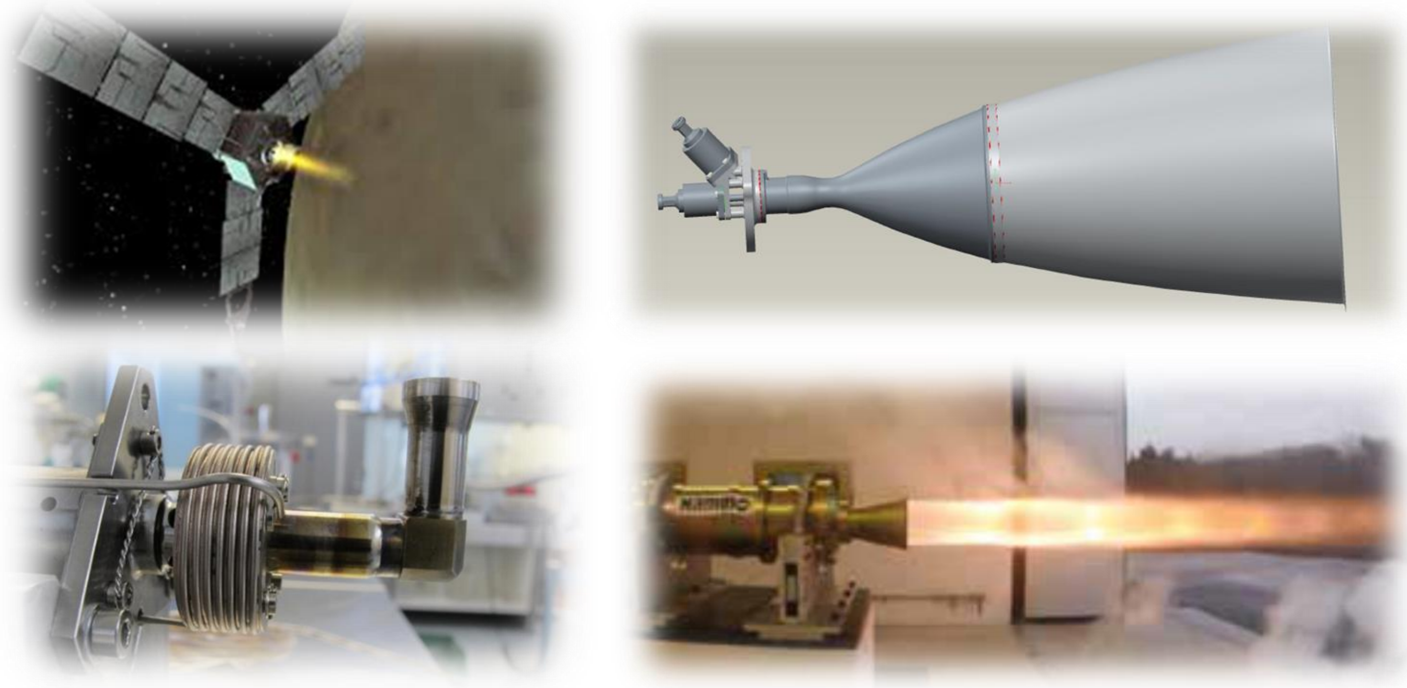
Nammo Westcott Ltd

Demisable Materials Compatibility for Tanks

Clean Space 25th October 2017 Adam Watts



SECURING THE FUTURE

The Point of the Study

- The ESA Clean Space initiative focuses on space debris mitigation by the use of graveyard and de-orbit strategies.

- Current technology uses high strength/low weight propellant tanks constructed from titanium alloys which, due to their high melting points, may and too often do survive re-entry.

- This study identified suitable propellant compatible tank construction materials which are fully demisable and therefore minimise risk to the Earth and its inhabitants from unwelcome attack from descending propellant tanks – sometimes full of non-compatible-with-human rocket fuels and acidic oxidiser.

A 600-pound stainless-steel fuel tank from a Delta II rocket, sits dented, gashed and rusty -- scarred by its descent from space to a farm near Georgetown, Texas, in 1997.

SECURING THE FUTURE

November 2011 – ‘The baffling metal sphere’, made a crater 30 cm deep and 4m wide where it fell in the Namibian desert – it was found 18m away from the impact crater

Mystery solved – a 39 litre titanium bladder tank for hydrazine that had survived a satellite re-entry .... Oooops!

SECURING THE FUTURE

Skylab

Skylab was the USA’s first and only space station orbiting Earth from 1973 to 1979. It fell back to Earth amid huge worldwide media attention. due to delays with the development of the Space Shuttle, Skylab's decaying orbit could not be stopped.

Skylab – uncontrolled re-entry

Skylab did not burn up as fast as NASA expected, and Skylab debris landed southeast of Perth in Western Australia

Objectives of the Compatibility Study

- Bibliographic review and database creation of historical compatibility testing (materials and methods).
- Compilation of a database of prospective alloys and surface treatments.
- Procurement, surface treatment, immersion test and post-test analysis of propellant and candidate materials and surface treatments.
- Creation of a list of immersion tested alloys plus surface treatments and their compatibility with the candidate propellants.

Documents – always fun!

Applicable Documents		
AD1	Performance SpecificationPropellant, Hydrazine	MIL-PRF-26536E
AD2	Performance SpecificationPropellant, Monomethylhydrazine	MIL-PRF-27404C
AD3	Performance Specification Propellant, Dinitrogen Tetroxide	MIL-PRF-26539F

Reference Documents		
RD1	Flammability, offgassing and compatibility requirements and test procedures	NASA-STD-6001B
RD2	Compatibility testing for liquid propulsion components, subsystems and systems	ECSS-E-ST-35-10C
RD3	Brown, C.T. Determination of Long-term compatibility of hydrazine with selected with selected materials of construction. Design Criteria and Guidance, AFRPL.	AFRPL-TR-76-33
RD4	Salvinski, R.J.; Vol. II: Materials Compatibility and Liquid Propellant Study, TRW, 1967.	NAS 7-436
RD5	Marsh, W.R.; Knox, B.P.; USAF Propellant Handbooks Hydrazine fuels, AFRPL, 1970.	AFRPL-TR-69-149
RD6	Flammability testing for the screening of space materials	ECSS-Q-ST-70-21C
RD7	Materials, mechanical parts and processes	ECSS-Q-ST-70C
RD8	Performance Specification Propellant, Unsymmetrical Dimethyl Hydrazine	MIL-PRF-26536E

Test Propellants

Propellant	Supplier	Amount	Batch	Specification
Hydrazine	Girling Holz (Cylinder)	105kg	EAL/SR/2014.013	MIL-PRF-26536F
MMH	Safran (Drum)	42kg	12TL050014	MIL-PRF-27404C
MON-3	Airbus Lampoldshausen	625kg	-	MIL-PRF-26539F

Discussions with ESA identified the fuels monomethyl hydrazine and anhydrous hydrazine, along with the oxidiser dinitrogen tetroxide as the propellants for study.

