HIGH STRENGTH ALUMINUM ALLOYS WITH EMPHASIS ON SCANDIUM ADDITION

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INTRODUCTION

Aluminium is perhaps the youngest among the large group of metallic elements. It was first commercially produced in the year 1886 and rose in prominence meteorically to occupy today the second position in the total weight produced, next only to steel. Aluminium is a silvery white ductile metal with a FCC structure. It has excellent electrical and thermal conductivity (next only to copper and silver). It has low density (2.7 g/cc) which gives it a very high specific modulus and strength. Pure aluminium is the soft metal with the modulus value of 70 GPa and the yield strength of about 40 MPa. One of the most important properties of aluminium is to form a thin protective oxide layer on the surface. This layer is tenacious, adherent, deformable and impervious to most corroding elements.

Aluminium is the common structural material because of the following properties.

- **Light weight :** Aluminium weighs roughly one third of iron and steel, but is one and a half times as heavy as magnesium. It finds application in reducing the weight of the component and structures particularly connected with transport, especially with aerospace application. High strength to weight ratio can be achieved in certain alloys, which show marked response to age hardening. High strength to weight ratio saves a lot commercially when dead weight is decreased and pay load of transport vehicle is increased. The ratio is of particular significance in engineering designs where stiffness is involved. For example, stiffness for equal weights similar beams are in ratio 1: 2.9: 8.2: 18.9 for steel, titanium, aluminium and magnesium, respectively.

- **Ease of fabrication and machinability :** It can be easily cast, rolled to any desired thickness (aluminium foils), stamped, drawn, spun, forged and extruded to all shapes.

- **High resistance to atmospheric corrosion :** It is due to thin, impermeable aluminium oxide layer on the surface.
- **Good thermal as well as electrical conductivity**
- **High metallic lusture**
- **Non magnetic and non sparking**

In annealed state, commercial purity aluminium (CPAl) is very ductile to be drawn to greater depths than Cu or brass. The strength of aluminium can be markedly increased by cold working with simultaneous loss of ductility. Annealed CPAl has tensile strength of 89.7 MN/m^2.

EFFECT OF ALLOYING ELEMENTS

Presence of alloying elements like Cu, Si, Mn, Mg, Zn, Cr, Ni etc, single or in combinations, added to commercial purity Al significantly influence the properties of the material. The effect of various alloying elements on commercial grade Al alloys, are given below:

- **Cu** is added up to 5.5% to improve dynamic fatigue, elastic properties, strength, hardness, but impairs ductility. It improves the castability and machinability. The resulting alloys are age hardenable to obtain optimum physical properties.
- **Mn** is added up to 1.5% to improve hardness, strength even at elevated temperatures; improves machinability without impairing corrosion resistance, but decreases ductility.
- **Si** is added up to 1% along with Cu and Mg to enhance the response to age hardening heat treatment.
- **Mg** is added up to 3% to increase strength, hardness and machinability. It improves corrosion resistance to salt sprays and mild alkaline solutions.
- **Zn** is added up to 6% but commonly along with Cu or Mg to increase strength and hardness with little loss of ductility.
- **Ni** is added up to 2 - 5% always along with Cu to increase strength and hardness, particularly at high temperatures, but lowers ductility and corrosion resistance.
- **Cr** is added in minute amounts up to 0.3% to act as grain refiners, to improve corrosion resistance and physical properties at elevated temperatures.

Among the different varieties of Al alloys, Al - Cu (2XXX) and Al - Zn-Mg (7XXX) alloys have been considered as high strength aluminium alloys and are mainly used for aircraft structural applications in the form of clad sheet, forgings and extrusions. An ultimate tensile strength (UTS) of more than 600 MPa is observed in some of these alloys. However, these alloys have problems because of susceptibility to stress corrosion cracking. Efforts have been made to develop new aluminum alloys. Addition of rare-earth elements like scandium, yttrium etc proved to be a potential development towards high performance aluminium based alloys. The history and importance of scandium additions to aluminum alloys are briefly discussed below.

