HG-SCC test method for aluminium alloys

Transmitted by JAPAN

GTR13 Phase2 Informal WG #3 : 26-28/Jun/2018 @ Seoul, KOR

Purpose of this document

【1】 What is the corrosion phenomenon to be considered when using aluminum alloy for CHSS?

【2】 What is the concern?

【3】 Why is the HG-SCC test method necessary?

【4】 What is a specific Japanese proposal?

5: Conclusions

■Hydrogen-embrittlement type SCC must be considered as a corrosion/SCC
automobile CHSS.
en moisture exists even
t type SCC in humid air is
roject.
all amount of water vapor
and therefore can become a humid gas environment.

alloy to CHSS,
to hydrogen-embrittlement type SCC

test method (HPIS E 103:2018)
hydrogen-embrittlement type SCC.

※ **SCC** : **S**tress **C**orrosion **C**racking
HG-SCC : **H**umid **G**as - **S**tress **C**orrosion **C**racking

1: Corrosion / SCC in automotive CHSS

- External environment : Corrosion by water/salt content
- Internal environment : Anode-dissolution type SCC
- Internal environment : Hydrogen-embrittlement type SCC

2: Concerns

- Hydrogen-embrittlement type SCC under humid gas environment

3: Proposal of HG-SCC test method (HPIS E 103:2018)

4: Verification of HG-SCC test method

5: Conclusions

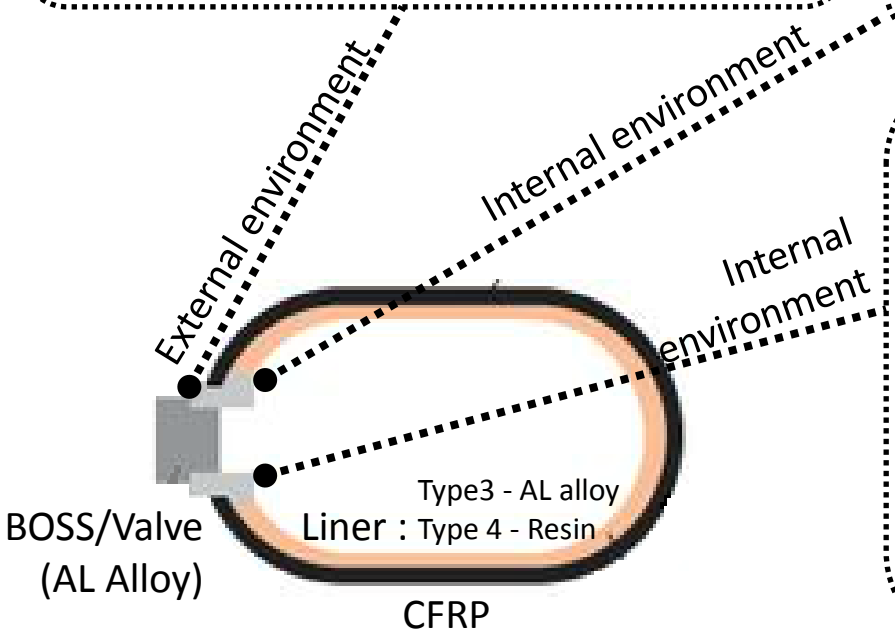
1: Corrosion / SCC in automotive CHSS

■ **Corrosion by water/salt content**

■ **Anode-dissolution type SCC**

$M \rightarrow M^+ + e^-$

$\frac{1}{2}O_2 + H_2O + e^- \rightarrow 2OH^-$



■ **Hydrogen-embrittlement type SCC**

$M + H_2O \rightarrow MO + H_2$ •••• (1)

$H_2 \rightarrow 2H$ •••• (2)

When aluminium alloy is used for automotive CHSS, there are 3 kinds of corrosion / stress corrosion cracking to be considered.

1: Corrosion / SCC in automotive CHSS

■Corrosion by water/salt content

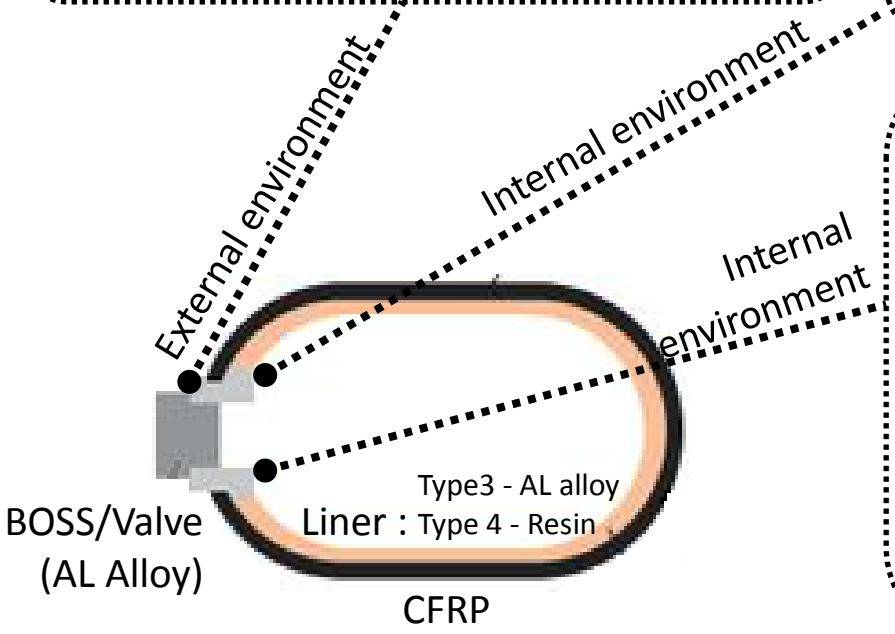
・OEM companies have criteria for corrosion by the external environment.

■Anode-dissolution type SCC

$M \rightarrow M^+ + e^-$

$\frac{1}{2}O_2 + H_2O + e^- \rightarrow 2OH^-$

・SCC does not occur in H_2 environment in which oxygen does not exist.