Aluminium was the preferred tank material, specifically alloys of aluminium-lithium and this study focussed upon these.

Aluminium Lithium Alloys

- Aluminium lithium alloys are a range of advanced aluminium alloys that usually contain around 2-3% lithium along with copper and magnesium alloying elements. Their key advantage over standard aluminium alloys is a lower density combined with improved elastic modulus. Resistance to fatigue cracking is also generally superior to standard 2000 and 7000 series aluminium alloys. Newer (third generation) aluminium lithium alloys have improved corrosion resistance and greater toughness than their predecessors.

- These properties make aluminium lithium particularly suitable to any application where weight to strength ratio is critical and fatigue cracking is a concern. Aerospace and motorsport are typical application areas as well as space exploration where these alloys have been extensively used.

Alloy Selection Criteria

Previous compatibility data available for the Alloy

- Positive/negative results?
- Validity/applicability of the testing
- Availability of the data

Material properties

- Does the Alloy meet the structural requirements for a pressurised propellant tank? (These structural requirements need to be determined)
- Can the Alloy be machined (spun/cast/forged) and made (welded) into components for and into a complete propellant tank? (Tank component manufacturing and complete tank construction methods need to be determined)

Alloys

- Composition of the Alloy
  - Does the Alloy contain elements that are perceived to reduce its compatibility with conventional rocket propellants?
  - If so, is there anything that can be done to the Alloy to potentially improve its compatibility e.g surface treatments?
- Availability
  - How easily can the Alloy be obtained both for this study and assuming it was to be used commercially to make ‘X’ number of propellant tanks per year?
  - Future availability of the Alloy must be considered. Is the Alloy being less commonly used? Will it no longer be commercially available in the foreseeable future?

The Al-Li Alloys chosen

Coupon 1 – Alloy 2055 supplier ALCOA

Coupon 2 – Alloy 2060 supplier ALCOA

Coupon 3 – Alloy 2070 supplier ALCOA

Coupon 4 – Alloy 2195 supplier MT Aerospace
A high strength, heat treatable aluminium lithium alloy containing around 1% lithium. Weldability is good and it finds many applications in aerospace, space and some military armour applications. Good fracture resistance at very low temperatures. The alloy composition of 2195 aluminium is:
Copper: 3.7 to 4.3%, Lithium: 0.8 to 1.2%, Zirconium: 0.08 to 0.16%

Coupon 5 – Alloy 2219 supplier MT Aerospace

Coupon 6 – Alloy 2050 supplier Constellium
The alloy 2050 was defined for a medium to high strength and high damage tolerance alloy intended to out-perform the property balance of 2xxx thin plate alloys and 7xxx thick plate alloys. Copper: 3.2 to 3.9%, Lithium 0.7 to 1.3%, Zirconium: 0.06 to 1.4%

Coupon 7 – Alloy 2198 supplier Constellium

Initial Alloy Information

- The obtainability of some of the initial Alloys proposed:
  - 2099: This is a commercially available product and can be easily obtained in plate form.
  - 2199: This is not currently a commercial product but it is very similar to 2099 and so is obtainable in plate form.
  - 2195: There are only small amounts of this alloy produced and it is in the US making it hard to obtain.
  - 2050: This alloy is made by a competitor of ALCOA (our preferred supplier), 2070 is a similar alloy made by ALCOA and is easily available in plate form. This is becoming a commercial alloy.
  - 2060: This is a sheet product available in sheets of 2mm - 8mm thickness. It is a commercial product used for aircraft fuselages and is easily obtainable.
  - 2219: This is not an Al-Li alloy and has a high copper content.