SCANDIUM- HISTORY

In the 19th century, the little village of Ytterby near Stockholm, Sweden played a remarkably large role in the quest for new elements. From the local mine, the mineral Ytterite was extracted, which was later renamed Gadolinite in honor of the Finnish chemist Johan Gadolin. From this mineral a long list of new earths was discovered, which in those days was regarded being equivalent to the discovery of an element. With an apparent lack of imagination, four of these new elements were even named after the village (Ytterbium, Yttrium, Erbium and Terbium). In 1871, Uppsala professor Lars Fredrik Nilson managed to split the earth ytterbia into a new ytterbia and a new element, which he named scandium after his homeland Scandinavia. In the meantime Mendeleev had introduced his periodic table of elements and Nilson was able to show that the properties of his scandium matched exactly those of eka-boron, a missing element predicted by Mendeleev.

Scandium is widely dispersed in minute quantities in the earth's crust. Only the mineral Thortveitite possesses a significant quantity of scandium oxide (30-40%). Consequently, scandium is not generally mined economically, but it is extracted mainly as a byproduct of iron, uranium or tantalum mining. The first pound of pure scandium was not produced until 1960. Due to its costs, applications of scandium were at first limited. It is used in mercury vapor lamps to imitate natural sunlight and has applications in laser research and aerospace technology. The demand for scandium increased however, when in 1971 Willey patented the first aluminum-scandium alloy. He found that adding minute quantities (0.1-1.0%) of scandium to a number of aluminum alloys, significantly improved their mechanical properties. Al-Sc alloys are characterized as having superior corrosion resistance and weldability; they are strong, light weight and very stable at elevated temperatures. Furthermore, Al-Sc alloys turned out to be well suited for superplastic forming operations. Nowadays, the alloys are used for instance to make sporting equipment that has to be light weight and very strong, e.g., bicycle frames and baseball bats. There is a growing interest from industry, but the price of aluminum-scandium master alloys is still too high for most commercial applications. However, efforts are underway to extend existing Bayer process plants to produce scandium from scandium oxide along with extraction of Al. This would reduce the scandium costs enormously and it is thus expected that scandium will be used much more extensively in the near future.

PHYSICAL AND CHEMICAL PROPERTIES - SCANDIUM

Before emphasizing about importance of Sc - Al alloys, it is required to know some of the physical and chemical properties of Sc. Sc has an atomic number of 21 with atomic weight 44.96. The crystal structure is hexagonal close packed and has a density of 2.99 g/cm^3. It has melting point of 1541^{o}C and boiling point of 2831^{o}C. The electrical resistivity of Sc at 20^{o}C is 66 μohm.cm and the specific heat at 25°C is 557 J/K/kg. The thermal conductivity at 0 -100°C is 15.8 W/m/K. In addition, while referring to the mechanical properties, the bulk and tensile modulus are 44.2 and 79.3 GPa respectively, with a hardness of ~80 BHN and has Poisson's ratio of 0.27.

While referring to the chemical properties, the Sc forms a white oxide and its solutions show no bands of light absorption. When calcined, it dissolves only slowly in nitric acid, even at boiling, but more readily in hydrochloric acid. It is completely precipitated from the solution of the nitrate by oxalic acid. This salt is very easily and completely decomposed at the temperature at which ytterbium nitrate is partially decomposed. With sulphuric acid it forms a salt that is as stable on heating as the sulphates from gadolinite or cerite and, like these, can be completely decomposed by heating with ammonium carbonate.

Some of the areas where scandium is used as an additive or dopant are

- Alloying element in Aluminium alloys.
- Dopant in garnets for lasers.
- Addition as metal and iodide to high intensity halide lamp to make the emitted light spectrum resemble that of sunlight.

APPLICATIONS

The main applications of aluminium-scandium alloy are in the area of aerospace industry for minor components, and unusual design sport equipments (bikes, baseball bats, firearms, etc.) which rely on high performance materials (Fig. 1).

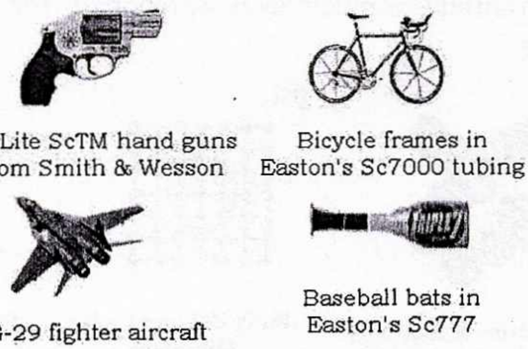

Fig. 1 : Components made from Sc-containing Al-alloys

There are several advantages of using Sc in Al-alloys and the effect of Sc addition depends upon the type and composition of the alloy. Addition of Sc to Al gives the highest increase in strength (per atomic percent) of all alloying element. In addition, it reduces the hot cracking during welding. The Al_3Sc dispersoid is coherent with Al matrix. This gives rise to age hardening behavior. The enhanced properties that could be achieved by the addition of Sc to Al are through superior fundamental dispersoid characteristics. A more important aspect of the greater thermal stability of the Al_3Sc dispersoids is their effectiveness at reducing recrystallisation. The above points have been discussed in details below:

Al_3Sc Dispersoids

Most of the beneficial effects from the Sc-addition are linked to the formation of the Al_3Sc phase in the alloy. In a typical processing route of a wrought aluminium alloy the Al_3Sc phase can form under three different conditions:

- During solidification after casting or welding, Al_3Sc particles can form in the melt and act as grain refiners. This requires that the alloy is hypereutectic with respect to Sc. For a binary Al-Sc alloy this means that the Sc content should be in excess of approx. 0.6 wt%, while in for instance an Al-Zn-Mg-Zr alloy an addition of 0.2 wt% Sc can be sufficient.
- High temperature processing of the alloy in the range of 400-600°C, for instance homogenization, hot rolling or extrusion can give a dense distribution of Al_3Sc particles. Typical particle diameters from such processes would be in the range of 20-100 nm. These particles will not have a significant direct strengthening effect on the alloy, but they will have a stabilizing effect on the grain structure/subgrain structure of the alloy. Good recrystallization resistance and enhanced superplasticity Sc-containing alloys are properties that are attributed to the distribution of Al_3Sc particles formed under conditions as mentioned above.
- Heat treatment in the range of 250-350°C can lead to significant precipitation hardening of an alloy supersaturated in Sc. The size of strengthening Al_3Sc precipitates is typically in the range of 2-6 nm and the precipitates are reported to be completely coherent with the aluminum matrix.

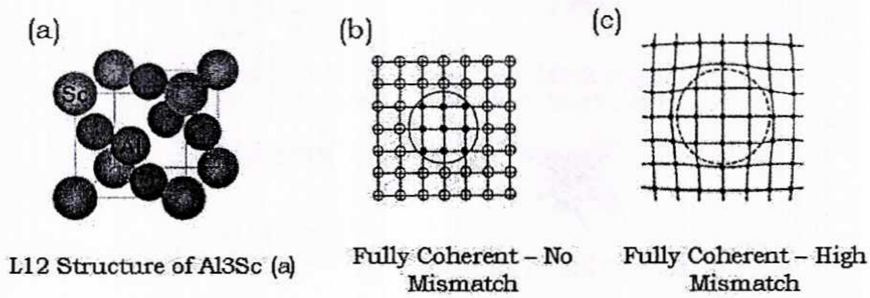

Fig. 2 : Schematic illustrations of Sc with Al

The Al_3Sc dispersoid is an $L1_2$-type phase (Fig. 2a) which is coherent with the aluminum matrix. An extremely high coherency mismatch is observed for the Al_3Sc phase resulting in significant lattice strain to block dislocation motion and to impede grain growth (Figs. 2b, 2c). This mismatch is 1.2% compared with 0.8% for Al_3Zr, one of the next most potent dispersoids.

A greater volume fraction of Sc can be added compared with other grain refining elements used in aluminum alloys (e.g. Zr, Ti, Mn, Cr). As shown in the Table 1 below, this is especially evident when the volume atomic percent maximum solubility is considered.

Greater volume fraction effectiveness is important to inhibit recrystallization and prevent subgrain annihilation and coalescence. The high coherency strain further impedes the motion of grain boundaries resulting in a finer grain structure and higher strength through the well known Hall-Petch relationship.