■Hydrogen-embrittlement type SCC

$M + H_2O \rightarrow MO + H_2$ •••• (1)

$H_2 \rightarrow 2H$ •••• (2)

※1,2

・If moisture is present, SCC may occur in H_2 environment via the two consecutive reactions (1) and (2), even without oxygen. (Direct cause of SCC is atomic H)

※3,4

・Embrittlement by H_2 gas (single reaction (2)) does not occur in aluminium alloys, unlike iron and bcc-base steel.

※1	G. A. Young, Jr. and J. R. Scully: Met and Mat. Trans. 33A(2002), 101-115.
※2	M. O. Speidel: The theory of stress corrosion cracking in alloys, ed. by J. R. Scully, NATO, p.289（1971）.
※3	G. Itoh: Materials for Storage and Safety of Hydrogen, Science & Technology, (2010)、234-244, ISBN:978-4-86428-004-4
※4	Safety Standard for Hydrogen and Hydrogen Systems, NASA（2005）

1: Corrosion / SCC in automotive CHSS

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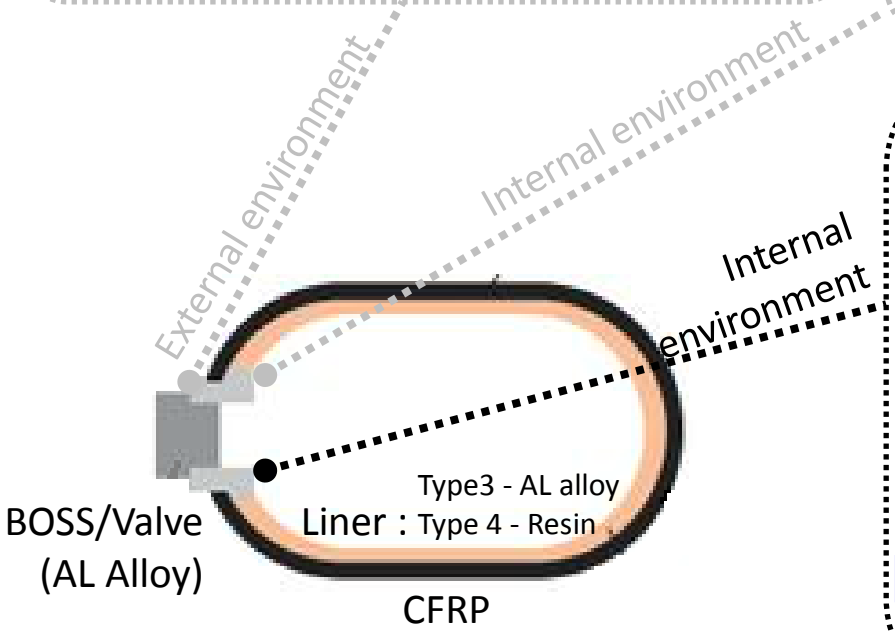

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・If moisture is present, SCC may occur in H_2 environment via the two consecutive reactions (1) and (2), even without oxygen.

・Embrittlement by H_2 gas (single reaction (2)) does not occur in aluminium alloys, unlike iron and bcc-base steel.

ISO7866 ANNEX B provides testing method for SLC(Sustained Load Cracking). **But it is not in a humid environment.**

There is a provision of the test method for each corrosion/SCC. However the humid environment condition is not considered in ISO7866 ANNEX B.

※ SCC : Stress Corrosion Cracking
HG-SCC : Humid Gas - Stress Corrosion Cracking

1: Corrosion / SCC in automotive CHSS

- External environment : Corrosion by water/salt content
- Internal environment : Anode-dissolution type SCC
- Internal environment : Hydrogen-embrittlement type SCC

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- Hydrogen-embrittlement type SCC under humid gas environment

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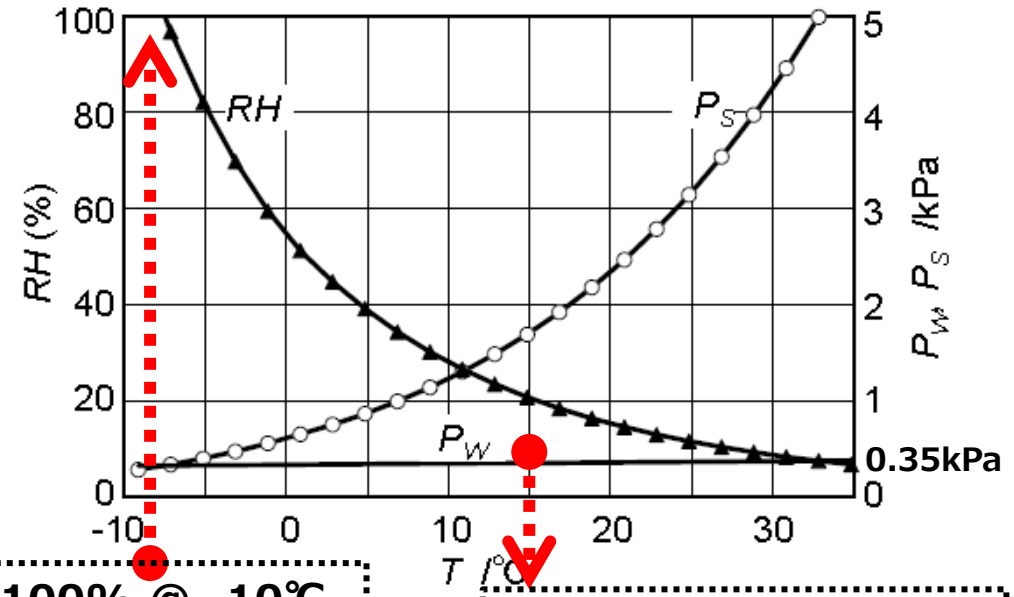
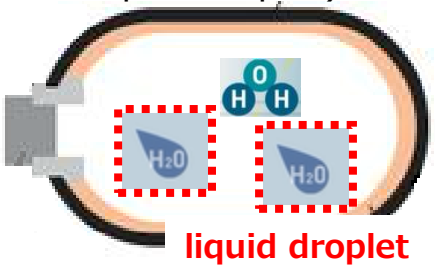
2: Concerns (Hydrogen-embrittlement type SCC under humid gas environment)