Sample material compositions considered

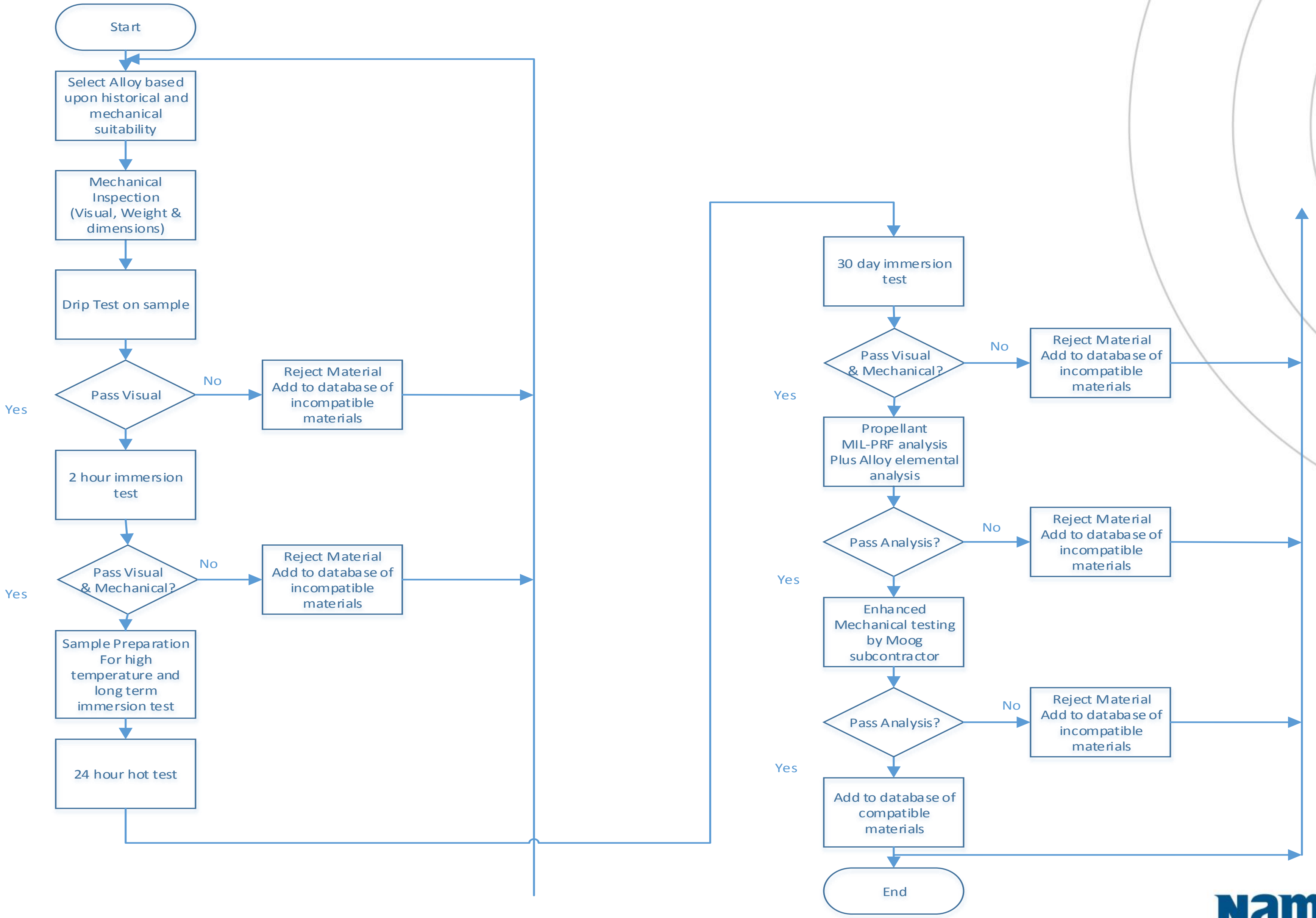
Element %		Aluminium			Aluminium-Lithium (*=ESA preferred alloy) Safety Tests to select AL-Li alloy?									Stainless Steel	
Symbol	**Name**	**1100**	**5052**	**6061**	**2050***	**2090**	**2091**	**2099***	**2195***	**2199***	**2219***	**2297**	**8090**	**304L**	**316**
Al	**Aluminium**	99.0 min	93.9-96.7	96.0-97.36	92.03-95.44	92.53-94.8	91.9 - 95.4	92.7-95.1	91.9 - 94.9	93.3-95.8	91.5-93.8	93.7-96.2	93-96.2		
Ag	**Silver**				0.20-0.70				0.25 - 0.60						
Be	**Beryllium**							<=0.0001							
Bi	**Bismuth**														
C	**Carbon**													<=0.03	<=0.03
Cr	**Chromium**		0.15–0.35	0.04–0.35	<=0.05	0.05	<= 0.10						<=0.10	18.0-20.0	18.0-20.0
Cu	**Copper**	0.05–0.20	0.1	0.15–0.40	3.2-3.9	2.4-3.0	1.8 - 2.5	2.4-3.0	3.7 - 4.3	2.3-2.9	5.8-6.8	2.5-3.1	1.0-1.6		
Fe	**Iron**	0.95 Si+Fe	0.4	0.7	<=0.10	0.12	<= 0.30	<=0.07	<= 0.15	<=0.07	<=0.30	<=0.10	<=0.30	65.05-71.05	60.05-67.05
Ga	**Gallium**				<=0.05										
Li	**Lithium**				0.70-1.3	1.9-2.6	1.7 - 2.3	1.6-2.0	0.80 - 1.2	1.4-1.8		1.1-1.7	2.2-2.7		
Mg	**Magnesium**		2.2–2.8	0.8–1.2	0.20-0.60	0.25	1.1 - 1.9	0.1-0.5	0.25 - 0.80	0.05-0.40	<=0.02	<=0.25	0.6-1.3		
Mn	**Manganese**	0.05	0.1	0.15	0.20-0.50	0.05	<= 0.10	0.1-0.5	<= 0.25	0.1-0.5	0.20-0.40	0.10-0.50	<=0.10	<=2.0	<=2.0
Mo	**Molybdenum**														2.0-3.0
N	**Nitrogen**													<=0.1	<=0.1
Ni	**Nickel**				<=0.05									8.0-12.0	10.0-14.0
P	**Phosphorous**													<=0.045	<=0.045
S	**Sulphur**													<=0.03	<=0.03
Si	**Silicon**	0.95 Si+Fe	0.25	0.40–0.8	<=0.08	0.1	<= 0.20	<=0.05	<= 0.12	<=0.05	<=0.20	<=0.10	<=0.20	<=0.75	<=0.75
Ti	**Titanium**			0.15	<=0.10	0.15	<= 0.10	<=0.1	<= 0.10		0.02-0.10	<=0.12	<=0.10		
V	**Vanadium**										0.05-0.15				
Zn	**Zinc**	0.1	0.1	0.25	<=0.25	0.1	<= 0.25	0.4-1.0	<= 0.25	0.2-0.9	<=0.10	<=0.05	<=0.25		
Zr	**Zirconium**				0.06-0.14	0.08-0.15	0.04 - 0.16	0.05-0.12	0.08 - 0.16	0.05-0.12	0.10-0.25	0.08-0.15	0.04-0.16		

ALCOA

🟩 **Oxidiser**

🟥 **Fuel**

Alloy Selection Logic Diagram



Start

Select Alloy based upon historical and mechanical suitability

Mechanical Inspection (Visual, Weight & dimensions)

Drip Test on sample

Pass Visual

No

Reject Material Add to database of incompatible materials

Yes

2 hour immersion test

Pass Visual & Mechanical?

No

Reject Material Add to database of incompatible materials

Yes

Sample Preparation For high temperature and long term immersion test

24 hour hot test

30 day immersion test

Pass Visual & Mechanical?

No

Reject Material Add to database of incompatible materials

Yes

Propellant MIL-PRF analysis Plus Alloy elemental analysis

Pass Analysis?

No

Reject Material Add to database of incompatible materials

Yes

Enhanced Mechanical testing by Moog subcontractor

Pass Analysis?

