

## Improvements in Corrosion Resistance Offered By Newer Generation 2x99 Aluminum-Lithium Alloys for Aerospace Applications.

James P. Moran<sup>1</sup>, Francine S. Bovard<sup>1</sup>, James D. Chrzan<sup>1</sup>  
Roberto J. Rioja<sup>1</sup>, Edward L. Colvin<sup>2</sup>,

<sup>1</sup>Alcoa Inc., Alcoa Technical Center, Alcoa Center PA, USA

<sup>2</sup>Alcoa Forgings and Extrusions, Lafayette, IN, USA

In recent years, several new-era (3rd generation) aluminum-lithium alloys have been developed for use in aerospace applications. Alloys of the 2x99 family, demonstrate significant improvements in corrosion performance, relative to the “legacy” alloys (e.g., 2x24, 7x75). This paper documents the excellent corrosion resistance of currently-available commercial 2x99 alloys and tempers. This includes assessments of stress corrosion cracking, exfoliation, intergranular corrosion and pitting corrosion, in both laboratory and seacoast exposure environments. In addition to the commercial tempers, the corrosion performance of 2x99 alloys is assessed as a function of the degree of artificial aging. Also, results from efforts to correlate seacoast exposure to laboratory test methods are provided.

**Keywords:** Alloy 2099, Alloy 2199, Corrosion, Stress Corrosion, Seacoast Exposure.

### 1. Introduction

Over the past decade or more, an extensive amount of research has been documented by the Aging Aircraft technical community, geared toward the characterization, monitoring, prediction, remediation, and prevention of aircraft corrosion. The vast majority of this work has focused on older military aircraft; hence most of the focus also has been on the “legacy alloys”, e.g., 2024-T3 and 7075-T6, which are well-known to exhibit poor corrosion performance. Beyond these legacy alloys, various newer alloys in the general 7xxx-T7x category have offered improvements in corrosion performance, and have been used extensively on newer aircraft structure. In recent years, Alcoa has been developing a series of new-era, 3rd generation Al-Li alloys [1-3]. These alloys offer superior corrosion resistance, as well as attractive mechanical properties and weight-savings opportunities [1-4]. This paper documents the corrosion performance of two of these new alloys. This includes characterization of the commercial tempers, and the effect of aging time on corrosion performance.

### 2. Experimental procedure

#### 2.1 Materials

Multiple lots of both Alloy 2099-T86 plate and Alloy 2199-T8 sheet were used in this study. 2099-T83 extrusions are also included. Their compositions are provided in Table 1. Details on fabrication and temper optimization for these alloys are included in a previous paper [4]. Details on which materials are used for various testing efforts are provided in Section 2.3.

**Table 1.** Chemical Composition Limits for 2099 and 2199  
(Composition in maximum weight percent unless shown as a range) [5].

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Zr	Li	Al
2099	0.05	0.07	2.4-3.0	0.10- 0.50	0.10- 0.50	0.40- 1.0	0.10	0.05- 0.12	1.6-2.0	Rem.
2199	0.05	0.07	2.3-2.9	0.10- 0.50	0.05- 0.40	0.20- 0.9	0.10	0.05- 0.12	1.4-1.8	Rem

#### 2.2 Corrosion Test Methods

A number of different corrosion test methods were employed in this study. They are all traditional methods used to study aerospace aluminum alloys. Some key details are provided below. Most are ASTM Standard methods, which are described in full detail in ASTM Standards, Volume 03.02 [6].

**2.2.1 ASTM G34:** *Standard Test Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys.* The EXCO test is a very commonly used laboratory test method for evaluating exfoliation resistance of 2XXX and 7XXX alloys. The method calls for exposure for 2 or 4 days (alloy dependant) in an acidic ( $\text{pH} < 1$ ) chloride/nitrate-based solution. After exposure, samples are compared and rated against a series of photographs provided in the standard.

**2.2.2 ANCIT :** *Aluminum Nitrate Chloride Immersion Test.* The ANCIT test is a derivative of the EXCO text, with a solution that is less-aggressive, with respect to pitting and general corrosion, but is equal with respect to exfoliation corrosion. The solution consists of the EXCO solution with a small addition of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . This raises the pH to approximately 3 thereby producing far less pitting as compared to standard EXCO. Previous work [7] demonstrated that ANCIT showed promise as an alternative to EXCO for earlier-generation Al-Li alloys. After exposure, the samples are rated against the same photographs in the EXCO test.