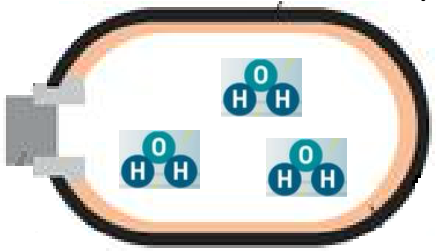


RH 100% @ -10℃
(Water vapor becomes liquid droplet)



Cool -ing

H_2 charging @15℃
(70MPa×5ppm =0.35kPa)
water vapor



G. Itoh ; Service Environment and Testing Method for Global Standardization of Aluminum Alloys Related to Hydrogen
ISSN 0892-4228, Corrosion Engineering, 2016, Vol.65, pp.339-346

Ps : Saturate water vapor pressure
Pw : Partial water vapor pressure
RH : Relative humidity

$$RH = \frac{Pw}{Ps} \times 100\ (\%)$$

■ **5ppm water vapor**
Regulated in ISO14687-2 and SAE J2719 as H_2 fuel specification

**When filling H_2 at room temperature and cooling it,
5 ppm of water vapor contained in H_2 becomes liquid droplet.
It should be considered that a humid environment exists in CHSS.**
(Water vapor is liable to form liquid droplets in high pressure environment.)

2: Concerns (Hydrogen-embrittlement type SCC under humid gas environment)

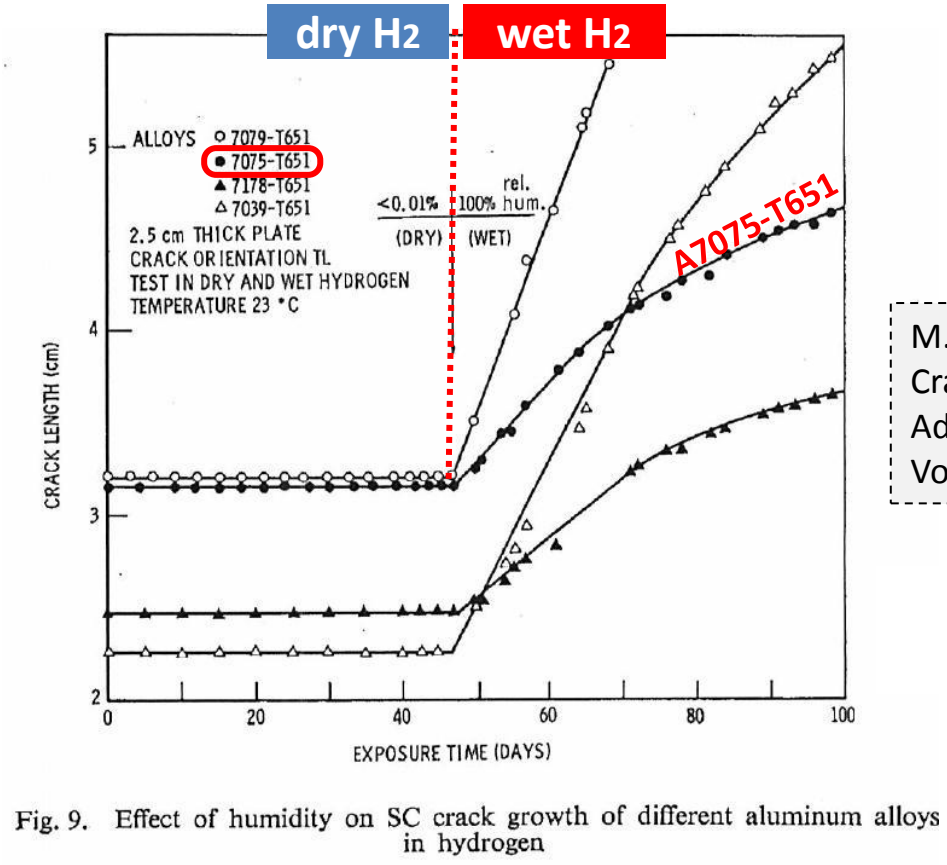


Fig. 9. Effect of humidity on SC crack growth of different aluminum alloys in hydrogen

M. O. Speidel and M. V. Hyatt: "Stress-Corrosion Cracking of High-Strength Aluminum Alloys", Advances in corrosion science and technology, Vol.2, Plenum Press, (1972), pp.115-335.

In some aluminium alloys, crack growth due to stress corrosion cracking is greatly accelerated under humid gas environment.

2: Concerns (Hydrogen-embrittlement type SCC under humid gas environment)