No

Reject Material Add to database of incompatible materials

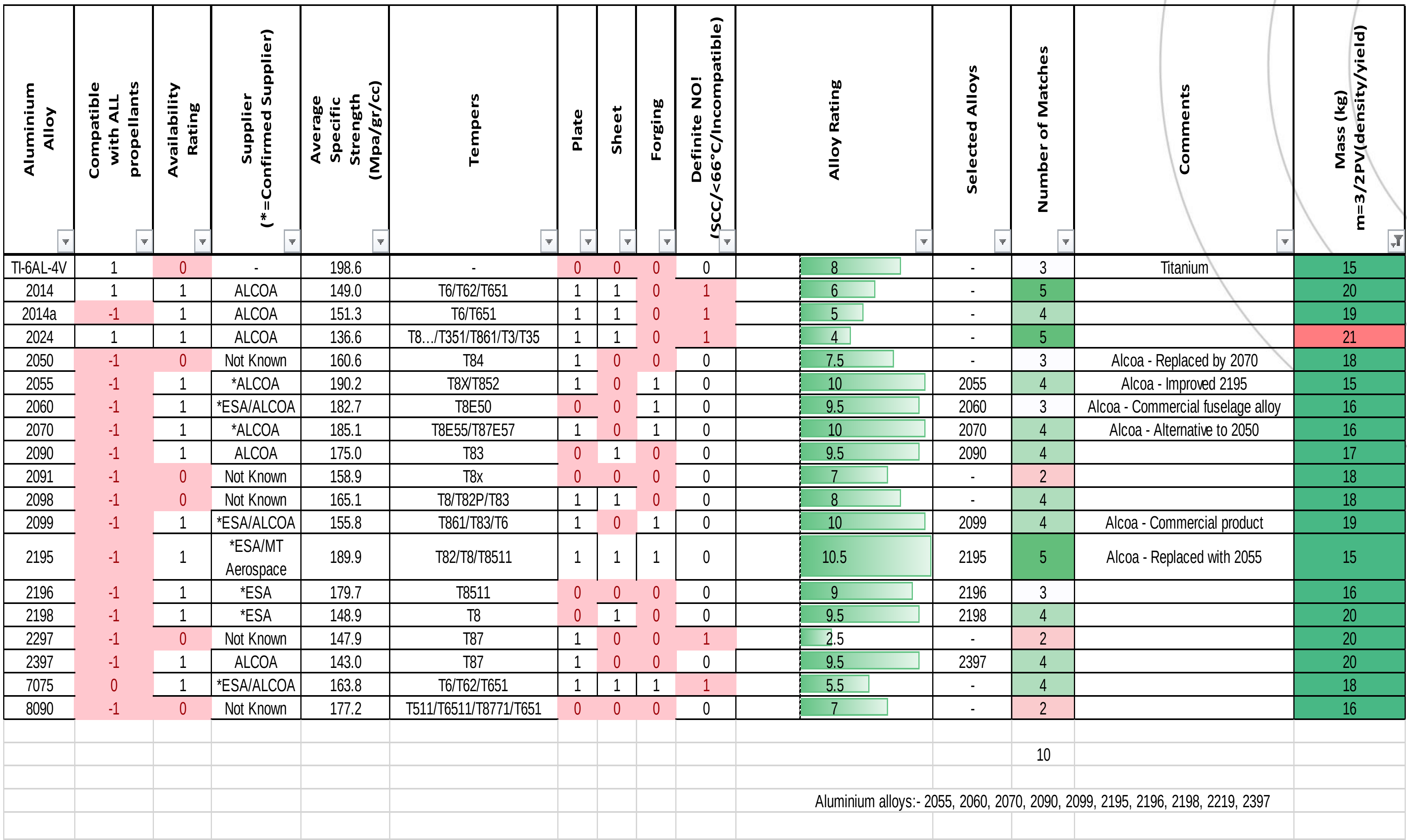
Yes

Add to database of compatible materials

End

SECURING THE FUTURE

The Alloy Selection



Aluminium Alloy	Compatible with ALL propellants	Availability Rating	Supplier (*=Confirmed Supplier)	Average Specific Strength (Mpa/gr/cc)	Tempers	Plate	Sheet	Forging	Definite NO! (SCC/<66°C/Incompatible)	Alloy Rating	Selected Alloys	Number of Matches	Comments	Mass (kg) m=3/2PV(density/yield)
TI-6AL-4V	1	0	-	198.6	-	0	0	0	0	8	-	3	Titanium	15
2014	1	1	ALCOA	149.0	T6/T62/T651	1	1	0	1	6	-	5		20
2014a	-1	1	ALCOA	151.3	T6/T651	1	1	0	1	5	-	4		19
2024	1	1	ALCOA	136.6	T8…/T351/T861/T3/T35	1	1	0	1	4	-	5		21
2050	-1	0	Not Known	160.6	T84	1	0	0	0	7.5	-	3	Alcoa - Replaced by 2070	18
2055	-1	1	*ALCOA	190.2	T8X/T852	1	0	1	0	10	2055	4	Alcoa - Improved 2195	15
2060	-1	1	*ESA/ALCOA	182.7	T8E50	0	0	1	0	9.5	2060	3	Alcoa - Commercial fuselage alloy	16
2070	-1	1	*ALCOA	185.1	T8E55/T87E57	1	0	1	0	10	2070	4	Alcoa - Alternative to 2050	16
2090	-1	1	ALCOA	175.0	T83	0	1	0	0	9.5	2090	4		17
2091	-1	0	Not Known	158.9	T8x	0	0	0	0	7	-	2		18
2098	-1	0	Not Known	165.1	T8/T82P/T83	1	1	0	0	8	-	4		18
2099	-1	1	*ESA/ALCOA	155.8	T861/T83/T6	1	0	1	0	10	2099	4	Alcoa - Commercial product	19
2195	-1	1	*ESA/MT Aerospace	189.9	T82/T8/T8511	1	1	1	0	10.5	2195	5	Alcoa - Replaced with 2055	15
2196	-1	1	*ESA	179.7	T8511	0	0	0	0	9	2196	3		16
2198	-1	1	*ESA	148.9	T8	0	1	0	0	9.5	2198	4		20
2297	-1	0	Not Known	147.9	T87	1	0	0	1	2.5	-	2		20
2397	-1	1	ALCOA	143.0	T87	1	0	0	0	9.5	2397	4		20
7075	0	1	*ESA/ALCOA	163.8	T6/T62/T651	1	1	1	1	5.5	-	4		18
8090	-1	0	Not Known	177.2	T511/T6511/T8771/T651	0	0	0	0	7	-	2		16
												10		

