Necessity of HG-SCC test method for aluminum alloys

Transmitted by Japan

7th Meeting of the informal working group on GTR No.13 (Phase 2)

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1. Background

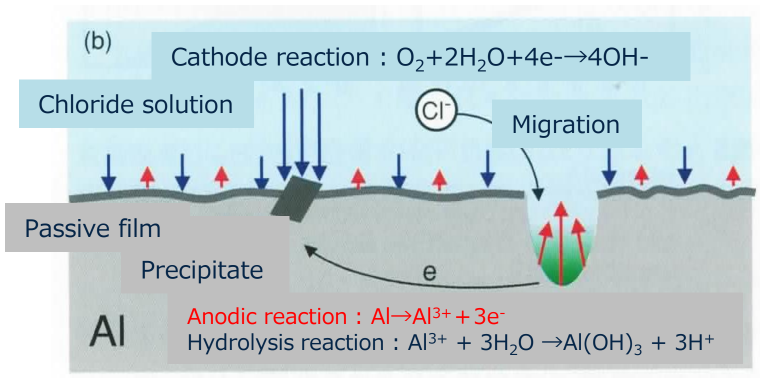
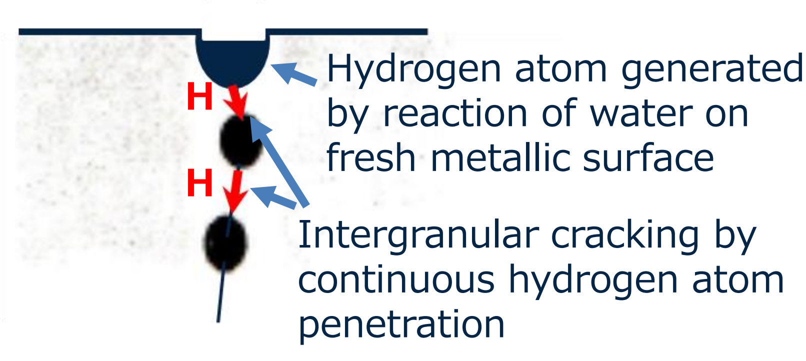
- Japan has been proposing Humid Gas Stress Corrosion Cracking (HG-SCC) test method at the previous GTR No.13 IWG. However the necessity of this test method does not seem to be understood by each country's representative.

- The common consensus of the necessity for HG-SCC test method is desirable, by sharing the target corrosion phenomena and the position of this test method.

2. Understanding on corrosion phenomena of aluminum alloys

SLC : Sustained Load Cracking
SCC : Stress Corrosion Cracking

■ 2 types of corrosion phenomena in aluminum alloys

Type	Anodic dissolution	SCC in humid gas environment
Principle	Electrochemical corrosion by salt water	SCC by the reaction of metallic Al and H_2O
		
Reaction	Anodic reaction : $Al \rightarrow Al^{3+} + 3e^-$ Cathode reaction : $O_2+2H_2O+4e^- \rightarrow 4OH^-$	$2Al+3H_2O \rightarrow Al_2O_3+$**6H**
Characteristics	• Need oxygen and solution • Need Cl^- (break passive film) • Not occur in high pressure H_2 (no oxygen and no solution) ⇒ **Occur only outside of containers** 	• Occur under the presence of H_2O • Crack growth by accumulation of hydrogen atoms at the crack tip (on fresh metallic surface), not by dissolution of metal into ion ⇒ **Occur both outside and inside of containers** 
Evaluation	Current test method applied by each car OEM	※**HG-SCC test method (Improved SLC test) proposed by Japan for GTR13**

※ **HG-SCC test method is different from H_2 compatibility test method in high pressure hydrogen gas environment.**

2-1. Relationship between SLC and SCC (in wide sense)