**2.2.3 ASTM G85-Annex 2:** *Modified ASTM Acetic Acid Salt Intermittent Spray* (also referred to as MASTMAASIS). This test method is an acidified salt spray test, with an intermit air purge. In this work, the dry bottom method was used (see ASTM G85 for more information on dry versus wet bottom options). This test environment was shown to correlate well with seacoast exposure for earlier-generation Al-Li alloys [8]. Samples are typically exposed for 2 – 4 weeks, and then rated against the same photographs in the EXCO test.

**2.2.4 ASTM G110:** *Standard Practice for Evaluating Intergranular Corrosion Resistance of Heat Treatable Aluminum Alloys.* Samples are immersed in a Chloride/Peroxide solution for 6 hours, then metallographically examined to determine the susceptibility of the sample to IG corrosion.

**2.2.5 ASTM G47:** *Standard Test Method for Determining Susceptibility to Stress-Corrosion Cracking of 2XXX and 7XXX Aluminum Alloy Products.* This method provides the details for conducting laboratory stress corrosion testing for aluminum alloys. The specimens used are 3mm diameter tensile bars, as described in ASTM G49. The test environment is alternate immersion in 3.5 wt% NaCl, as described in ASTM G44.

**2.2.6 Seacoast Exposure:** Alcoa maintains a seacoast exposure test station in Point Judith, Rhode Island, USA. The station is directly on the Atlantic Ocean, in an area with a rocky coastline, which promotes a spray containing high chloride concentration into the prevailing winds across the station. The site is downwind from major metropolitan areas so the atmosphere contains other contaminants such as acid rain components. Both stressed and unstressed specimens were exposed.

## 2.3 Types of Corrosion Evaluated

**2.3.1 Exfoliation:** Exfoliation corrosion of Alloy 2199 was studied using all three exfoliation test methods above (Sec. 2.2.1 to 2.2.3), and was also evaluated at the seacoast. The alloy was tested in both the commercial T8 temper, as well as in a number of intermediate aging times, from T3 to T8. Both the T/10 and T/2 planes were tested. 2099-T83 Extrusions were also exposed at the seacoast.

**3.2.2 Stress Corrosion Cracking:** The SCC performance of Alloy 2099 was studied using the ASTM G47 method (Sec. 2.2.5), and was also evaluated at the seacoast. The alloy was tested in both the commercial T86 temper, as well as in a number of intermediate aging times, from T3 to T86. Stress was applied in the Short Transverse direction, at multiple stress levels ranging from 25-50ksi (100-345MPa). Stress levels varied with aging time, with higher stress levels used as aging time (hence yield strength) increased. Production T86 material was tested at 50ksi.

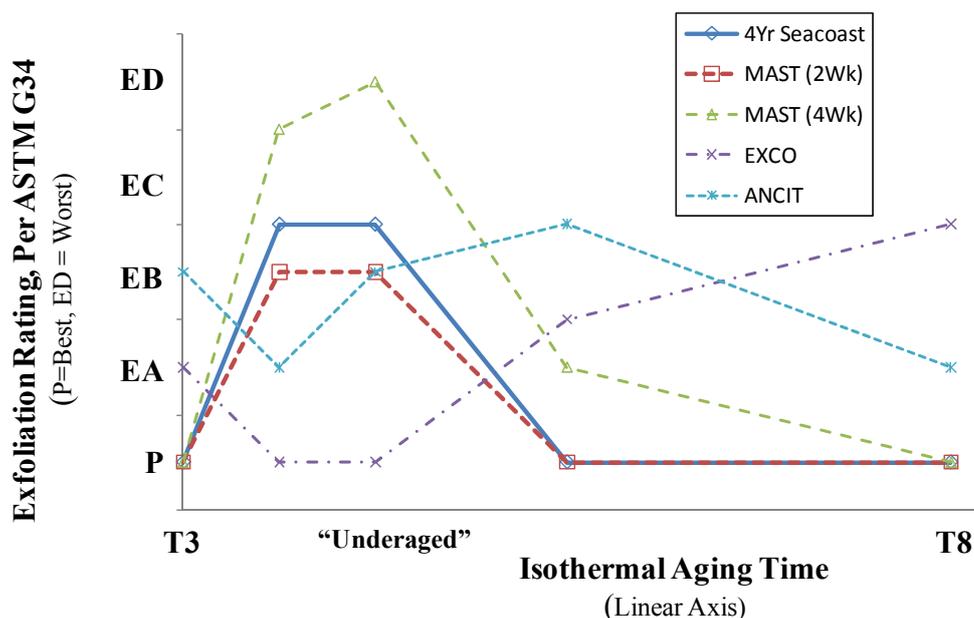
**3.2.3 Intergranular Corrosion:** The susceptibility of Alloy 2199 was studied using ASTM G110 (Sec 2.2.4), and was also evaluated at the seacoast. Both the commercial T8 and under-aged aging conditions were evaluated.