Aluminium alloys:- 2055, 2060, 2070, 2090, 2099, 2195, 2196, 2198, 2219, 2397

Surface Treatments

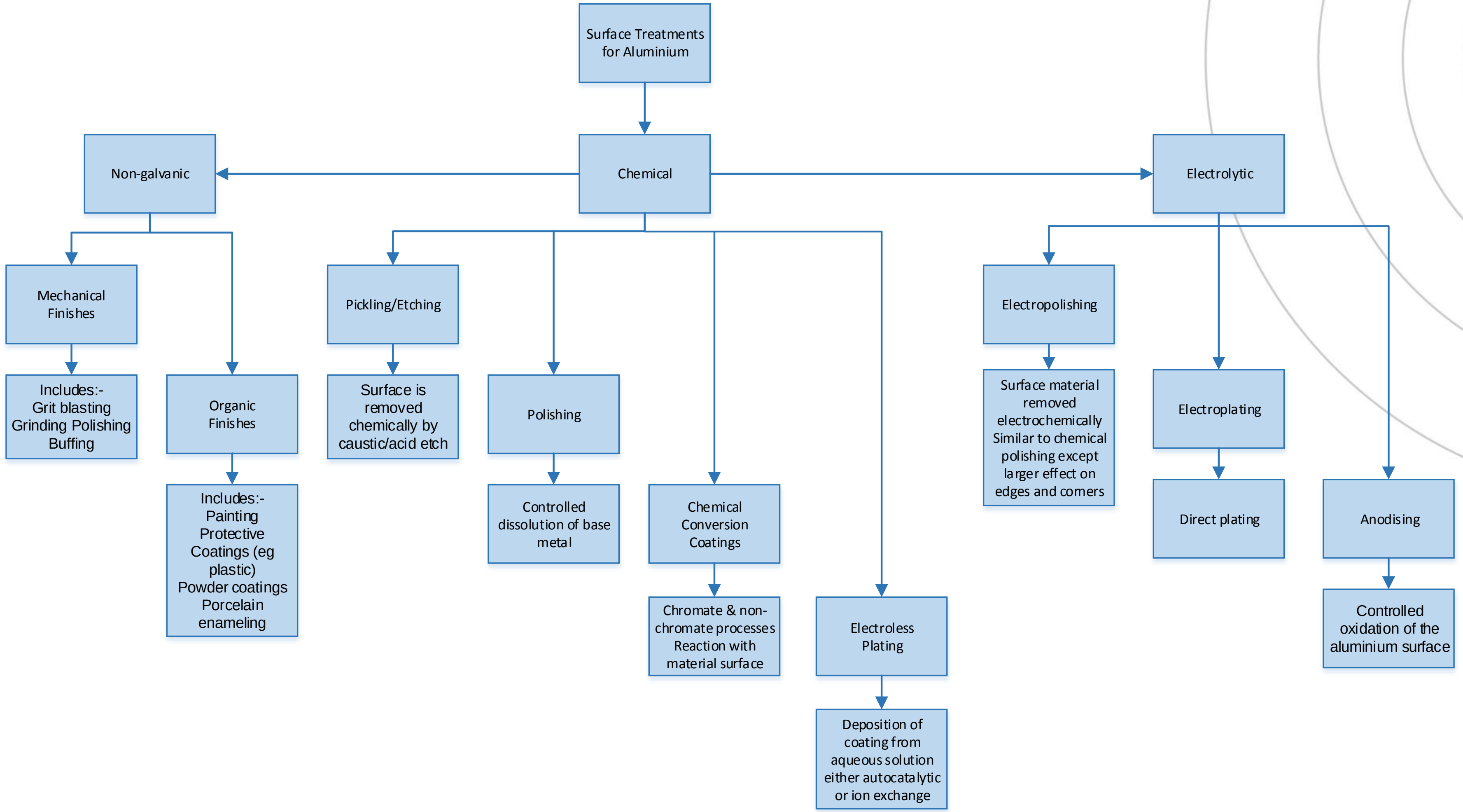
1. Mechanical finishing to achieve the standard for space hardware of 0.4 micron surface roughness and cleaning as per 205909-5146 “ESA Demisable Materials Study – Test Procedure D4”. This is to be performed on all coupons including those subject to further surface treatment so as to achieve a standard for comparison.
2. A pickle/passivation technique (7% solution of 6:1 HNO3 (69%) : HF (38-40%) in demineralised water for 15 minutes) to remove weld scale/dealloy (remove incompatible alloy components) from the material surface.
3. A chemical conversion coating - Chemetall Gardobond x4707 treatment.
4. ESA requested a proposed hard anodise was replaced with a pickle/passivate treatment using tri-sodium phosphate (Na_3PO_4). In addition to the acid pickle/passivation technique, ESA were keen to try one based upon an alkali or base solution. It was felt that the acid treatment was more suitable for oxidiser and an alkali treatment for fuels.

Surface Treatments

The Chemetall Gardobond x4707 treatment.

- Coating consists of titanium/zirconium.
- Formed by a reaction between alloy surface and coating fluid.
- 5 to 20 mg/m^2 (very thin) – this may not be a problem as the coating could be applied to the internal surface of the assembled tank which is unlikely to be damaged.
- Usually used as a treatment prior to coating/anodising/painting.
- Activation time is NOT critical, although there is a minimum required contact time for the reaction to take place.
- Longer immersion times have no beneficial or detrimental effect and will not increase coating thickness.
- Some testing may be required to verify coating adhesion to the al-li alloys.