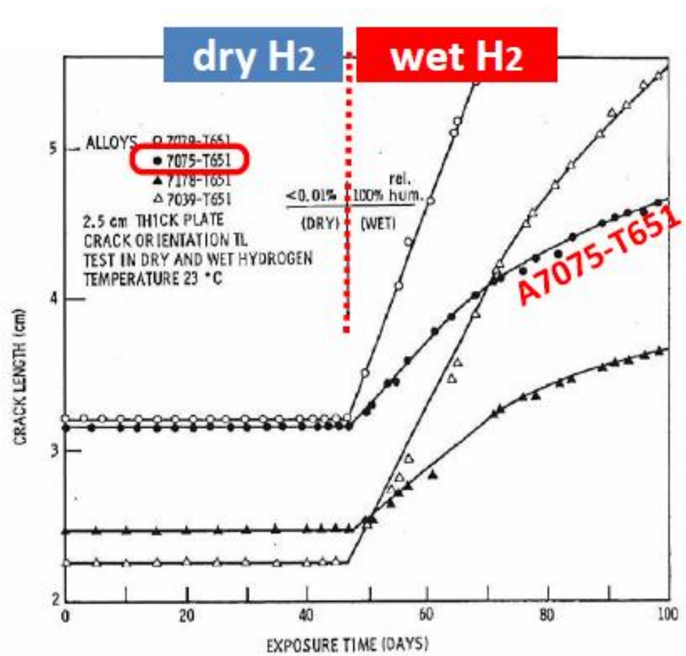
1. Understanding until 2001

- EIGA report :
  RECOMMENDATIONS FOR AVOIDANCE OF SUSTAINED LOAD CRACKING OF ALUMINIUM ALLOY CYINDERS (Doc 57/18 (2011), the first publication at the end of 1990s)
  - Investigation for the accidents of 6351 and 6082 containers as SLC.
  - Intergranular cracking is accelerated by the lead with intermetallic inclusions.
  - The manganese and silicon based intermetallic precipitates also affect the cracking.

- KHK report :
  Investigation of aluminum alloy containers for scuba (2001)
  - Investigation for the accidents of 6351 scuba containers as SCC (scuba containers are normally used in corrosive environments).
  - Intergranular cracking is accelerated due to coexistence of corrosive environment.

2-1. Relationship between SLC and SCC (in wide sense)

1. Understanding until 2001



- Crack grows rapidly in some aluminum alloys under environment with only water vapor.

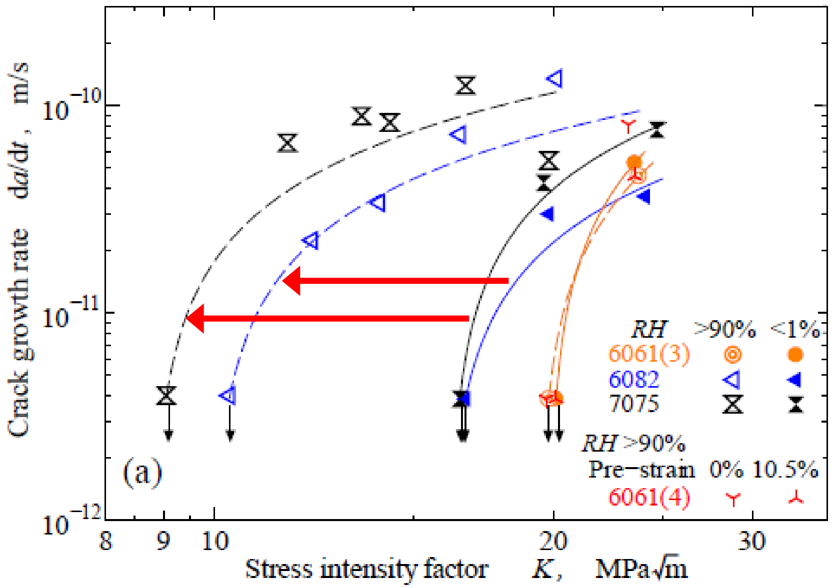
The phenomena that have been categorized as SLC might have been affected by humidity in air?

To clarify this, crack growth behavior have been investigated for many aluminum alloys in NEDO project in Japan.

M. O. Speidel and M. V. Hyatt: "Stress-Corrosion Cracking of High-Strength Aluminum Alloys" in Advances in Corrosion Science and Technology, Vol.2, ed. By M. G. Fontana and R. W. Staehle, Plenum Press, (1972), pp. 115-335.
M. O. Speidel: "Current Under standing of Stress Corrosion Crack Growth in Aluminum Alloys" in The theory of stress corrosion cracking in alloys, ed. by J.C. Scully, North Atlantic Treaty Organization, Scientific Affairs Division (1971), pp. 288-344.

2-1. Relationship between SLC and SCC (in wide sense)

2. Recent Understanding



Ogawa. T, et al. Effect of Chemical Composition and Relative Humidity on the Humid Gas Stress Corrosion Cracking of Aluminum Alloys.
Pressure technology, High Pressure Institute of Japan (2018)

- Crack growth was observed at much lower K values in humid air than in dry air.