### 3. Results and Discussion

#### 3.1 Effect of Aging on Exfoliation of Alloy 2199

Figure 1 illustrates the effect of aging time on the exfoliation performance for Alloy 2199, in the three laboratory tests and after 4 years of seacoast exposure. For the seacoast samples, there is a clear trend in exfoliation resistance, with the more under-aged tempers being highly susceptible, but continued aging toward the T8 temper results in immunity to exfoliation (a “P” rating designates only pitting, no exfoliation). Figure 2 provides macro and micro photos of the under-aged and the commercial T8 conditions. Note that even in the under-aged condition, the sites of exfoliation are isolated and few; however, the morphology clearly indicates exfoliation susceptibility. In contrast, the surface of the T8 sample exhibits no exfoliation, with large areas of the original machined surfaces still clearly visible. There are some discrete sites of corrosion, but optical cross-sections reveal these are only shallow pits.

Figure 1 also provides a comparison of the various lab test methods. Note that the MASTMAASIS test method (Sec 2.2.3) demonstrates excellent correlation to seacoast results. This is consistent with earlier findings [8]. The 2-week MASTMAASIS exposure matches more directly to the 4-year seacoast data, but both 2-week and 4-week results exhibit the same trend with aging time. With longer seacoast exposure, it may well be that the 4-week data will match more directly. Neither EXCO nor ANCIT correlate well with seacoast results, in fact the EXCO test is particularly misleading because it provides a non-conservative result for under-aged samples. This could lead decision makers to choose an inappropriate temper or alloy.

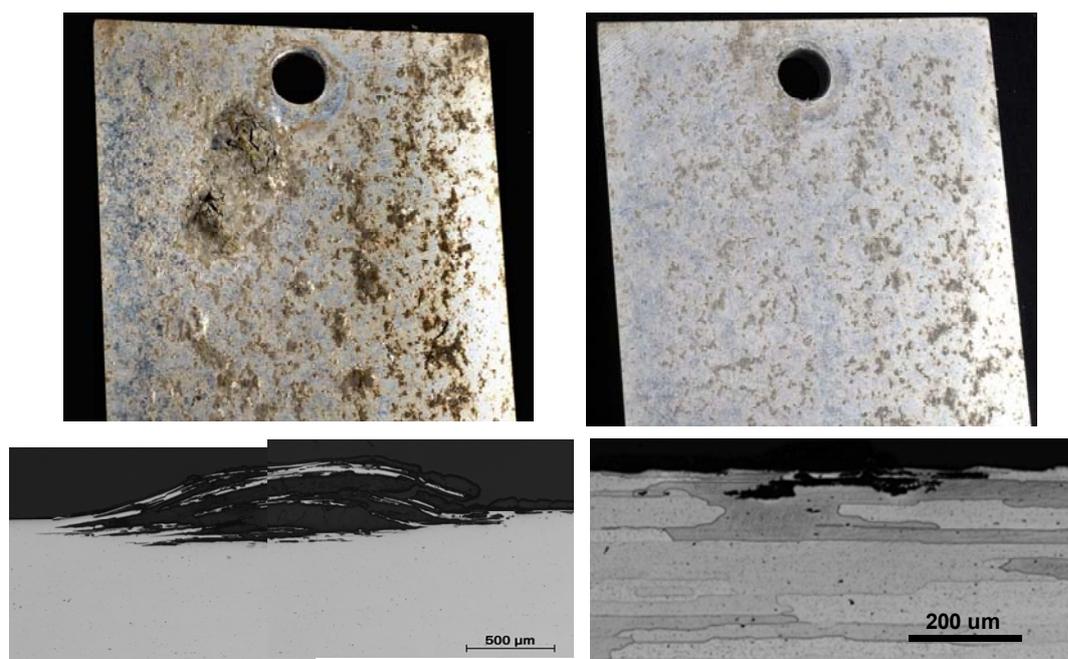


**Figure 1:** Comparison of exfoliation data for Alloy 2199, in various accelerated laboratory tests, and seacoast exposure, as a function of aging time, from T3 to T8. Note some values are mid-way between letter-grades. The values shown are an average of duplicate samples.