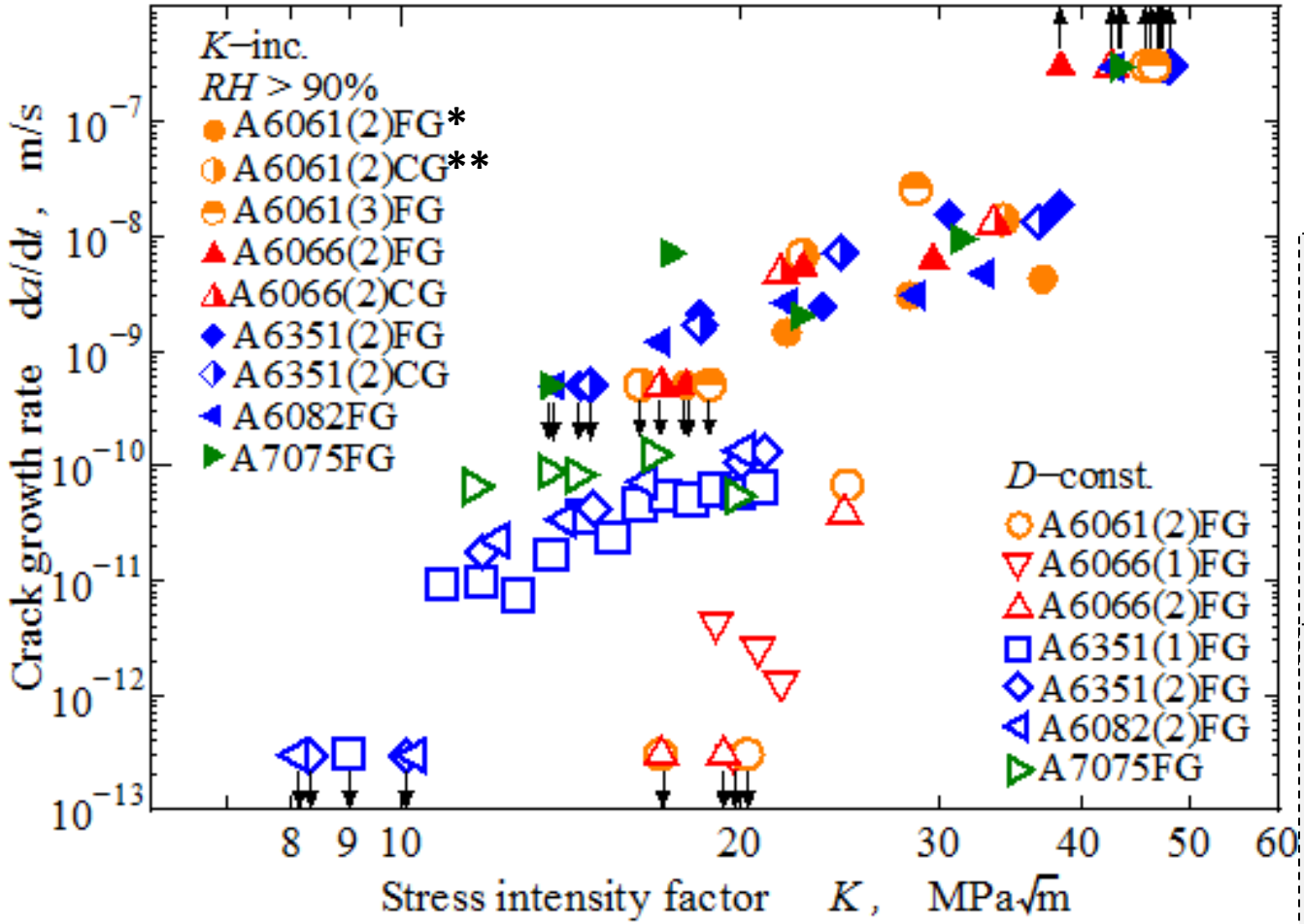


Fig.2 SCC characteristics of the standard alloys.

FG *
Fine Grain
CG **
Coarse Grain

■**Test method & data of A6061, A6066, A6351**

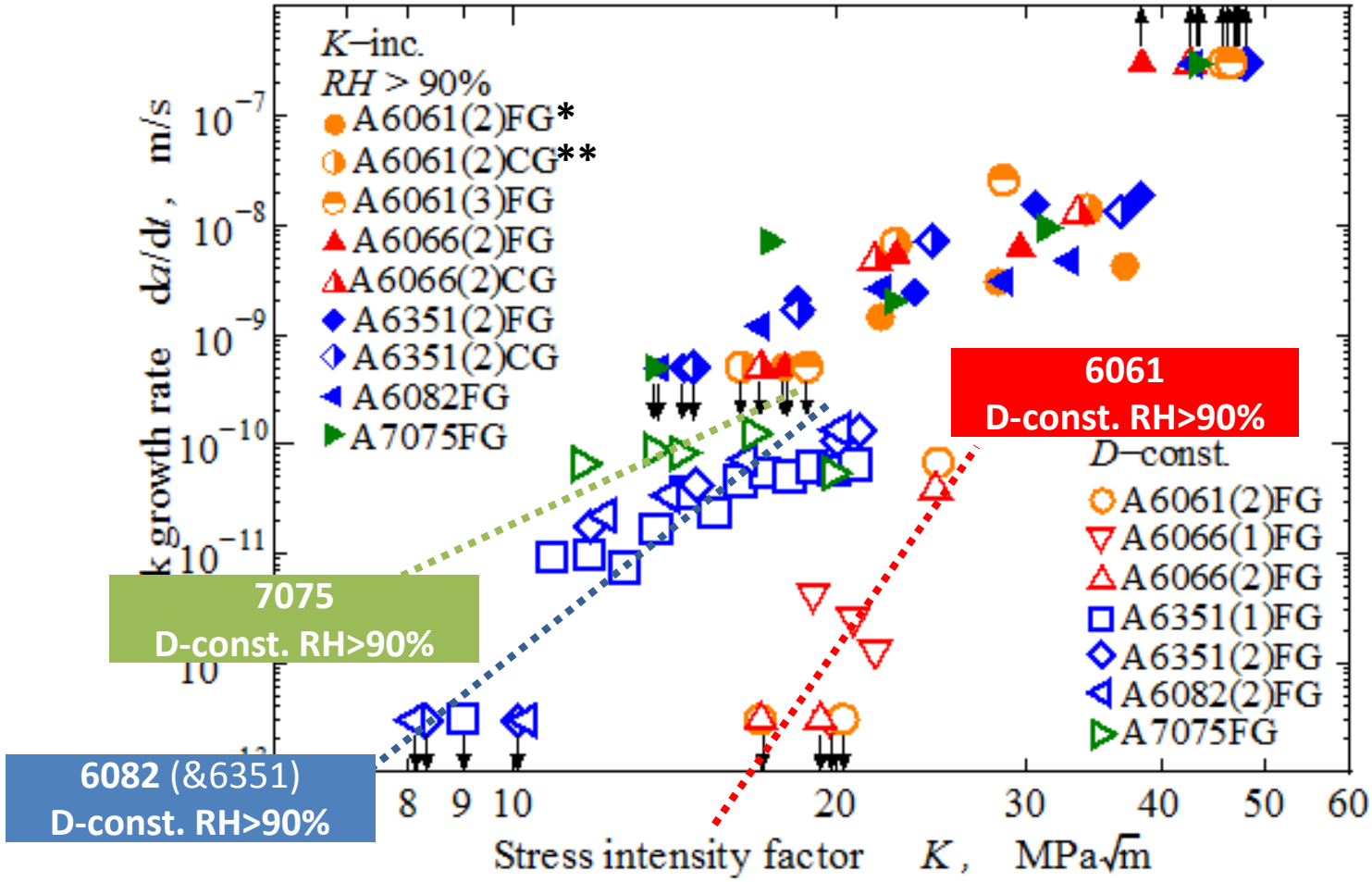
Study on Evaluation Methods for Stress Corrosion Cracking and Fatigue Crack Growth of Aluminum Alloys for Hydrogen Containers
T. Ogawa et al.:
JHPI Vol.54 No.6 2016
http://doi.org/10.11181/hpi.54.277