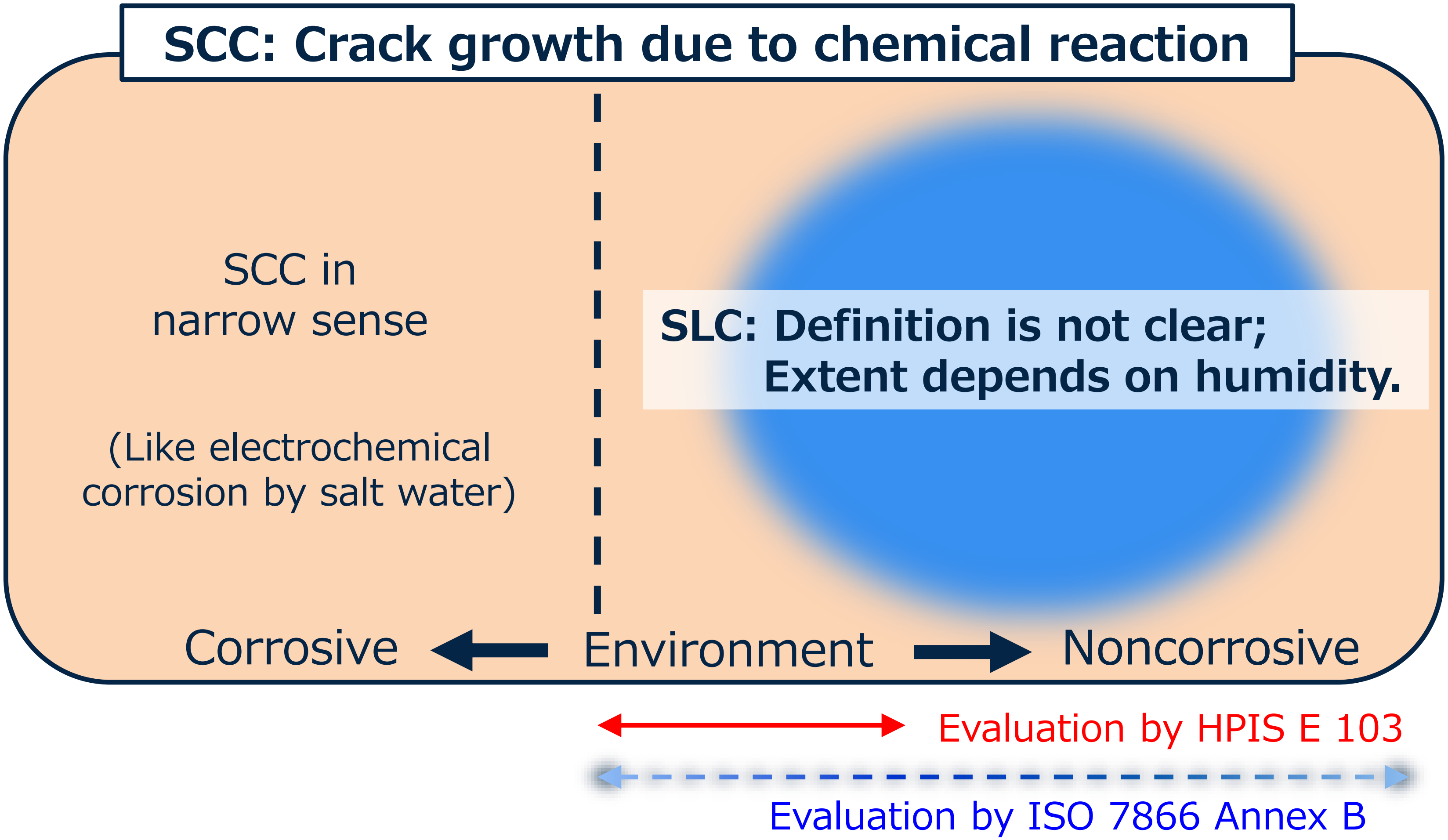
The cracking behavior must be evaluated under a controlled humidity (ISO 7866 Annex B is not enough). For safety, environments with high humidity will be necessary for screening aluminum alloys.