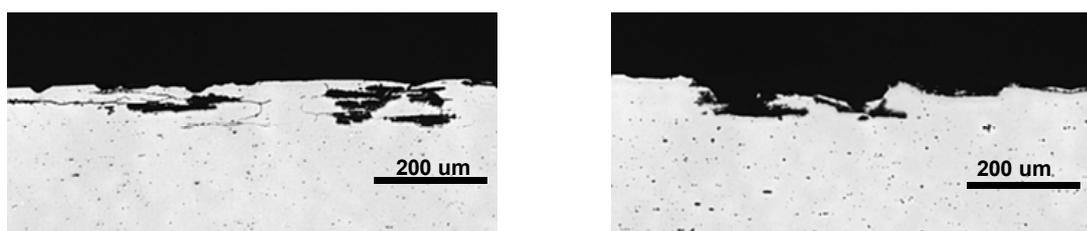
#### 3.2 Effect of Aging on Intergranular Corrosion of Alloy 2199

Figure 3 illustrates the corrosion morphology exhibited by Alloy 2199 in both under-aged and the commercial T8 aging conditions, after exposure in ASTM G110. Note that in the under-aged temper, there is a mixture of mild intergranular corrosion and pitting, while in the T8 temper, only pitting is observed. This is a similar finding to that seen in Figure 2. While the under-aged seacoast panel exhibits an exfoliation morphology, this is a form of intergranular attack. Hence the under-aged temper is exhibiting IG forms of attack in both seacoast and G110 environments. In contrast, the T8

temper exhibits a pitting morphology in both seacoast and G110 environments. These results indicate that both MASTMAASIS and G110 are useful test methods to evaluate susceptibility to intergranular forms of corrosion for Alloy 2199, and that commercially produced 2199-T8 exhibits only pitting corrosion. Note also that the pitting can develop an “under-cutting” morphology, as seen in the T8 micrographs of both Figures 2 and 3. These under-cutting sites tend to be isolated to within discrete grains, and have not been generally found to propagate beyond these discrete grains. The reason that only certain grains exhibit this under-cut pitting is not well-understood to date, but is an area of active research.



**Figure 2:** Comparison macro-photos and optical cross-sections for the under-aged (left side) and T8 (right side) aging conditions, after 4 years of seacoast exposure.

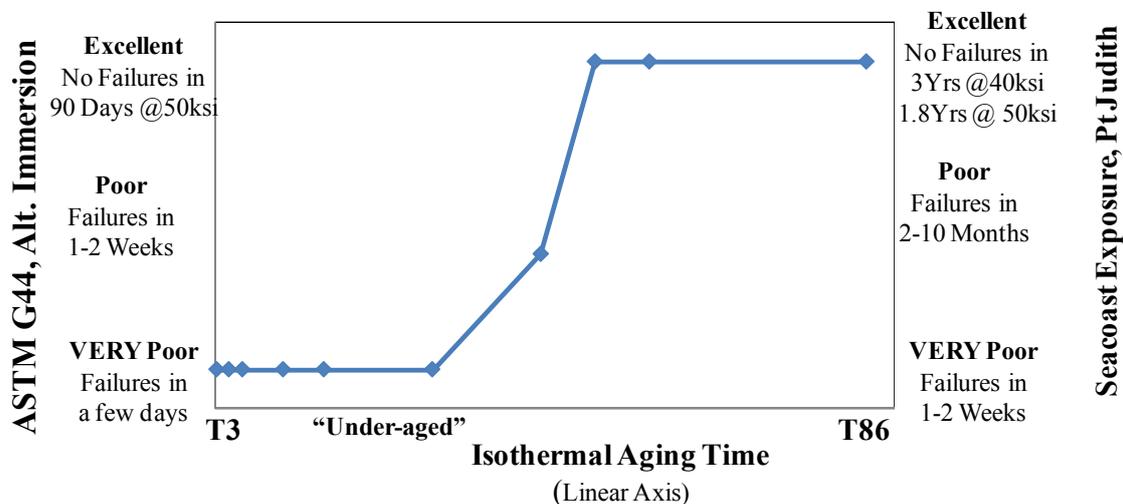


**Figure 3:** Comparison optical cross-sections for the under-aged (left side) and T8 (right side) aging conditions, after a 6 hour exposure to ASTM G110.

