapped at the interfaces of ferrite/sigma. In case of DP8 weld metal, the results were as same as that of Fig.10.

4. Conclusions

Hydrogen behavior in duplex stainless steel and weld metals was investigated by means of internal friction measurements. The internal friction measurements were conducted over the temperature range from 77 K to 373 K by using an inverted torsion pendulum for a frequency of 1.5 Hz.

(1) A significant peak appeared at 245 K after hydrogen charging for 329J1 base metal and 329J3L and J4L weld metals. The peak height increased with increasing hydrogen concentration. The peak was associated with hydrogen in austenite.

(2) As the specimens were heated at 1023 K for various times, the sigma phase precipitated in the ferrite at the ferrite/austenite interface. The broadening of the internal friction peak at 245 K and scattering of the internal friction value took place by hydrogen charging for the sigma phase precipitation. Overlapped two peaks of the peak associated with hydrogen in austenite and the peak associated with hydrogen in sigma phase were observed.

(3) The precipitation of sigma phase caused suppression of hydrogen diffusion in duplex stainless steel and weld metal. It is considered that hydrogen was dissolved in the sigma phase on the basis of the hydrogen content measurement and internal friction measurement.

Acknowledgement

This work was supported by A Grant-in-Aid for Cooperative Research Project of Nationwide Joint-Use Research Institute on Development Base of Joining Technology for New Metallic Glasses and Inorganic Materials from The Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1) T.Kuroda, K. Nakade and K. Ikeuchi, Welding in the world, 44, (2000) 17-22.
2) T.kuroda, K.Ikeuchi, K.Oe, K.Nakade.,Proceedings from Materials Solutions Conference ’99 on Joining of Advanced and Specialty Materials, 1-4 November (1999), Cincinnati, Ohio.
3) J.O.Nilsson, Mater. Sci. and Tech., 8, (1992), 685 -699.
4) J.O.Nilsson and A.Wilson, Mater.Sci.and Tech., 9 , (1993), 545- 554.
5) R.A.Walker, Mater.Sci.and Tech., 4, (1988) 78-84.
6) D.J.Kotecki, Welding Journal, 10 (1986) 273s.
7) T.Kuroda and C.D.Lundin, Journal of Society Material Science Japan, 43 (1994) 562.
8) J. A. Peterson, R. Gibala, and A.R. Troiano, Journal of The Iron and Steel Institute (1969), 86.
9) H.Asano, K. Sumida and M.Otsuka, J. Japan Inst. Metals, 41 (1985) 671.
10) R.Gibala., Transaction of the Metallurgical society of AIME, 239 (1967) 1574.
11) M.Kazaoka and H.Asano, J.Japan Inst.Metals, 50 (1986) 391.
12) T.Kuroda, Y.Kikuchi and A.Kasahara, Materials Sci. Research international, 4-3, (1998) 217-222.
13) T.Kuroda, A.Kasahara, K.Nakade; Quatt. J. Japan Welding Society, 17- 3 (1999) 474-483.