Surface Treatments



Surface Treatments for Aluminium

Chemical

Non-galvanic

Electrolytic

Mechanical Finishes

Includes:-
Grit blasting
Grinding Polishing
Buffing

Organic Finishes

Includes:-
Painting
Protective Coatings (eg plastic)
Powder coatings
Porcelain enameling

Pickling/Etching

Surface is removed chemically by caustic/acid etch

Polishing

Controlled dissolution of base metal

Chemical Conversion Coatings

Chromate & non-chromate processes
Reaction with material surface

Electroless Plating

Deposition of coating from aqueous solution either autocatalytic or ion exchange

Electropolishing

Surface material removed electrochemically
Similar to chemical polishing except larger effect on edges and corners

Electroplating

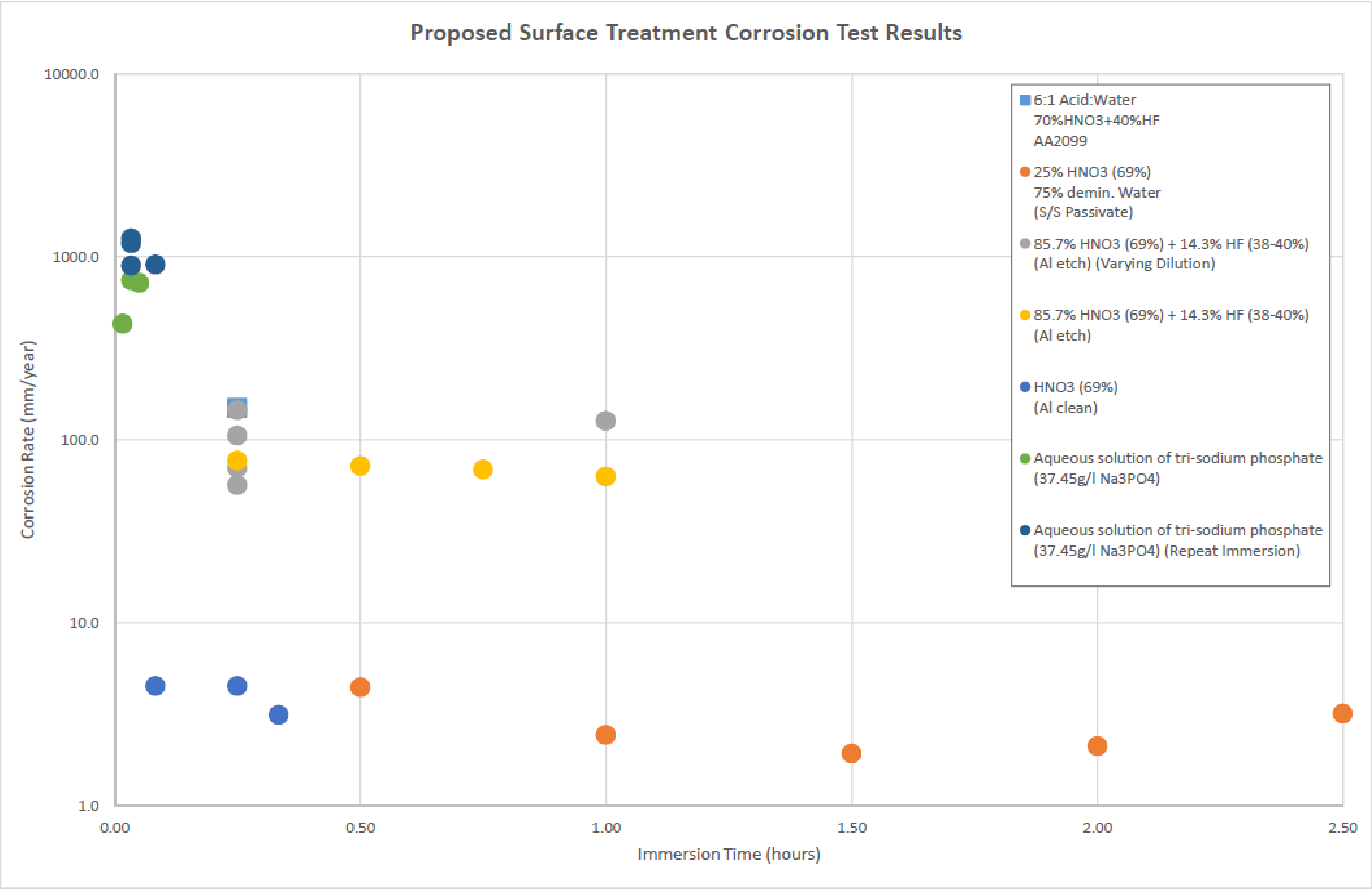
Direct plating

Anodising

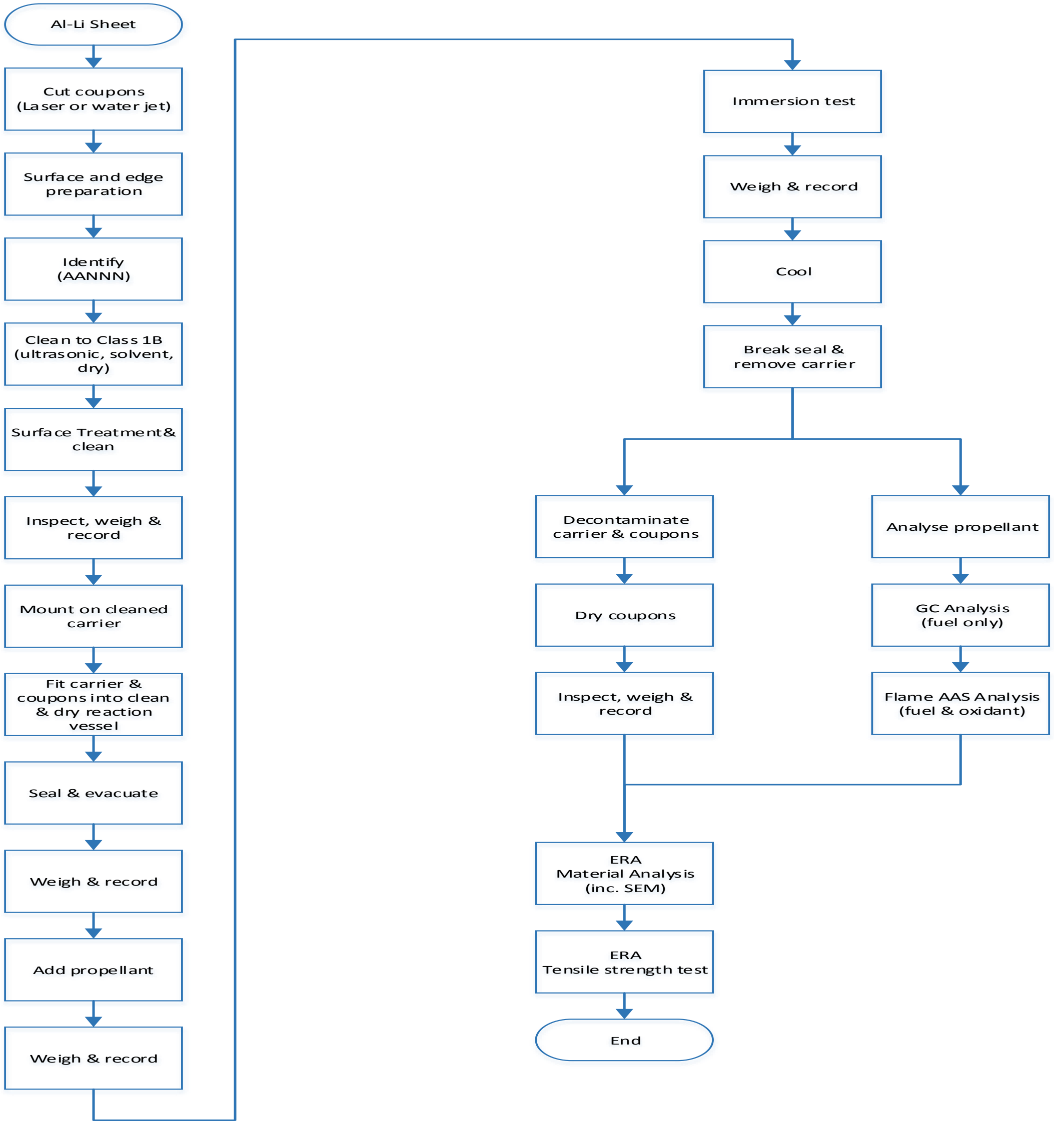
Controlled oxidation of the aluminium surface

Surface Treatments

Surface Treatments for Aluminium					
Surface Treatment Type	**Subset**	**Pros**	**Cons**	**Comments**	**Selection**
Non-Galvanic	Mechanical Finishes	Simple to perform on pre-assembled components.	Cannot perform on internal surface of welded tank.	Sub-assemblies only.	Y
	Organic Finishes	Simple to perform on welded tank.	Unlikely to have long term resistance to propellant.		N
Chemical	Pickling/Etching	Surface dealloying to reduce incompatible constituents at the surface. Weld scale removal.	Difficult to inspect. Surface contact times for aggressive chemicals need to be controlled.	S/S tanks use this. Small amount could be loaded into assembled tanks and tank spun to clean weld area only. Could also be performed at sub-assembly level.	Y
	Polishing	Smooth surface finish.	Difficult to inspect. Surface contact times for aggressive chemicals need to be controlled.		?