■ **Data of A6082, A7075**

Effect of Chemical Composition on the Characteristics of Humid Gas Stress Corrosion Cracking of Al-Mg-Si Alloys
T. Ogawa et al.:
JSME Kanto Annual meeting
@March 16, 2017 – Paper OS0501-04

In Japanese papers, basic data on stress corrosion cracking under humid gas environment of aluminium alloys have been acquired.

2: Concerns (Hydrogen-embrittlement type SCC under humid gas environment)



FG *
Fine Grain
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Fig.2 SCC characteristics of some commercial alloys

As a result, some aluminium alloys are prone to stress corrosion cracking under humid gas environment.

2: Concerns (Hydrogen-embrittlement type SCC under humid gas environment)

■ Corrosion by water/salt content

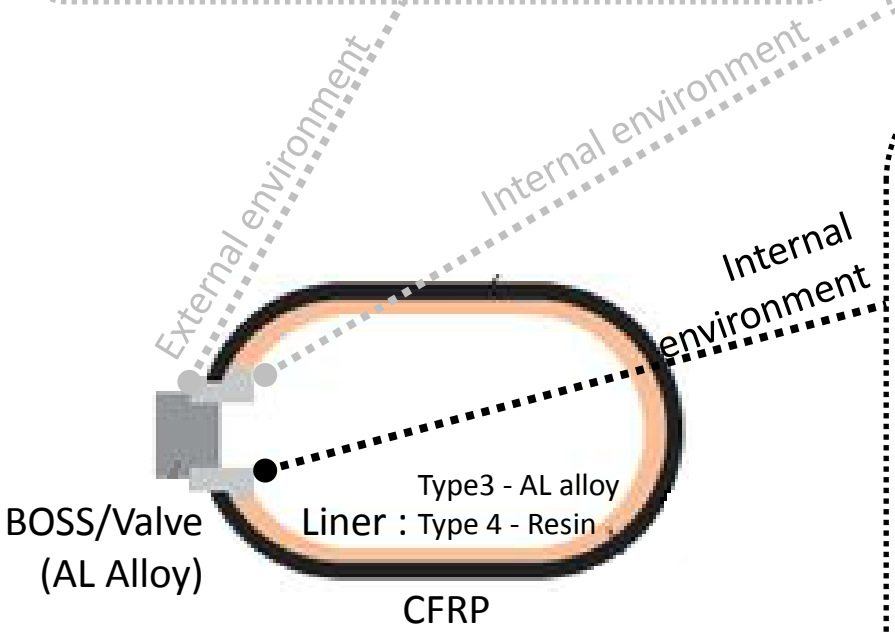
・OEM companies have criteria for corrosion by the external environment.

■ Anode-dissolution type SCC

$M \rightarrow M^+ + e^-$

$1/2O_2 + H_2O + e^- \rightarrow 2OH^-$

・SCC does not occur in H_2 environment in which oxygen does not exist.



■ Hydrogen-embrittlement type SCC

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・If moisture is present, SCC may occur in H_2 environment via the two consecutive reactions (1) and (2), even without oxygen.

・Embrittlement by H_2 gas (single reaction (2)) does not occur in aluminium alloys, unlike iron and bcc-base steel.

ISO7866 ANNEX B provides testing method for SLC(Sustained Load Cracking). But it is not in a humid environment.

Some aluminium alloys are prone to SCC under humid gas environment.

If an aluminum alloy with poor SCC characteristics is used for CHSS, hydrogen-embrittlement type stress corrosion cracking (HG-SCC) can develop serious trouble of boss and valve.

※ SCC : Stress Corrosion Cracking
HG-SCC : Humid Gas - Stress Corrosion Cracking

1: Corrosion / SCC in automotive CHSS

- External environment : Corrosion by water/salt content
- Internal environment : Anode-dissolution type SCC
- Internal environment : Hydrogen-embrittlement type SCC

2: Concerns

- Hydrogen-embrittlement type SCC under humid gas environment

3: Proposal of HG-SCC test method (HPIS E 103:2018)

4: Verification of HG-SCC test method

5: Conclusions

3: Proposal of HG-SCC test method (HPIS E 103:2018)

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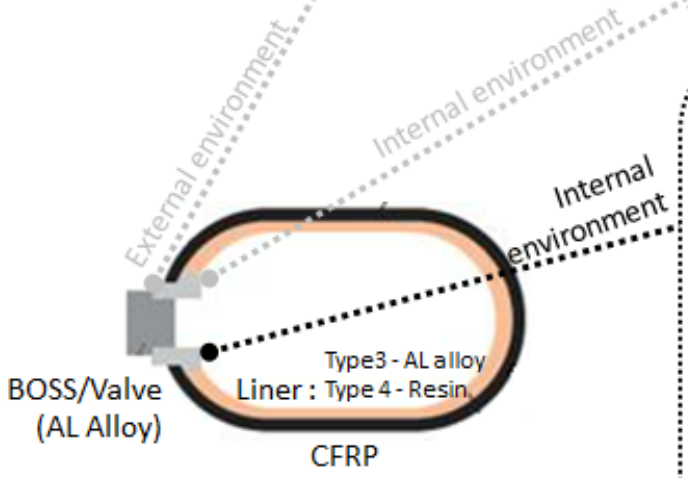

■ **Hydrogen-embrittlement type SCC**

$M + H_2O \rightarrow MO + H_2$ •••• (1)

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- If moisture is present, SCC may occur in H_2 environment via the two consecutive reactions (1) and (2), even without oxygen.
- Embrittlement by H_2 gas (single reaction (2)) does not occur in aluminium alloys, unlike iron and bcc-base steel.