### 3.3 Effect of Aging on Stress Corrosion of Alloy 2099

Figure 4 illustrates the stress corrosion cracking (SCC) performance of Alloy 2099, as a function of aging time, as tested in both laboratory alternate immersion testing (ASTM G47) and at the seacoast. This plot is a schematic rendering, that incorporates the results of multiple stress levels and replicates. The stress levels vary from 25 to 40ksi, depending on aging time. While there are subtle effects of stress level, the general trends of SCC susceptibility are far more dependent on aging time, and can therefore be represented in this schematic format. Note that a similar trend is seen for SCC as was seen for exfoliation. In under-aged conditions, the alloy exhibits a high susceptibility to SCC. But with continued aging toward T86, the SCC resistance improves significantly, with the commercial T86 temper exhibiting immunity to SCC at 50ksi for 90 days in alternate immersion and more than 1.8 years (thus far) at the seacoast, with additional seacoast testing at 40ksi still in test at

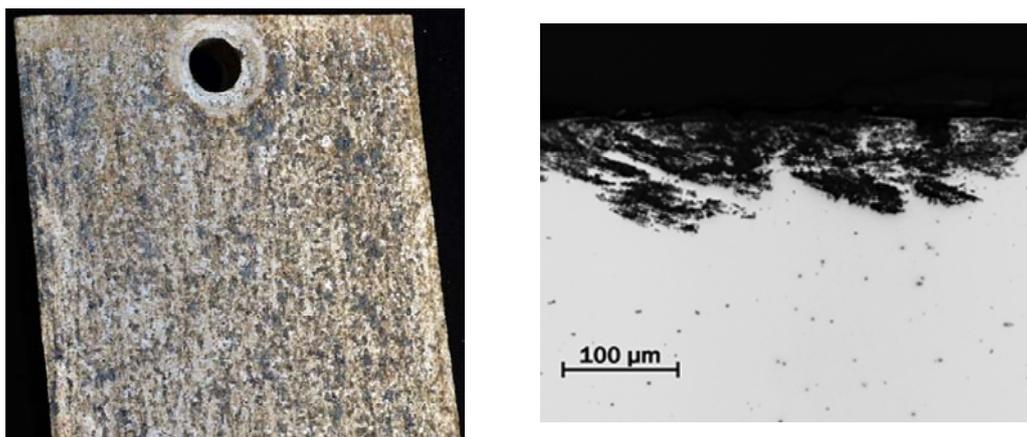
more than 3 years (thus far). Figure 4 also demonstrates that alternate immersion correlates very well with seacoast results.



**Figure 4:** Comparison of Short Transverse SCC Data for Alloy 2099 plate, in Alternate Immersion and Seacoast Exposure, as a function of aging time, from T3 to T86. The trends shown summarize testing performed at 2-3 stress levels, from 25 to 40ksi.

### 3.4 Long-Term Seacoast Exposure of 2099-T83 Extrusions

The sample illustrated in Figure 5 is a 2099 pre-cursor extrusion alloy that was a part of the alloy development efforts for 2x99 alloys. Its composition is within the range for Alloy 2099. The aging practice for this sample is not identical to the current T83 practice; however based on the comparative temperatures and times, it is deemed to have similar or perhaps slightly less equivalent aging time as the T83 practice. This sample has been exposed at the seacoast for more than 19 years. It exhibits essentially no evidence of exfoliation or intergranular corrosion, as seen by both the macro-photo and optical cross-section of Figure 5.



