The Properties and Application of Scandium-Reinforced Aluminum

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Scandium-reinforced aluminum alloys represent a new generation of high-performance alloys that display numerous advantages over high-strength aluminum alloys. Scandium-reinforced alloys are much stronger than other high-strength alloys, exhibit significant grain refinement, strengthen welds, and eliminate hot cracking in welds. These alloys also exhibit a good resistance to corrosion as shown by recent studies. A review of their mechanical, microstructural, and corrosion characteristics shows that scandium-reinforced allovs can be usefully employed in aerospace, sports, transportation, and process

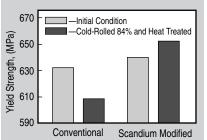


Figure 1. The yield strength of conventional and scandium-modified experimental 7XXX alloy in the initial and cold worked 84% and heat-treated conditions.

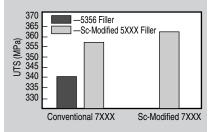


Figure 2. The ultimate tensile strength of a 7000 series weldment is considerably higher when a scandium-modified 5000 aluminum filler metal is used compared to a conventional 5356 filler material. The difference is even more pronounced when the base metal is also modified by scandium. industries. The information on scandiumreinforced alloys is scanty; very little has been published on the mechanical, microstructural, and corrosion behavior of these alloys. The following fills this gap.

INTRODUCTION

Scandium, a novel alloying element for aluminum, is mined and processed in Zhovti Vody, Ukraine, the only primary scandium mine in operation in the world. The mine has a proven minable scandium reserve of 7.58 million t of ore grading at 1.5 g/t of scandium, likely to yield 907,185 t of final Al-Sc product. Initial mining and processing of the complex ore and refining of scandium concentrates have resulted in the Al-Sc master alloy. Ashurst Technology Ltd. developed a fully integrated program aimed at the worldwide commercialization of scandium alloys.1 The development of Al-Sc alloys first flourished in the Soviet Union, where military demand was the main driving force. At the time of the Soviet Union break-up, scandium alloys were on the verge of major application in MIG 29 fighters because of their advantages over the low density and high strength of Al-Mg, Al-Li, and other recent alloys. Scandium, with its unique strength and weight-saving characteristics, has been introduced as a potent alloying element in several aluminum alloys (e.g., A15052 and Al7075) in recent years, bringing about dramatic improvements in their mechanical and physical characteristics. It has been possible to achieve an ideal combination of strength, density, and thermal stability because of the unique precipitation-hardening characteristics of scandium. These alloys are gaining a wide popularity in aeronautical, automotive, and transportation industries.

ADVANTAGES OF SCANDIUM ADDITION

Scandium-reinforced aluminum alloys offer design engineers several significant advantages over other highstrength aluminum alloys, including:

• Inhibition of recrystallization. Transition metals such as zirconium, chromium, manganese, vanadium, or titanium are not very effective at inhibiting recrystallization because most of the highstrength and precipitationhardenable aluminum alloys are solution-heat-treated at tempera-

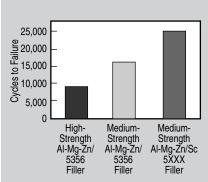


Figure 3. The fatigue life of a high-strength aluminum-magnesium-zinc alloy almost triples when it is welded by a scandium-modified 5000 series filler metal.

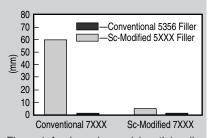
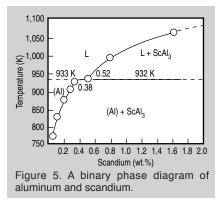


Figure 4. As shown by crack length in millimeters, the Houldcroft test greatly favors the scandium-modified vs. conventional filler metal in the welding of a 7000 series aluminum alloy.