ISO7866 ANNEX B provides testing method for SLC(Sustained Load Cracking). But it is not in a humid environment.

Some aluminium alloys are prone to SCC under humid gas environment.

Japan propose HG-SCC test method (HPIS E 103:2018) to evaluate hydrogen-embrittlement type SCC under humid gas environment.

HG-SCC test method is an extension of ISO 7866 ANNEX B with humid gas environmental conditions added.

(SLC can also be evaluated at the same time by HG-SCC test method)

Outline of HG-SCC test methods for aluminium alloys

Standard Test Method for Humid Gas Stress Corrosion Cracking of Aluminium Alloys for Compressed Hydrogen Containers (HPIS E 103:2018)

※**HPI** = **H**igh **P**ressure **I**nstitute of Japan

■ Section 1 : Scope

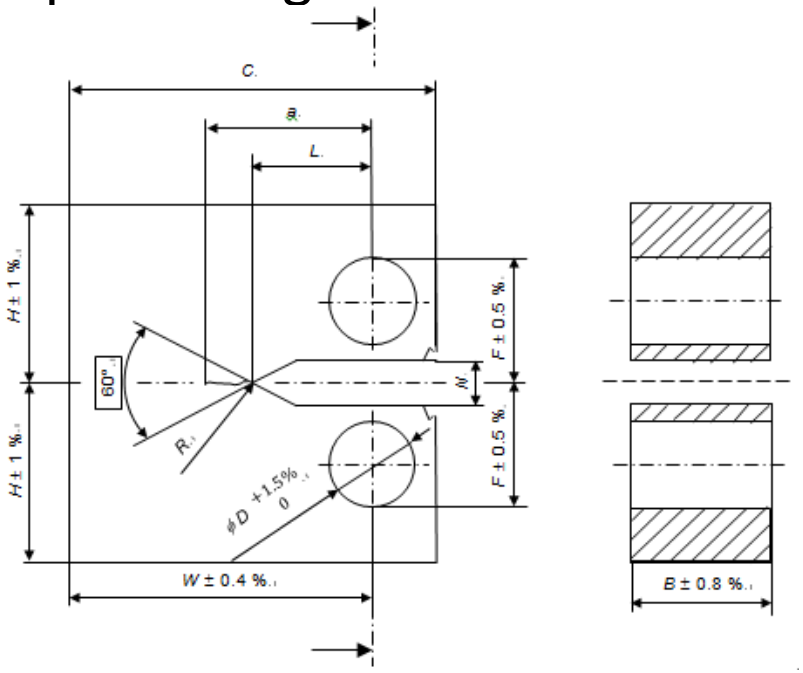
This standard specifies the test method for humid gas stress corrosion cracking (HG-SCC) and the qualification criterion of aluminium alloys for compressed hydrogen containers for automotive use.

■ Section 4 : Principle

A fatigue pre-cracked specimen is loaded by a constant-load or constant-displacement method to a K_{IAPP} equal to a defined value. Then, the specimen is maintained in the loaded state at prescribed environment for a prescribed duration. After the test duration, the specimen is examined as to whether or not the cracking has extended from the initial fatigue pre-crack. If the crack extension length does not exceed a prescribed value, the material of the specimen is considered suitable for compressed hydrogen containers as far as the required resistance to crack extension under loading is concerned.

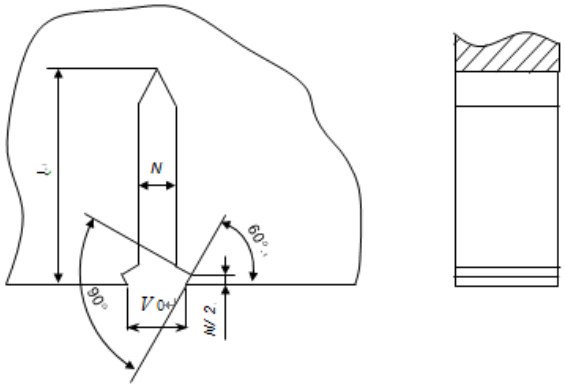
Outline of HG-SCC test methods for aluminium alloys

■ A.1 Specimen geometries



Where, W : net width
C : total width = $1.25W$
B : thickness = $\frac{W}{20} \sim \frac{W}{2}$
H : half-height = $0.6W$
D : hole diameter = $0.25W$
F : half-distance between outer edges = $1.6D$
N : notch width = no more than $0.065W$
R : notch radius = preferably no more than 0.1 mm
L : effective notch length = $0.25W \sim 0.40W$
a : effective crack length = $0.45W \sim 0.55W$

Figure A.1 - Proportional dimensions and tolerances of compact specimen



Where, V_0: knife edge spacing

Figure A.2 - Knife edge for location of displacement gauges

Outline of HG-SCC test methods for aluminium alloys

■ Test Method (Loading)

c) Loading is performed as follows.