Table 1 : Solubility limits of various elements to Al

Alloying element	Solubility (wt%)	Solubility (vol. atomic%)
Sc	0.50	0.30
Ti	0.18	0.05
Zr	0.15	0.08
Mn	0.30	0.15
Cr	0.25	0.13
V	0.10	0.05

GREATER THERMAL STABILITY

The Al - Sc phase diagram (Fig. 3) below shows the Al - Al_3Sc eutectic reaction to take place at an unusually high temperature. This high solidification temperature improves heterogeneous nucleation of grains, resulting in a refined grain size (and reduced hot cracking). A reduction in hot cracking is

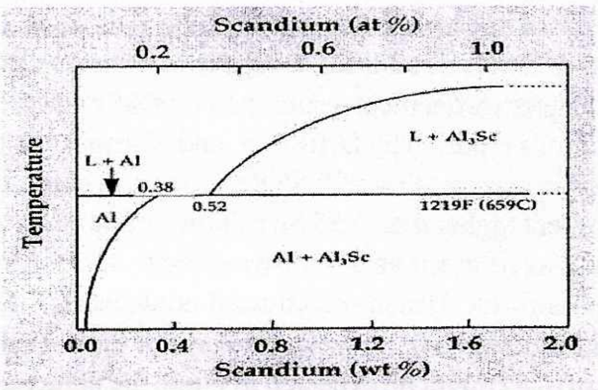

Fig. 3 : Al - Sc Phase diagram

especially important for welding of high strength alloys. Most of the high strength aluminum alloys are not weldable and the addition of Sc can improve the weldability of many of these alloys.

Perhaps a more important aspect of the greater thermal stability of the Al_3Sc dispersoids is their effectiveness at reducing recrystallization. Alloys that are heavily cold worked (such as extruded and/or drawn bats, bike frames, and tubes) contain sufficient stored energy to cause recrystallization. This results in substantial strength loss. Designers know that thin-walled products have less strength than thicker sections due to this softening effect. The addition of Sc can eliminate this problem in many combinations of alloy, heat treatment, and mechanical working. Table 2 shows the effective recrystallization temperature performance of different dispersoids:

Table 2 : Recrystallisation temperatures of Al for various elements

Element	Recrystallization Temperature (^{o}C)
Mn	325
Cr	325
Zr	400
Sc	600

GRAIN REFINEMENT

The grain refinement studies on Al, using TiBAl and various Sc additions show that, Sc additions (>1 wt%) to molten Al showed better grain refinement results as compared with Al, that was grain refined by adding 0.2 wt% of TiBAl master alloy. This significant amount of grain refinement was clearly seen in the 2 minute sample and the grain refinement effect was maintained up to 120 min. This type of grain refiner was mostly referred as ideal grain refiner. Similarly, the addition of 2 wt% Sc to molten Al showed a drastic change in grain refinement and considered best among all the known grain refiners (Fig. 4a). Moreover, grain-refining results of 2 wt% Sc addition to Al matrix are almost similar to 1 wt% Sc addition levels. It was observed that the 2 wt% of Sc addition gave marginally better grain refinement results than 1 wt% Sc added samples. The present results support the observations reported by Drits et al. and Norman et al., that Sc additions in amounts less than the eutectic composition of 0.55 Sc, exhibits a columnar grain structure, whereas increasing the Sc content higher than 0.55 Sc exhibits a fine equiaxed grain structure. The formation of such equi-axed grain structure was due to the formation of intermetallic particles of the $L1_2$ Al_3Sc phase in the Al melt, which acted as nucleating sites during solidification. Also, due to the similarities between the crystal structures of the a-Al and Al_3Sc phases, the heterogeneous nucleation of α-Al might be expected to guide the epitaxial growth of α-Al on the Ll_2 Al_3Sc particles. In the present investigation Sc addition in different concentrations higher than 0.6 wt% to molten Al exhibited similar results. The SEM image of Al - 2Sc master alloys is shown in Fig. 4b.

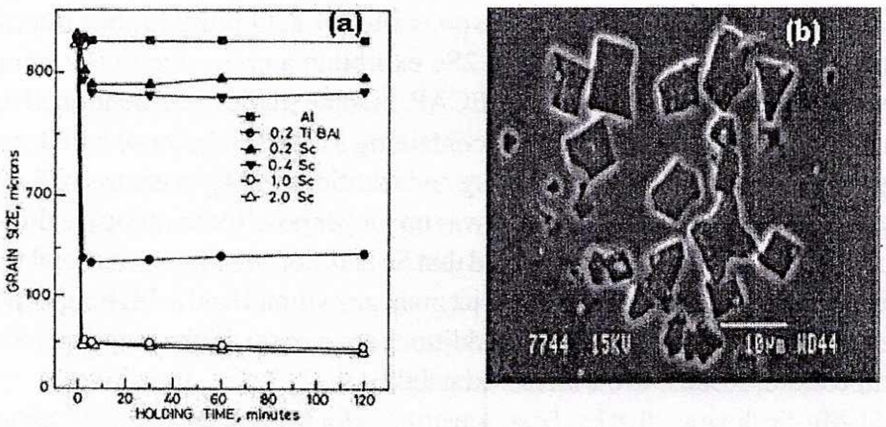

Fig. 4 : (a) Grain refinement on Al with addition of various master alloys and (b) SEM image of Al-2Sc master alloy