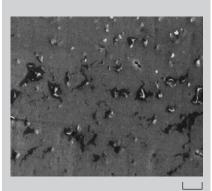
tures well above their recrystallization temperatures. Surprisingly, scandium increases the recrystallization temperature of aluminum alloys to above 600°C, well above the temperature range of heattreatable aluminum alloys. It has been observed that the addition of scandium with zirconium is more effective than the addition of scandium alone.²

- Small additions of scandium in the range of 0.2-0.6 wt.% bring about a high specific-strengthening effect.3 An Al-5.25Mg alloy containing 2.5% magnesium showed a yield strength of 365 MPa, more than double the strength of the scandium-free alloy. Scandium provides the highest increment of strengthening per atom percent of any alloying element when added to aluminum.4 Al-Mg-Sc alloys are capable of developing strength and fracture toughness similar to that of Al 2024-T3 alloy. The effect of scandium addition on the yield strength of conventional and scandium-modified experimental 7XXX alloys is shown in Figure 1.2
- Scandium has the ability to refine grain size. It is a strong modifier of cast structure, and the addition of scandium makes it possible to obtain continuously cast billets with a non-dendritic structure.⁵
- Reduction and elimination of hot cracking in welds. The scandium modification of welding filler alloys as well as base alloys are capable of preventing hot cracking. Aluminum alloy 2618 is known to be hot-crack sensitive, and, when welded with conventional filler, it develops a high level of cracking.² However, its cracking susceptibility was reduced when the conventional

filler was replaced with scandiummodified filler. Welding studies on Al 7XXX by conventional filler alloys and scandium-modified fillers have shown the capability of scandium to convert non-weldable alloys to alloys with a promising degree of weldability. In addition, the weldment tensile strength of Al 7XXX is significantly improved when welded with modified 5XXX alloys versus conventional 5XXX filler (Figure 2).⁶ Strength is further improved when scandium is added to Al 7XXX.

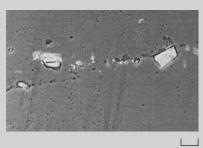
Because of these advantages, the scandium-modified aluminum alloys have a promising potential for military and commercial aerospace applications including bulk heads, heat shields, sheet for upper skin, fuel and exhaust systems, and in automotive and transport systems.

The addition of scandium also improves fatigue life.⁶ Medium- to high-strength Zr-Mg-Al alloys failed at 16,000 cycles, indicating their limitation for intended applications. Surprisingly, the fatigue life was increased to 25,000 cycles with a scandium-modified filler



10 *µ*m

Figure 6. A SEM micrograph showing Mg_2Si (dark) precipitates. Black (Fe) and white particles contain Mg, Ti, and Sc.



10 *µ*m

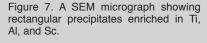




Figure 8. A photomicrograph showing the pinning of grain boundaries by dislocations.



Figure 9. A TEM micrograph of Al-2.5Mg-0.5Sc alloy showing a high dislocation density at the sub-grain boundaries.

metal (Figure 3). In a Houldcroft welding test, cracking was significantly reduced by a scandium-modified filler metal. When both the filler and base metal are modified by scandium, cracking is eliminated (Figure 4).⁶

OPTIMUM AMOUNT OF SCANDIUM

The Al-Sc binary phase diagram is shown in Figure 5.7 As observed from the figure, Al-Sc is slightly hypereutectic and hence, very small amounts of Al₃Sc precipitate could form prior to the solidification of the aluminum phase. The aluminum-rich side of the Al-Sc phase diagram shows a eutectic point at 655°C. The system has also a very narrow freezing range. The maximum equilibrium solubility of scandium in aluminum is 0.35–0.4 wt.%. With cooling rates in solidification corresponding to the continuous casting of ingots, a supersaturated solution of scandium (up to 0.6%) with aluminum is obtained.⁵ An equilibrium phase Al₃Sc with Li₂ structure precipitates in cast alloys. The supersaturated solution of scandium in aluminum is unstable compared with

the solid solution of other transition metals. The rate of incubation preceding decomposition is three to four orders of magnitude shorter compared to Al-Mn and Al-Zr alloys and the rate of decomposition is five to six times higher compared to Al-Mn and Al-Zr alloys.8 The stability of a solid solution of scandium in aluminum drops with an increase in scandium content under conditions of long, high-temperature heating such as those as encountered in production of billets. Under such conditions, decomposition and coagulation of Al₂Sc secondary particles occurs. In view of these findings, the optimum limit for scandium is 0.6%. The desirable limit is, however, 0.1–0.5%.5

Experience accumulated over a few years has shown that a lower content of scandium can have a very strong modifying effect when zirconium is present.⁹ In the presence of zirconium, a non-dendritic structure is formed with a scandium content as low as 0.2%, whereas, without zirconium, more than 0.5% scandium is required to obtain a non-dendritic structure. The synergistic interaction between scandium and

zirconium is effective in inhibiting recrystallization through the formation of extremely fine $Al_3(Zr_xSc_{1-x})$ particles. These particles are less prone to coagulation compared to Al_3Sc particles.