1) The value of K_{IAPP} obtained by the following equation given in B.6.2 of ISO 7866:2012 is loaded.

$$K_{IAPP} = 0.056\sigma_{0.2} \quad \text{———— (2)}$$

K_{IAPP} : initial stress intensity factor at the tip of the crack (MPa$\sqrt{m}$)
$\sigma_{0.2}$: 0.2% proof stress (MPa)

A.2 Constant-load testing

For loading under constant load conditions, load P shall be determined by the following equations specified in Figure 13 of ISO 7539-6:2011.

$$P = \frac{31.62 K_{IAPP} B \sqrt{W}}{Y} \quad \text{———— (A.1)}$$

$$Y = \frac{(2+x)(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4)}{(1-x)^{3/2}}$$

$$x = \frac{a}{W}$$

P : load (N)
K_{IAPP} : initial stress intensity factor of the tip of the crack (MPa$\sqrt{m}$)
B : thickness (mm)
W : net width (mm)
a : effective crack length (mm)

A.3 Constant-displacement testing

For loading under constant displacement conditions, crack mouth opening displacement V shall be determined by the following equations given in B.6.4 a) of ISO 7866:2012.

$$V = \frac{K_{IAPP}\sqrt{W}}{0.032 E f(x)} \quad \text{———— (A.2)}$$

$$f(x) = \frac{2.24(1.72 - 0.9x + x^2)(\sqrt{1-x})}{9.85 - 0.17x + 11x^2}$$

$$x = \frac{a}{W}$$

$$V = V_f - V_0$$

V : crack mouth opening displacement (mm)
V_f : knife edge spacing under loading (mm)
V_0 : knife edge spacing under no load (mm)
K_{IAPP} : initial stress intensity factor of the tip of the crack (MPa$\sqrt{m}$)
W : net width (mm)
a : effective crack length (mm)
E : longitudinal elastic modulus (MPa)

Outline of HG-SCC test methods for aluminium alloys

■ Test environment and period

The test environment and period shall be as follows.

a) Temperature: 25℃ ± 5℃ for the entire duration of the test.

b) Atmosphere and humidity: no generation of dew in air measuring 85 % or higher in relative humidity for the entire duration of the test.

c) Test period: 90 days (in accordance with B.6.6 of ISO 7866:2012)

■ Qualification of materials

The applicability of materials shall be judged as follows.

a) The crack extension (a_{scc} - a_{pre}) by HG-SCC is examined to exceed 0.16 mm or not.
NOTE The threshold value of "0.16 mm" is specified in B.7.3 of ISO 7866:2012.

b) The actual applied value of K_{IAPP} (defined as K_{IA}) is calculated by using a_{pre} and the applied load.

c) The validity of materials is judged by comparing KIA with KIAPP as well as (a_{scc} - a_{pre}) with 0.16mm.

For detailed information on HG-SCC test method (HPIS E 103:2018), see below.

■ *Full text of draft version*

https://wiki.unece.org/display/trans/GTR13-2+2nd+session

Appendix of " GTR13-2-06 HG-SCC test method for aluminum alloy.pdf "

■ *Part of the official issue version (HPIS E 103:2018)*

http://www.hpij.org/publication/?action=common_download_main&upload_id=1946

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3: Proposal of HG-SCC test method (HPIS E 103:2018)

4: Verification of HG-SCC test method

5: Conclusions

4: Verification of HG-SCC test method

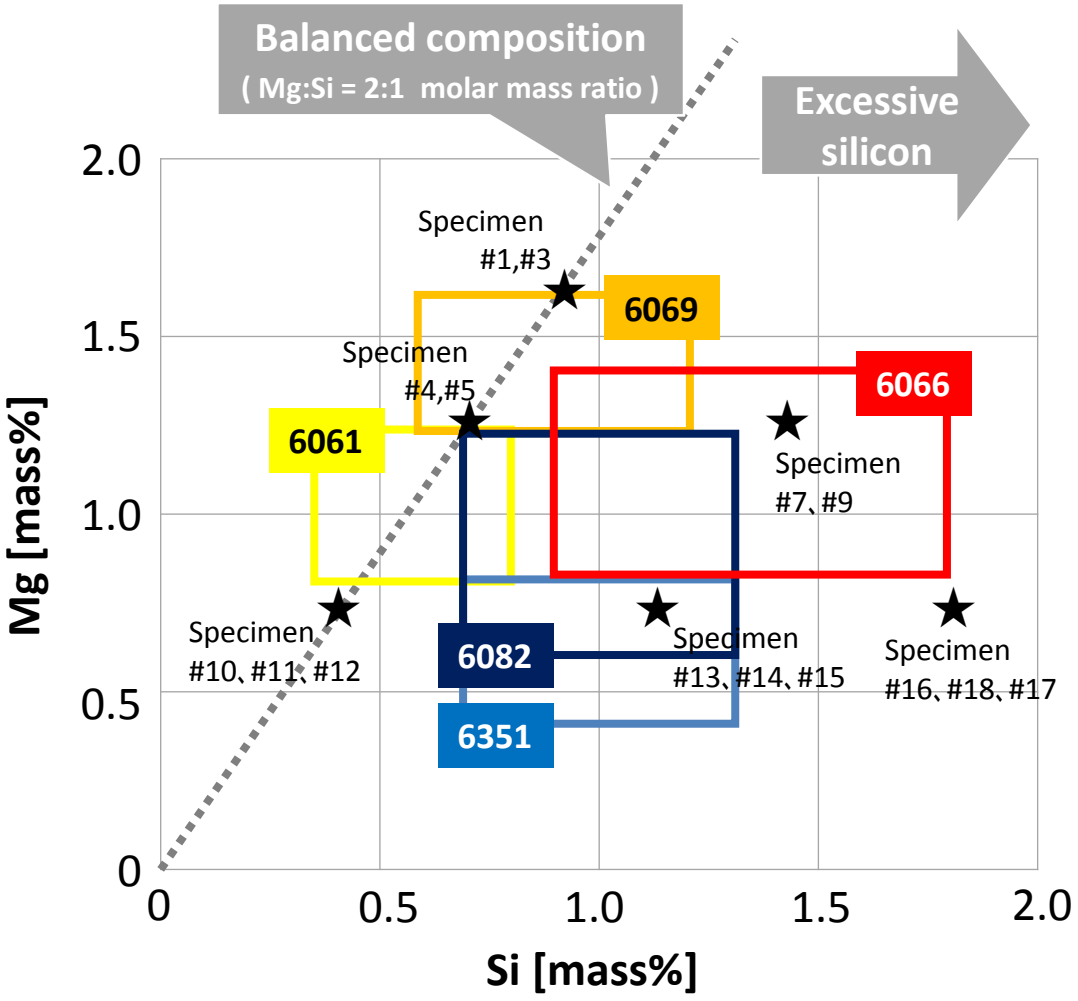
- **6000 series** (Al-Mg-Si-(Cu)) **aluminium alloys with 18 kinds of compositions were prepared, and the judgment whether the pre-crack grows or not during the sustained loading was successfully made by the HG-SCC test method.**