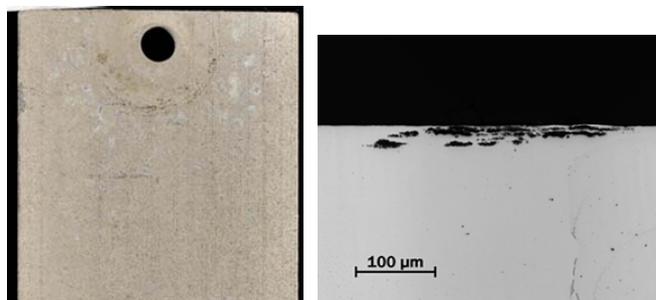
**Figure 5:** Macro-photos and optical cross-section of a 2099 Pre-cursor extrusion alloy, after 19+ years of exposure at the seacoast.

Figure 6 illustrates a production lot of 2099-T83 extrusion, after 5 years of seacoast exposure. As for the 19-year sample in Figure 5, there is again no evidence of exfoliation or IG corrosion.

### 3.5 Comparison to Incumbent Legacy Alloys

Figure 7 provides photographs that illustrate the typical corrosion behavior of 7xxx-T6 and 2x24-T3 alloys after seacoast exposure. The 7150-T6 sample, exposed for four years, is coated, but

the coating is breached at a fastener, thereby promoting the severe exfoliation corrosion that is inherent to this alloy/temper. The 2024-T3 sample is bare, and also clearly demonstrates severe exfoliation after only 1 year of exposure. This severe exfoliation is well-known for these alloys and tempers [9].



**Figure 6:** Macro-photo and metallographic cross-section of a 2099-T83 Extrusion, after 5 years of exposure at the seacoast.



**Figure 7:** Photos of 7150-T6 (left) and 2024-T3 (right), after seacoast exposure. 4 years for 7150, 1 year for 2024.

#### 4. Summary

The corrosion performance of new-era, 3rd generation 2x99 Al-Li alloys was investigated, both in the commercial T8x tempers, and as a function of the degree of artificial aging (T3 to T8x). The results indicate that while under-aged tempers are susceptible to intergranular forms of corrosion, the commercially produced T8x tempers provide exceptional resistance to stress corrosion, exfoliation and intergranular corrosion, even after many years of seacoast exposure. The results are far superior to the incumbent, legacy 7xxx-T6 and 2x25-T3 type alloys. Excellent correlation was found between well-established laboratory accelerated test methods and long-term seacoast exposure. This provides good confidence that we have a suite of laboratory test methods that can be used to evaluate corrosion performance as additional similar alloys and tempers are developed. The exceptional corrosion resistance exhibited by the 2x99-T8x alloy class, along with their attractive mechanical properties and weight-savings opportunities, should prove advantageous for new aircraft designs, and provide an opportunity for significant increases in the time-intervals for aircraft inspection and reduced maintenance costs.

#### References

- [1] Rioja, R.J., Cho, A., Colvin, E.L., Vasudevan, A.K., U.S. Patent 5,137,686, 1992
- [2] Rioja, R.J., Bowers, J.A., James, R.S., U.S. Patent 5,066,342, 1991
- [3] Rioja, R.J., Cho, A., Bretz, P.E., U.S. Patent 4,961,792, 1990
- [4] C. Giummarra, R.J. Rioja, G.H. Bray, P.E. Magnusen, J.P. Moran, 11th Int'l Conf.on Aluminum Alloys, *Aluminum Alloys*, Ed. by J. Hirsch, B. Skrotzki, G. Gottstein, (WILEY-VCH, 2008) pp. 176-188.
- [5] *International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys*, The Aluminum Association, 2006
- [6] ASTM Volume 03.02 *Corrosion of Metals; Wear and Erosion*, 2009, ASTM-International.
- [7] S. Lee, B. W. Lifka, "Modification of the EXCO Test Method for Exfoliation Corrosion Susceptibility in 7XXX, 2XXX and Aluminum Lithium Alloys," *ASTM STP 1134-New Methods for Corrosion Testing of Aluminum Alloys*, Ed. by V. S. Agarwala and G. M. Ugiansky, (1996), ASTM.
- [8] E.L. Colvin, S.J. Murtha, *Proc. 5th Int. Al-Li Conf.* eds., T.H.Sanders, E.A. Starke, Jr. (Birmingham, AL: Material and Component Engineering Publications Ltd., 1989), p. 1,251-1,260.
- [9] R. Kinzie: Proc. 6th Aging Aircraft Conference, San Francisco, CA, USA, September 2002, FAA/DoD/NASA.