This effect of humidity is based on the chemical reaction:
$2Al+3H_2O \rightarrow Al_2O_3+$**6H** (ref. P4)

The phenomenon should be classified as SCC in wide sense.

2-1. Relationship between SLC and SCC (in wide sense)

Crack growth by continuous static stress



- ISO 7866 Annex B : humidity is not controlled ➡ not enough for SCC evaluation
  Result varies with humidity.
- HPIS E 103 : under high-humidity condition ➡ appropriate for SCC evaluation

3. Past accident cases

- Some accidents that seem to be caused by HG-SCC occurred in scuba containers of 6351 alloys.

Accident cases of cylinder made of aluminum alloy for SCUBA

From accident Investigation Committee in KHK (11.2001)

No.	Date (M/D/Y)	Place of occurrence	Human damage	Material	Manufacturing date	Duration of use	Damage condition	Handling condition
1	6.4.1994	Miami, Florida, USA	Severe:1	**A6351**	11.1982	11.5 years	Rupture	During refilling
2	7.1996	Alabama, USA	Unknown	**A6351**	Unknown	Unknown	Rupture	During refilling
3	5.30.1997	Vestfold, Norway	None	A5283	1973	24 years	Rupture	During storage
4	1.1998	New South Wales, Australia	Unknown	**A6351**	10.1982	15.3 years	Rupture	During storage
5	2.1.1998	Riviera Beach, Florida, USA	Severe:1 Slight :2	**A6351**	Unknown	Over 10 years	Rupture	During refilling
6	8.1998	Tairua, New Zealand	Injury	**A6351**	10.1980	18 years	Rupture	During refilling
7	12.1998	Tampa, Florida, USA	None	**A6351**	Unknown	Unknown	Rupture	During refilling
8	3.2000	Key Largo, Florida, USA	Severe:1	**A6351**	1987	13 years	Rupture	During refilling

Appearance of the broken container

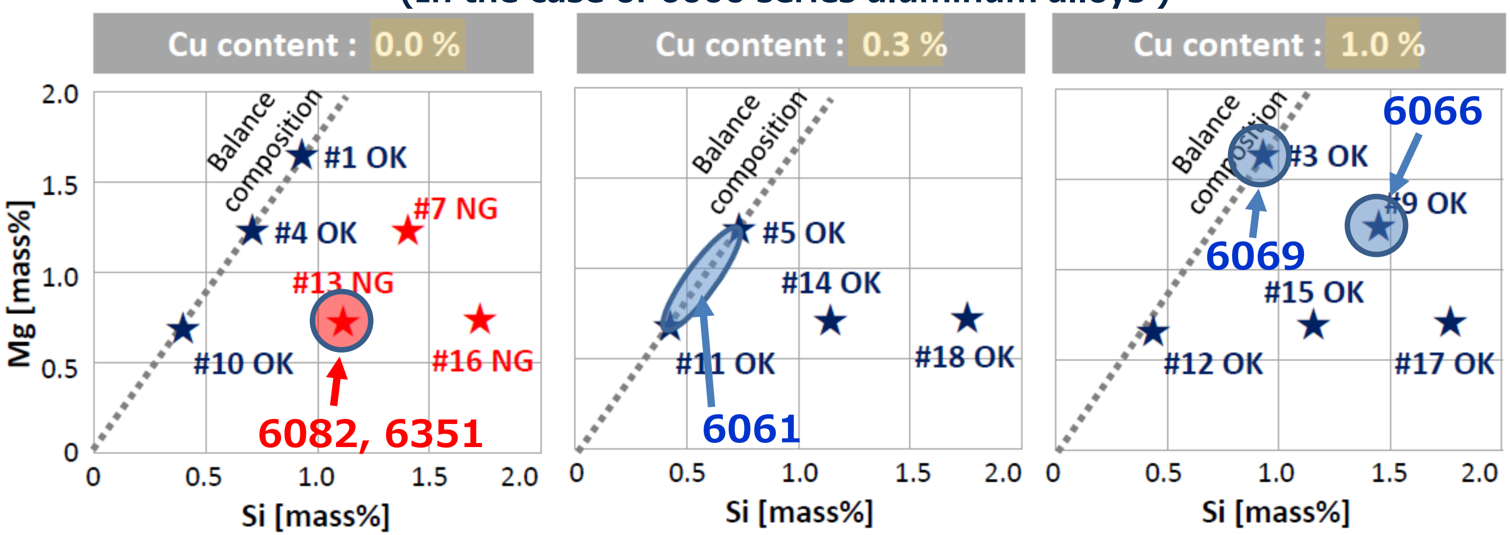
4. Position of HG-SCC test method

- Only for aluminum alloys
  - Application to other metals such as stainless steel is unnecessary.
- Effective for evaluating safety when expanding the types of aluminum alloys
  - In addition to existing 6061-T6 alloys, HG-SCC test has been done for other various alloys (see below) in humid air in Japan.
  - It does not greatly inhibit future expansion of material types.