- **Thus, HG-SCC test has been concluded to be useful as a assessment test on aluminium alloys for CHSS.**

- **Furthermore, the following important facts have been revealed:**
  - **① Alloys with balanced composition** (Mg/Si atomic ratio=2) **are highly resistant to hydrogen-embrittlement type SCC.**
  - **② Adding Cu to the alloy improves the resistance to hydrogen-embrittlement type SCC (Si-excess alloys without Cu are irresistant).**

The following 2 pages introduce the verification test results.

4: Verification of HG-SCC test method



Specimen Group	Cu Content %
Specimen #1, #4, #7, #10, #13, #16	0.0
Specimen #5, #11, #14, #18	0.3
Specimen #3, #9, #12, #15, #17	1.0

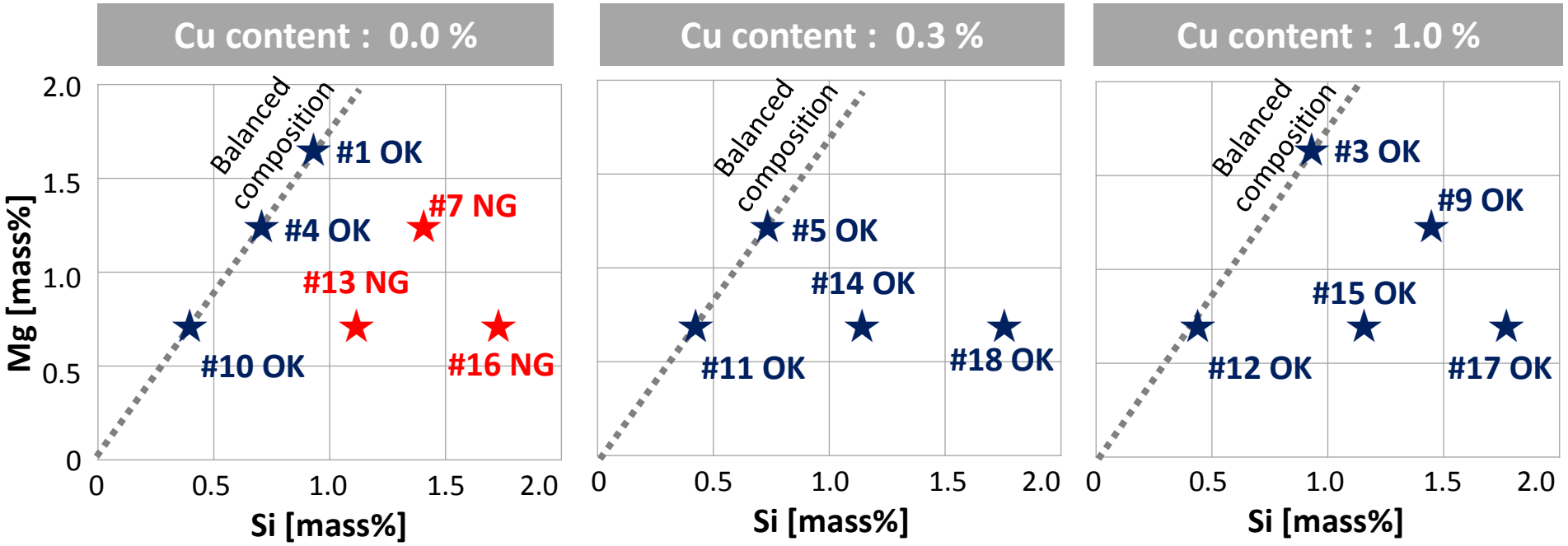
Standard alloy	Cu content %
6061	0.15 – 0.40
6066	0.7 – 1.2
6069	0.55 – 1.0
6351	≤ 0.01
6082	≤ 0.01

In order to verify the usefulness of the HG-SCC test method, 6000 series (Al-Mg-Si-(Cu)) **aluminium alloys with 18 kinds of compositions were prepared, and HG-SCC test was performed on each specimen.**

4: Verification of HG-SCC test method

Result of HG-SCC test sorted by main chemical contents (Mg, Si, Cu)

- Test condition : 25℃, RH85 %, 90 days
- Qualification : The crack extension is examined to exceed 0.16 mm or not.



- **The alloys with balanced composition** (Mg/Si atomic ratio=2) **are highly resistant to hydrogen-embrittlement type SCC.**
- **Adding Cu to the alloy improves the resistance to hydrogen- embrittlement type SCC (Si-excess alloys without Cu are irresistant).**

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5: Conclusions

5: Conclusions

- Hydrogen-embrittlement type SCC must be considered as a corrosion/SCC problem when applying an aluminium alloy to automobile CHSS.
- Hydrogen-embrittlement type SCC occurs when moisture exists even without oxygen.
- The occurrence of the hydrogen-embrittlement type SCC in humid air is verified in the course of the Japanese NEDO project.
- Hydrogen gas supplied to CHSS contains a small amount of water vapor and therefore can become a humid gas environment.

Prior to the application of an aluminium alloy to CHSS,
it is necessary to confirm the resistance to hydrogen-embrittlement type SCC under humid gas environment.

Japan propose to include HG-SCC test method (HPIS E 103:2018) in GTR13-Phase2 that can evaluate hydrogen-embrittlement type SCC.

Thank you!!