MICROSTRUCTURE

A microstructural examination by optical microscopy reveals little in alloys containing less than 0.6 wt% of scandium. Al-Mg alloys containing 6% magnesium show β -Al-Mg (Al_gMg₅) precipitate.¹⁰ The combination of Mg (0.6-1.2%) and Si (0.4-1.1%) results in the formation of a Mg₂Si metastable phase.11 The dark Mg₂Si particles are shown in Figure 6. A scanning electron microscopy examination of the Al-2.5Mg-0.15Sc alloy revealed rectangular precipitates containing iron, aluminum, and scandium particles as confirmed by electron dispersive spectroscopy (EDS) analysis (Figure 7).8 Transmission electron microscopy (TEM) studies on the microstructure of the alloys containing higher scandium contents (1%) were also conducted. After cold rolling to 85% and aging to peak hardness at 320°C, Al-4Mg-1Sc showed a sub-grain

	Yield Strength	Tensile Strength	Elongation	Strain Hardening Exponent	Tear Strength*	Unit Propagation Energy**
Alloy	(MPa)	(MPa)	(%)	(n)	Yield Strength	$(kJ/m)^2$
A1-0.5Sc	286	297	14.5	0.026	1.74	319
Al-2.5Mg-0.5Sc	341	370	13.5	0.051	1.95	317
Al-4Mg-0.5Sc	381	443	14.5	0.072	1.93	270
Al-6Mg-0.5Sc	381	467	10.5	0.101	1.22	84

* Tear strength = maximum load divided by net cross-sectional area + bending stress.
** Unit propagation energy = integral of load deformation curve after crack propagation divided by the total area
of the specimen.

Table II. Mechanical Properties of AI-Sc and AI-Mg-Sc Alloys (WR/A)						
Alloy	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)	Strain Hardening Exponent (n)	<u>Tear Strength</u> Yield Strength	Unit Propagation Energy (kJ/m) ²
Al-0.5Sc	298	319	10.5	0.008	1.59	193
Al-2.5Mg-0.5Sc	376	401	8.5	0.052	1.74	113
Al-4Mg-0.5Sc Al-6Mg-0.5Sc	414 433	460 503	9.5 10.5	0.064 0.074	1.68 1.33	114 100

Table III. Mechanical Properties of AI-Mg-Sc Alloys				
No.	Alloy	Yield Strength MPa	Ultimate Tensile Strength MPa	Elongation %
1	Al-0.5Sc	158.63	213.80	14
2	Al-2.5Mg-0.5Sc	202.08	265.35	10
3	Al-4Mg-0.5Sc	215.87	272.43	9.5
4	Al-6Mg-0.5Sc	255.19	286.22	9

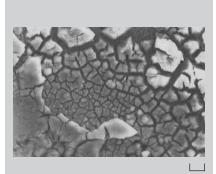
Table IV. Corrosion Rates of Al-Mg-Sc
Alloys in 3.5 wt.% NaCl ¹⁷

	Corrosion Rate			
Alloy	(mm/year)	(mdd)		
Al-2.5Sc	0.023	1.477		
Al-2.5Mg-0.10Sc	0.031	1.980		
Al-2.5Mg-0.15Sc	0.046	2.914		
Al-2.5Mg-0.30Sc	0.038	2.460		

Table V. Pitting Data on Al-Mg-Sc Alloys ¹⁷					
Alloy	E (V)	E _{pp} (V)	E _{corr} (V)		
Al-2.5Sc	-0.521	-0.697	-0.643		
Al-2.5Mg-0.10Sc	-0.578	-0.713	-0.659		
Al-2.5Mg-0.15Sc	-0.518	-0.694	-0.628		
Al-2.5Mg-0.30Sc	-0.670	-0.729	-0.742		

size of 1 µm, however, it was difficult to resolve the structure. It was only after overaging for 5,500 min. at 320°C that coherent precipitates of Al₂Sc (15 nm diameter) were observed. The poor aging response of deformed samples was attributed to the discontinuous precipitation of Al₃Sc.¹¹ It was also found that coherent precipitation is possible only under high super saturation in alloys with 1% of scandium content. In another study, microstructural studies on an Al-1.0Sc chill-cast alloy showed the presence of Al₂Sc. The particles of Al₂Sc were found to be highly faceted with a cubic morphology.10 By x-ray diffraction, the structure of Al₂Sc was found to be face-centered cubic with a lattice parameter of 0.4105 nm. It had a Li₂-type ordered structure. In samples aged for 3 h and 100 h, a large number of rod-shaped dendritic or spherical precipitates were observed.11