Result of HG-SCC test classified by alloy composition (Mg, Si and Cu)

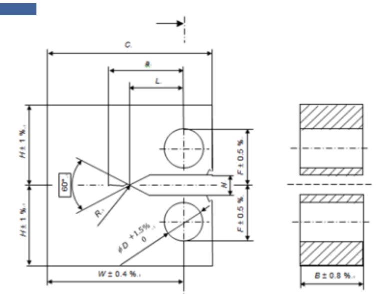
- Test condition : 25℃ , RH85 %, 90 days
- Qualification : The crack extension exceeds 0.16 mm or not.

(In the case of 6000 series aluminum alloys)



5. Progress of IWG discussion

■ Summary of HG-SCC test method (HPIS E 103:2018)



Example of specimen (CT)

□ The test conditions

a) Temperature: 25˚C ± 5˚C

b) Atmosphere and humidity: 85 % or higher in relative humidity in air

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

SLC(Sustained Load Cracking) test

□ How to judge

The crack extension exceeds 0.16 mm or not under applied stress intensity factor value (K_{IApp}=0.056 $\sigma_{0.2}$)

ref) K_{IApp}: equivalent to $\sigma_{0.2}$ at the tip of a crack of 1mm length

■ Progress of IWG discussion

GTR13 IWG	Proposal from Japan	Discussions
1st～3rd	• Introduce corrosion mechanism and verification test results • Explain Japanese standard (HPIS)	• Need additional verification in humid H_2 • Question of influence of 5ppm H_20 at room temp in H_2 of FCV
4th	• Introduce additional verification test plan in humid H_2	• Also need verification by other test lab
5th	• Introduce verification test plan by Japan, SNL(US) and MPA Stuttgart(Germany)	Request continuous discussion from Japan because of importance of HG-SCC test method

6. Plan of verification test (in humid hydrogen gas environment)

- **objective : Confirm whether the same results as the evaluation under humid air environment can be obtained also under humid hydrogen environment.**

◎Samples
A6061-T6 / A6082-T6 / A7075-T6

◎Specimen shape
½ inch compact tension (CT) specimen based on ISO 7539-6

◎Test type
Stepwise-load test or rising-load test.