	Chemical Conversion Coatings	Process self-limiting. Non-Chromate process available. Self-healing of small scratches.	Chromate process has H&S implications.	Chemetall Gardobond x4707 includes titanium.	Y
	Electroless Plating	No power supply required. Process self limiting?	Coatings generally incompatible with propellants. Surface contact times may need to be controlled to achieve uniform thickness.		N
Electrolytic	Electropolishing	Smooth surface finish Larger effect on corners & burrs Process controlled by applied voltage and duration	Will this work for tank internals?		?
	Electroplating	Process controlled by applied voltage and duration	Coatings generally incompatible with propellants		N
	Anodising	Prior use with propellants	Will this work for tank internals?	Historical testing recorded no benefits	Y


Proposed Surface Treatment Corrosion Test Results
10000.0
1000.0
100.0
10.0
1.0
Corrosion Rate (mm/year)
0.00
0.50
1.00
1.50
2.00
2.50
Immersion Time (hours)
■ 6:1 Acid:Water 70%HNO3+40%HF AA2099
● 25% HNO3 (69%) 75% demin. Water (S/S Passivate)
● 85.7% HNO3 (69%) + 14.3% HF (38-40%) (Al etch) (Varying Dilution)
● 85.7% HNO3 (69%) + 14.3% HF (38-40%) (Al etch)
● HNO3 (69%) (Al clean)
● Aqueous solution of tri-sodium phosphate (37.45g/l Na3PO4)
● Aqueous solution of tri-sodium phosphate (37.45g/l Na3PO4) (Repeat Immersion)

Test Procedure



Al-Li Sheet

Cut coupons (Laser or water jet)

Surface and edge preparation

Identify (AANNN)

Clean to Class 1B (ultrasonic, solvent, dry)

Surface Treatment& clean

Inspect, weigh & record

Mount on cleaned carrier

Fit carrier & coupons into clean & dry reaction vessel

Seal & evacuate

Weigh & record

Add propellant

Weigh & record

Immersion test

Weigh & record

Cool

Break seal & remove carrier

Decontaminate carrier & coupons

Dry coupons

Inspect, weigh & record

Analyse propellant

GC Analysis (fuel only)

Flame AAS Analysis (fuel & oxidant)

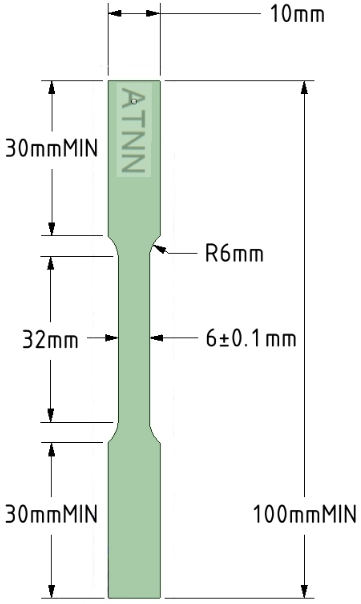
ERA Material Analysis (inc. SEM)