Efforts have been made to study the precipitation sequence in Al-Sc alloys by positron lifetime measurements.12 It was observed that coherent Al₂Sc precipitates were formed from solutiontreated alloys at around 300°C in alloys containing 0.006 wt.% scandium and 0.03 wt.% scandium. The technique is very cumbersome and it has not been widely used. The precipitation process has also been investigated by resistivity and hardness measurements.13 Investigation into alloys containing 0.090 wt.% scandium and 0.15 wt.% scandium showed that the equilibrium Al₂Sc phases with Li, structure precipitates homogeneously without the formation of any metastable phase and the Al₃Sc phase



 $10 \ \mu m$ Figure 10. A SEM micrograph showing oxide layer mudcracking.



Figure 11. The formation of gelatinous $AI(OH)_3$ in the form of mothballs and its cracking.

maintained coherency with the matrix for a long aging time.

It is a common observation that Al₂Sc precipitates are very effective in pinning grain boundaries and thus maintaining a fine grain size. The dislocations that emerge from deformation are the favorable sites for the nucleation of Al₃Sc precipitate. The coherent small Al₂Sc precipitates are highly effective in impeding the grain boundary motion. The effect of grain size and pinning down of grain boundaries on the strengthening mechanisms of Al-2.5Mg-3Sc alloys9 has also been observed by the authors.14 The pinning down of the grain boundaries by Al₂Sc precipitate is shown in Figure 8 and the high dislocation density at the sub-grain boundaries is shown in Figure 9.

STRENGTHENING EFFECT

As stated previously, scandium is said to produce the highest increment of strengthening per atom percent when added to aluminum, increasing strength both by solid solution and precipitation hardening of Al₃Sc particles. These particles pin the dislocation cell structure. One disadvantage of using Al-Mg alloys is the loss in strength they exhibit during the process of recovery of ductility and toughness. Scandium addition minimizes these losses. Despite the low solubility of scandium and, hence, a limited volume fraction of Al₃Sc phase, it produces a significant strength increment. The other advantage of scandium is its capability to provide thermal stability by a substantial increase in the re-crystallization temperature. The Al₂Sc precipitate is also highly resistant to coarsening, unlike the traditional precipitate phases. Data on mechanical properties of Al-Mg-Sc alloys is not abundant.10

The mechanical properties of five Al-Sc and Al-Mg-Sc alloys (warm rolled and aged [WR/A] and warm rolled/cold rolled and aged [WR/CR/A]) are shown in Tables I and II.

Both the tear and tensile strength increase with increasing magnesium content, as does the difference between the yield strength and tensile strength. The strain-hardening coefficient has a lower value for Wr/Cr/A alloys with 4% and 6% magnesium because of the hardening that occurs during cold-rolling operation. One point of interest is a very low value of n(0.01) for the magnesiumfree Al-0.5Sc alloy that is suggestive of strengthening by coherent particles, which may shear during the deformation process.10 A similar behavior is observed in Al-Li alloys.¹⁵ Crack propagation toughness as shown by the tearstrength/yield-strength ratio increases with magnesium content and then drops suddenly above 4% for WR/A treatment. It may be attributed to the presence of microvoids at a higher magnesium level. When interpreting the data and comparing it with conventional aerospace alloys, it is fair to say that Al-4Mg-0.5Sc alloys compete favorably with the conventional aerospace alloys like 2024 and 7075. Beyond the scope of this review, it may also be mentioned that the Al-4Mg-0.5Sc alloys are capable of producing superplasticity.

The nature of artificial aging response by the alloys Al-0.5Sc and Al-4Mg-0.5Sc was investigated. An aging temperature of 561K was considered adequate,¹⁶ and peak hardness was produced by aging times in the range of 10–20 h. The yield strength was raised by at least 100 MPa for the Al-0.5Sc alloy.¹⁶ The increase in strength was due to the precipitation of Al₃Sc particles both within the grains and at grain boundaries. Mechanical properties of Al5052 containing 0.1% scandium and 0.15% scandium were evaluated by the authors. These are shown in Table III.