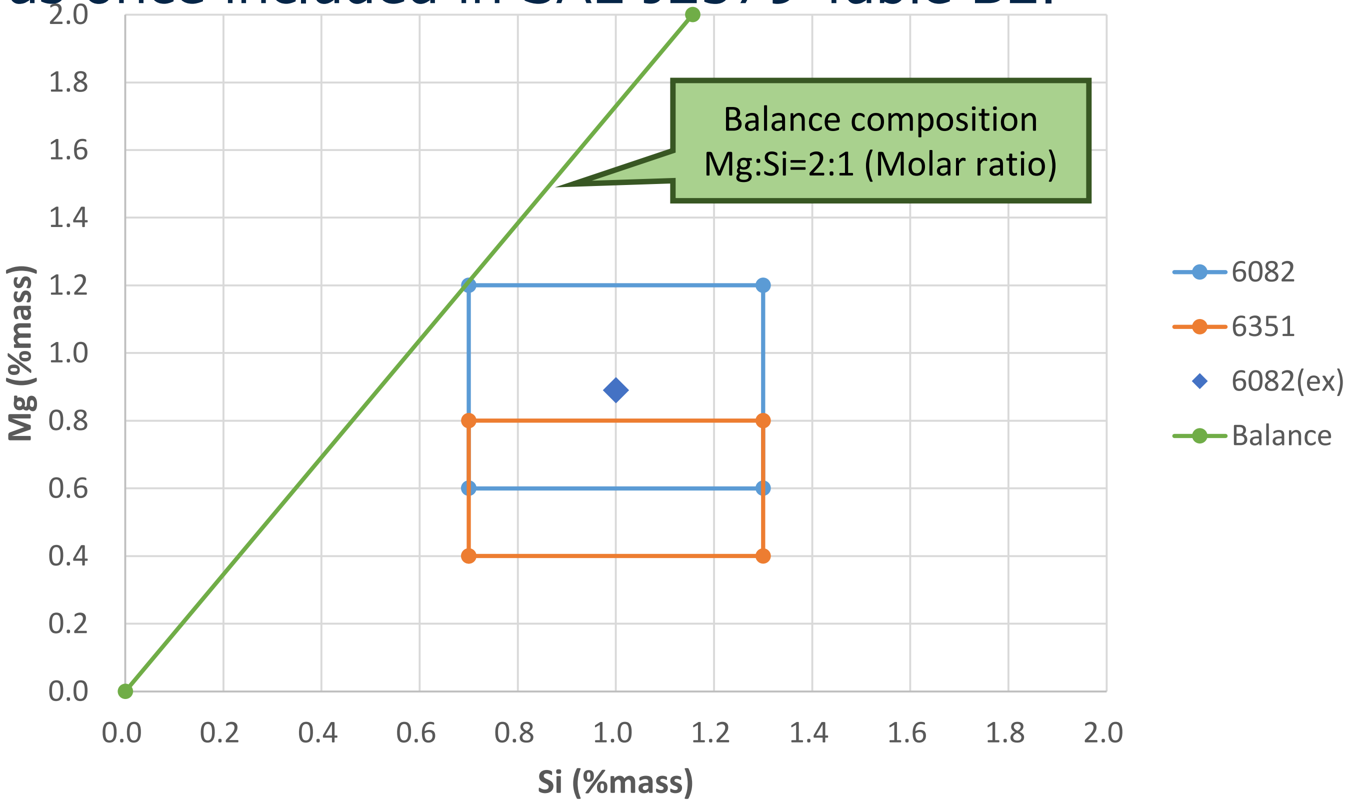
◎Gas condition
・High purity hydrogen gas (Pure H_2)
10MPa, G1 grade (99.99999%; 7N), Frost point: -80°C* (～0.004ppm H_2O)
・Humid hydrogen gas (Wet H_2)
10MPa at 20°C, Frost point: -15°C (24.7～27.3ppm H_2O*)
(* GAS specification)

◎Temperature
・Room temperature (ambient temperature)
・Low temperature : -15°C±1°C