The presence of Al_3Sc in Al has shown improved tensile properties. Homogenization at 460°C was responsible for further increase in tensile properties probably due to the presence of fine Al_3Sc precipitates and redistribution of Al_3Sc particles that would have been acted as nucleating sites during solidification of Al.

EFFECT OF Sc ON Al-Mg ALLOYS

Aluminium alloys with magnesium as the major alloying element constitute a group of non-heat treatable alloys with medium strength, high ductility, excellent corrosion resistance and weldability. Wrought Al-Mg alloys are used as structural materials in marine, automotive, aircraft and cryogenic applications while the cast forms are used mainly for their corrosion resistance in dairy, food handling and chemical processing applications. Unlike the heat treatable alloys, these materials derive their strength primarily from solid solution strengthening by Mg, which has a substantial solid solubility in aluminium. However, in order to obtain strength levels approaching the regime of the precipitation hardening alloys, high Mg levels are required. Such high levels of Mg pose processing challenges and can increase the susceptibility of the alloys to stress corrosion cracking.

An effective alternative method to increase the strength of aluminium alloys (including Al-Mg alloys), first proposed by Willey in 1971, involves the addition of scandium as an alloying element. The fine dispersion of Al_3Sc precipitates is known to inhibit recryztallization even at large levels of plastic deformation and high annealing temperatures, enabling the use of strain hardening to push the strength of Al-Mg alloys to the levels achieved by traditional precipitation hardening.

Many researchers have also studied the addition of Sc to Al-Mg alloys. They suggested that equal channel angular pressing (ECAP) is responsible for achieving higher ductilities. In some experiments, it is shown that Al-3Mg-0.2Sc exhibited a grain size of 0.2 micron and tensile elongations of>2000% when subjected to ECAP. In some studies, it is mentioned that the optimum super plasticity was achieved in an alloy containing 3wt% Mg because smaller amounts of Mg yield larger grain sizes in ECAP processing and additions of Mg in excess of 3 wt% reduced the melting temperature of the alloy so that it was no longer possible to optimize the amount of Sc in solid solutions. In addition, they also stated that Sc addition are more beneficial than Zr additions in providing arrays of precipitates that restrict grain growth and lead to high super plastic ductilities at elevated temperatures. When both the additions are present, higher super plasticity is achieved at high temperature, because of the increased stability of $Al_3(ZrSc_{1-X})$ precipitates. In a partial ternary diagram Al-Mg-Sc diagram that has been constructed for Mg contents up to 26 wt% and Sc contents up to 3 wt% indicated that in alloys with Mg contents up to ~10 wt% and 0.3 wt%Sc, α-Al would be the first phase to solidify. The main difference between the microstructures of Al - Mg and Al - Mg - Sc is the presence of discontinuous precipitation at the cell boundaries in the latter alloy. The fine precipitates forming the fan shaped array and mostly these are Al_3Sc precipitates.

ECAP STUDIES ON Al & Al - Sc ALLOYS

Equal channel angular pressing (ECAP) is a well-known severe plastic deformation process in which the material is subjected to pass through a die with two channels connected at two specific angles and with the same cross sectional area. By this, microstructural changes take place, ultra fine grain structure is possible and properties like strength, toughness, super plasticity improves. In view of keeping these important properties, ECAP has been given much interest by many researchers that are also led to fabricate large bulk samples with ultra fine sizes. In general, the grain sizes less than 1 micron are referred as ultra fine grain size. During the ECAP, large strains are generated because the repeated pressings are not allowing any change in the material dimensions and causing dislocation cells of sub micron size. As the strain increases, the dislocation cell gradually turns into an independent grain, producing an ultra fine grain size of below one micron. The Sc additions to Al-Mg and Al-Si alloys showed improved mechanical properties and further improvement has been reported when the alloys are subjected to ECAP.

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