An outstanding contribution of scandium to the modification of aluminum alloys is its novel effect in preventing strength loss after thermal processing and its resistance to crystallization even after 75-85% cold reduction, in which range conventional alloys are completely recrystallized. The data reported only limits to few alloys and the effect of age hardening of alloying elements, and secondary particles such as Al₂Sc on the mechanical properties is not fully understood. Several areas need to be fully explored, such as the superplastic forming nature of Al₂Sc precipitate, temperature dependence of mechanical properties, and the effect of alloying elements like titanium, chromium, vanadium, and hafnium.

CORROSION BEHAVIOR

The existing interest in Al-Mg-Sc alloys is centered around their excellent combination of physical and mechanical properties, but not their service performance in a corrosive environment. It is therefore of prime interest to evaluate the corrosion performance of Al-Mg-Sc alloys. The author has recently reported the only information on the corrosion behavior of Al-Mg-Sc alloys.17 The weight-loss studies conducted in 3.5 wt.% NaCl showed that the corrosion rate decreased as the exposure period increased. For instance, the corrosion rate of the alloy Al-2.5Mg-0.1Sc decreased from 2.4 mdd to 1.44 mdd (0.038 mm/y to 0.023 mm/y) after an exposure period of 800 h. This has been attributed to the build-up of a protective film of either Bayerite (β -Al₂O₂.3H₂O) or Boehmite (γ -Al₂O₃.H₂O). The surface of Al-Mg-0.1Sc was covered with a film of boehmite as identified by EDS studies.

Table IV, which summarizes the corrosion rates the alloy, shows it provides good resistance to corrosion typical of other Al-Mg alloys such as 5456 and 6061, which are well known for their performance in seawater service.

Pitting studies were conducted by

ASTM cyclic-polarization technique. Age hardening did not seriously affect the pitting potential. The pitting data obtained from polarization studies is reported in Table V.

The pitting potential of Al-Mg-Sc alloys meets the criteria that E_{corr} be more negative to E_p for good pitting performance. On comparing the pitting potentials of well-known commercial aluminum alloys such as Al6061, Al6013, Al2024, and Al5456 with Al-2.5Mg-0.1-0.3Sc alloys, it is observed that pitting potentials of Al-Mg-Sc alloys are more positive, suggesting a good pitting resistance of these alloys.

The pitting morphology on the Al-2.5Mg-0.1-0.3Sc alloys was studied by scanning electron microscopy.¹⁷ The maximum pit depth on these alloys compared favorably with the pitting depths observed in Al6061 and Al6013. One reason for good resistance to localized corrosion is that the Al₂Sc precipitates are of a very small size (8-10 nm) and they are coherent with the matrix. One would expect fewer flaws and lesser discontinuities at the precipitate/oxide electrolyte interface compared to Al2024, Al6061, and Al6013, which contain much larger precipitates of ClAl₂ and CuMgAl. It has been shown that an increase in the precipitate size decreases the pitting potential and increases the susceptibility to pitting. Pits on the alloy surface are covered by Al(OH)₃. The gelatinous Al(OH)₃, which is pumped by pits, dries up eventually in the form of mud cracking (Figures 10 and 11).

APPLICATIONS

With the passage of time and new developments, scandium has found a wide range of applications. A leading sports company successfully employed scandium alloys in the production of softball and baseball bats. This success was followed by the manufacture of mountain and road bicycle frames and components. The bicycle frames showed a 12% reduction in weight, a 50% increase in yield strength, and a 24% improvement in fatigue life over the best-selling aluminum bicycle. Potential aerospace applications include bulk heads, heat shields, forgings and extrusions for seat tracks, wheels, running gear, and fuel and exhaust systems.

Scandium alloys are promising for automotive and air transportation applications because of their capability of weight reduction on critical moving parts. Scandium alloys could also be used in wheels, bumpers, frames, pistons, and air bag canisters. The aluminum scandium welding wire provides a very strong bonding while welding aluminum. This alloy could also be used in the cylinders of diesel engines for power boats. Because of the good corrosion resistance shown by recent studies, scandium alloyed with aluminum could also be used in a saltwater environment (e.g., heat exchanger tubes in desalination plants). The potential of scandium alloys is highly promising, but, like new technologies, it is going to take time and painstaking research and development efforts to convince the designers to

use these alloys in a wide spectrum of applications.

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