◎Test schedule
・Pretest 2019.10
・Test 2019.11～

6-1. Comparison of chemical composition between 6351 and 6082

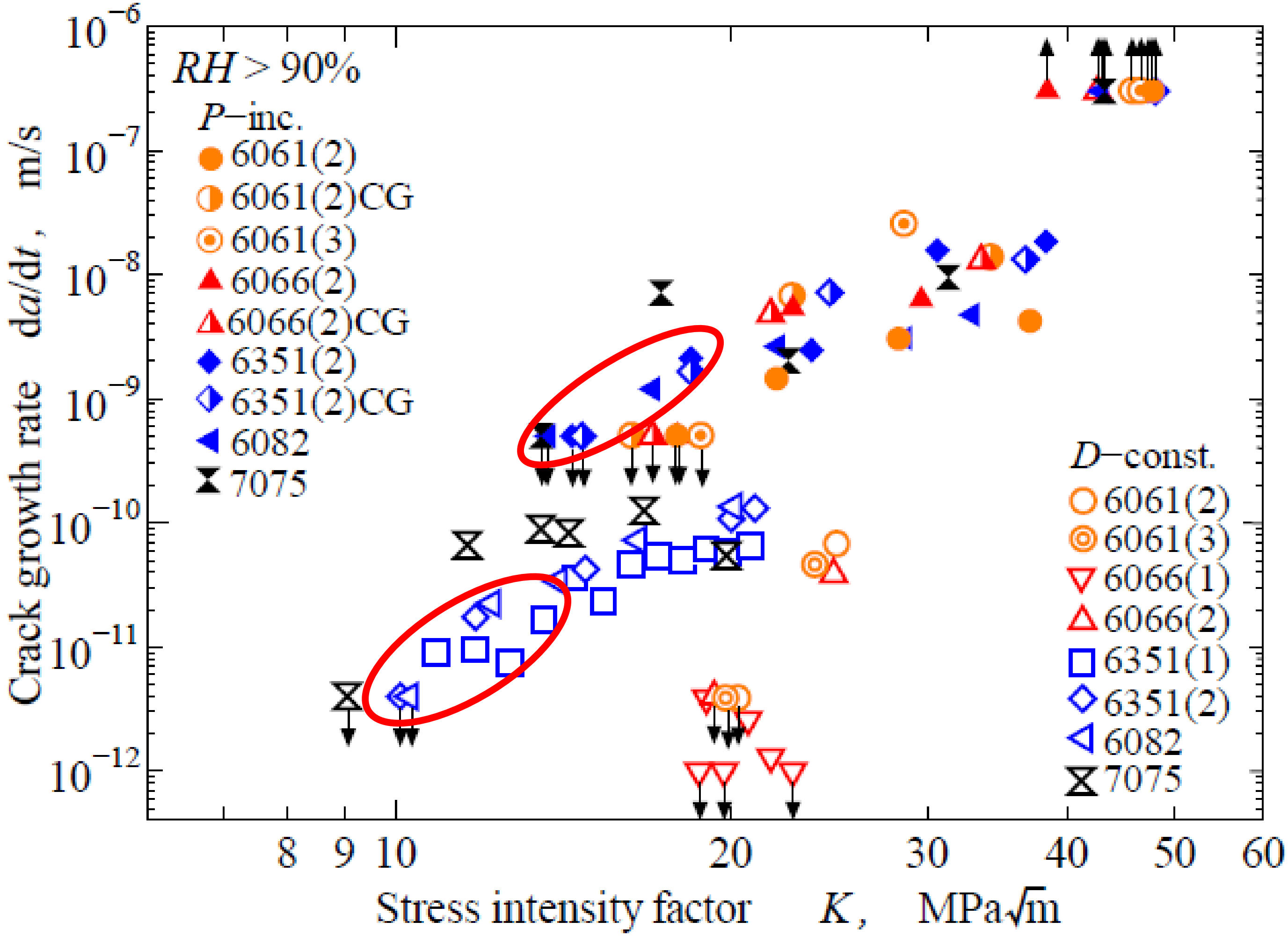
- 6082 has almost the same chemical composition as 6351.
- 6082 was once included in SAE J2579 Table B2.



	Si	Mg	Cu	Fe	Mn	Cr	Zn	Ti
6351	0.7-1.3	0.4-0.8	<0.1	<0.5	0.4-0.8	-	<0.2	<0.2
6082	0.7-1.3	0.6-1.2	<0.1	<0.5	0.4-0.8	<0.25	<0.2	<0.1
6082(ex)	1.0	0.89	<0.01	0.23	0.71	0.14	<0.01	0.03

6-2. HG-SCC characteristics of the standard alloys

- 6082 and 6351 have almost the same HG-SCC characteristics.
  ➡ Evaluation of 6082 can be regarded as equivalent to evaluation of 6351.



Ogawa. T, et al. Effect of Chemical Composition and Relative Humidity on the Humid Gas Stress Corrosion Cracking of Aluminum Alloys. Pressure technology, High Pressure Institute of Japan (2018)

(Reference) Verification tests of the other test labs

- Validation test plan at Sandia National Laboratories (US)
  - ✓ Constant displacement SCC test in high pressure humid hydrogen environment (30ppm H_2O, 70MPa) : end of December

- Validation test plan at MPA Stuttgart (Germany)
  - ✓ HG-SCC test in humid air environment based on Japanese proposal (HPIS E 103:2018) : end of March, 2020
    (1st data : end of December)

7. Summary

- 2 types of corrosion phenomena exist in aluminum alloys.
  - The anodic dissolution corrosion by salt water occur outside of the containers. It is possible to evaluate this phenomenon using the current test method applied by each car OEM.
  - The stress corrosion cracking in humid gas environment (HG-SCC) may occur both outside and inside of the containers. Since it is difficult to detect HG-SCC especially inside of the containers, new test method at material level is necessary.

- This HG-SCC test method is for evaluating safety of aluminum alloys in humid gas environment. It does not greatly inhibit future expansion of material types.

- In addition to evaluation in humid air environment, other verification tests in humid hydrogen gas environment have been planned for validation of HG-SCC test method.
  - Japan will show some of the test results at the 8th GTR No.13 IWG in March 2020.

Thank you for your kind attention