ERA Tensile strength test

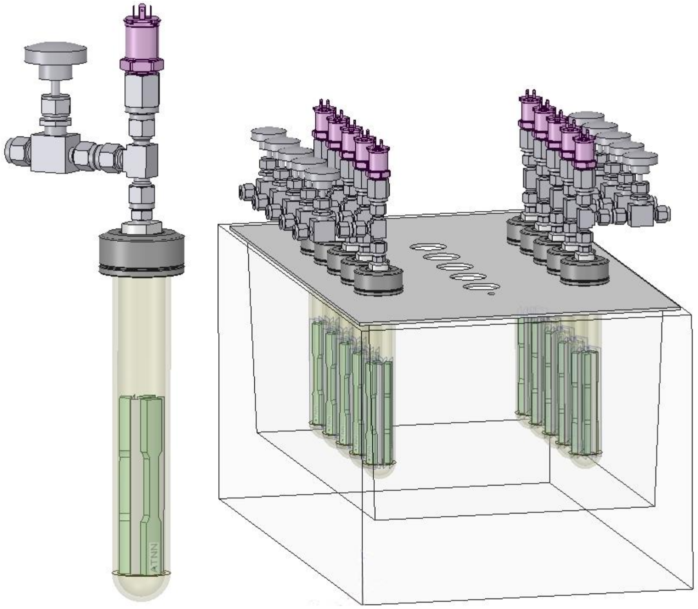
End

Compatibility Testing - The Kit

Tests conducted in temperature controlled water baths within fume cupboards

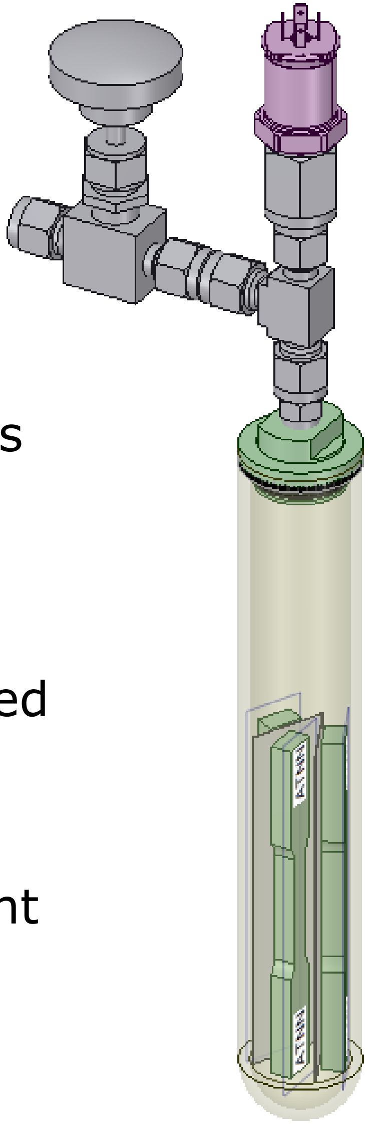


Coupon



Test Equipment

- 15.5 bar pressure rated borosilicate glass reaction vessel (RV)
- 0 – 20 bar Omega pressure transducer
- Needle valve for pressure release
- PTFE shim material coupon spacer
- 3 similar alloy and surface treatment samples per RV
- Filled under vacuum
- Vial pressure monitored and logged
- Water bath temperature monitored and logged
- Volume to surface area ratio recorded
- Propellant Control RV with no samples
- Coupon Control reaction RV with no propellant
- Water bath temperature and RV pressures (max. 16 channels) recorded at 0.1Hz



Immersion Testing

- Test Equipment
  - Reaction Vessels
  - Data Acquisition System
  - Temperature and pressure transducers calibrated prior to immersion test with traceable standards
  - Flame atomic absorption spectrometer (FAAS)
  - Multi-element Lumina Hollow Cathode lamps and FAAS comparator standards

Coupon Tests (per alloy)

Test	Propellant	Surface Treatment					Totals
		Untreated	1	2	3		
Reference Pull-Test	N/A	3	3	3	3	*	12
48 hours @ 21°C	None	3	3	3	3	**	12
"	N_2H_4	3	3	3	3		12
"	MMH	3	3	3	3		12
"	MON-3	3	3	3	3		12
1 month @ ambient°C	None	3	3	3	3	**	12
"	N_2H_4	3	3	3	3		12
"	MMH	3	3	3	3		12
"	MON-3	3	3	3	3		12
Spares	N/A	3	3	3	3		12
						***	120
Totals		30	30	30	30	120	

*	Surface treatment assumed to change material strength?
**	Either 1 coupon per propellant OR 3 coupons for one propellant
***	Coupon requirement could be reduced by selective application of surface treatment(s) or reduction of reference pull-tests

Achievements

- Open-source literature was investigated to compile a database of previously tested propellant compatible propellant tank materials, surface treatments and test methods.

- Material property information for compatible alloys was combined with that of 3rd generation Al-Li alloys and ranked/rated to produce a short list of prospective candidates for testing with propellants.

- 10 alloys from this list were selected for further study – 3 of these proved to be unobtainable.

- In addition to the untreated alloy, three surface treatments were evaluated (acid, alkali, and a chrome-free aluminium pre-treatment).

Achievements cont …

- Material was procured and processed to produce test coupons for immersion test in MIL-PRF propellants:- mono-methyl hydrazine, anhydrous hydrazine and dinitrogen tetroxide (MON-3).
- Six immersion tests were performed with coupons immersed in propellant for up to 1 month at 71±1.0° C (equivalent to 3 years immersion at ambient temperatures).
- Propellant and coupon characteristics were measured pre and post-immersion test. Conditioning temperature and coupon/propellant container pressure were monitored throughout the test. In addition the propellant was analysed for dissolved alloy constituents.
- Finally a subset of coupons which appeared unaffected after immersion have been subjected to mechanical testing and metallurgical analysis.

Conclusions ... Hooray!

- None of the aluminium alloys 2055, 2060, 2070, 2195, 2219 and 2198 exhibited any significant negative properties after testing and all are considered suitable for use with the propellants mono-methyl hydrazine, hydrazine and mixed oxides of nitrogen (MON-3) for up to 3 years.

- AA2050 is declared to be not compatible with hydrazine. The difference in compatibility between two very similar alloys (i.e. 2050 vs 2055) is not well understood.

- Therefore the study has identified a number of aluminium-Lithium alloys suitable construction material for tanks, valves and pipework or any other space qualified components which are in contact with the storable bipropellants hydrazine, monomethyl hydrazine and dinitrogen tetroxide and are required to be light weight and demisable.