Assessment of Scandium Additions in Aluminum Alloy Design

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Abstract

Scandium is claimed to improve casting, welding, strength, corrosion resistance and formability of aluminum alloys. The main effect appears to be a powerful effect of inhibiting recrystallization both alone and in combination with other dispersoid formers, such as zirconium. Improved cast grain refinement may be the mechanism of improved welding characteristics. The choice of alloy system is found to be very important. There is an interaction between scandium and copper, but only limited other solute interactions. The use of more than 0.1 wt.% scandium when copper is a major solute addition requires very careful design. Scandium appears better suited for the Al-Mg and the low, or copper free, Al-Zn-Mg alloy systems.

Keywords *scandium, recrystallization, alloy development, precipitation, dispersoid*

Introduction

Scandium, once quite rare, is now increasingly available and several new patents on either articles of use or composition have been issued.[1,2,3,4] On a weight basis, Al_3Sc is reported to provide the largest increase in strength of any aluminum alloy addition. Al_3Sc is claimed to function as a powerful dispersoid to control recrystallization, and to impart superplastic deformation.[5,6] Perhaps due to its effect on cast grain refinement; it is reported to be an effective alloy addition for weldable alloys[1], however, other considerations, such as the shape of the liquidus and solidus phase boundaries, are important in weldable alloys. This paper systematically assesses the effect of scandium on precipitation and strengthening, and solute interactions occurring with other alloy additions in aluminum alloys.

Al-Sc Binary Precipitation

Several groups have examined the aluminum-scandium system.[4,7,8,9,10,11] The maximum equilibrium solubility of scandium in aluminum is 0.21 at. % (0.31 wt. %) at the eutectic temperature of 655°C, or 659°C, and the eutectic composition is 0.36% Sc (0.48 wt.%). The unconstrained misfit of the Al_3Sc in a pure aluminum matrix is +1.3% based on reported lattice parameters.[7] Transmission electron microscopy shows strain contrast of small precipitates contrast consistent with a coherent particle of this magnitude of misfit strain. Large incoherent Al_3Sc precipitates/dispersoids are spherical.[9,12,13] Since the lattice parameter of Al_3Sc is larger than the aluminum matrix, the addition of solute such as magnesium will further reduce the precipitate misfit, or change its sign. The Al_3Sc precipitates in an Al-6.5 wt.% Mg alloy are reported to have almost zero misfit.[14] Although scandium is a powerful precipitation hardener, its low solid solubility and limited volume fraction of Al_3Scmake it a more attractive dispersoid former.[4,15]

Precipitation of Al_3Sc

The precipitation of scandium is somewhat similar to the precipitation of Al_3Zr in aluminum. Both alloys form uniform spherical $L1_2$ precipitates in the matrix, and discontinuous precipitation in relatively high solute contents, or under slow solidification conditions.[16,17,18] However, Al_3Sc is an coherent equilibrium $L1_2$ phase and Al_3Zr is a non-equilibrium phase that transforms to an incoherent DO_{23} phase under slow solidification, high solute content, or aging at high temperature for long times. The $L1_2$ Al_3Zr phase is reported to be incoherent and to precipitate heterogeneously.[19]

The nucleation kinetics of precipitation of coherent Al_3Sc are quite rapid, at least an order of magnitude faster than Al_3Zr precipitation. Al_3Sc precipitation is probably strongly influenced by excess vacancy concentration. The precipitation is very slow below ~ 250°C where maximum hardness is not attained after 275 hrs. The nose of the CT curve is between 450-550°C.[13] Maximum hardness in binary alloys is reported to occur on aging at 250°C-350°C. Softening occurs at shorter times than required for loss of coherency, and is probably associated with precipitate impingement. Coarsening of Al_3Sc is very slow until coherency is lost.[8,12,13,20] Nucleation at 300°C is complete within 3 hours aging and subsequently only coarsening occurs, with moderately small (~<100mn) coherent particles present after up to 1667 hours aging. Coarsening markedly increases upon aging over 300°C-350°C. In an Al-0.3 at.% Sc alloy, the $L1_2$ phase becomes incoherent on aging for 50 hours at 400°C, at an average particle size of ~20nm. This transition occurs at shorter times at higher temperatures and is not observed after well over 100 hours at lower temperatures. Rapid coarsening of the phase accompanies the onset of loss of coherency, though its spherical shape persists.[12] Coherency loss and increased inter-particle spacing due to coarsening may allow recrystallization in deformed alloys.

There is evidence that Al_3Sc precipitation is accelerated by deformation. Drits measured the matrix lattice parameter of a range of Al-Sc alloys containing up to 0.75 (wt.?)% under various types of preheating and deformation. Extruding an as-cast ingot after only induction heating to the extrusion temperature of 300°C resulted in a matrix lattice parameter essentially that of pure aluminum. This indicates no scandium in solid solution. A similar ingot given a more conventional preheating of 30 hours at 380°C followed by reheating 6 hours at 400°C showed larger lattice parameter, indicating some scandium is still solid solution.[5] Nayayama, et al.[21] reported that the hardening effect of Al_3Sc is additive to the effect of θ' precipitation in a dilute aluminum-copper alloy. But when practical levels of copper are used, this effect is countered by the reaction of scandium with copper to reduce the available solute for precipitation hardening.

The Effect of Primary Alloy Additions

Magnesium

Much of the available work has been done in the Al-Mg-Sc system.[22,23,24,25] Magnesium does not strongly influence the kinetics of precipitation of Al_3Sc, or interact with scandium. The effect of Al_3Sc on recrystallization in Al-Mg is dramatic. A study of recrystallization of binary Al-Sc alloys and ternary Al-Mg-Sc alloys found recrystallization is accelerated by magnesium relative to the binary Al-Sc alloy; however, scandium significantly increases recrystallization temperature of the Al-Mg alloys.[26]. An Al-2 wt.% Mg -0.2 wt. % Sc alloy warm rolled 80% reduction could not be recrystallized below 550°C. The same warm rolled alloy containing zirconium and scandium could not be recrystallized below 590°C. Only by additionally cold rolling the latter alloy an additional 75% reduction and holding over 10 hours at [illegible]°C, could significant recrystallization be obtained.[27] Suitable TMP can produce an ultrafine grain rostructure exhibiting superplastic behavior at moderately high temperature.[28]

Copper

More than about 0.1 wt. % scandium and more than ~3.5-4.0 wt.% Cu will result in the formation of a ternary Al-Cu-Sc phase. This W-phase is reported approximately as $ScCu_{6.6-4}Al_{5.4-8}$.[29,30,31] The Sc-Cu interaction reduces the amount of copper available for precipitation hardening but otherwise does not interact with precipitation of θ', or θ''. The eutectic temperature for Al-$AlCu_2$ is 548°C limits the maximum solution heat treatment temperature relative to scandium. The equilibrium solubility of scandium at 548°C in aluminum is only ~0.13 wt. %. Increased scandium content can produce insoluble Al_3Sc constituent, or lower melting point eutectic reaction. Addition of even 0.2 wt.% Sc to 6013 (nominal 1 wt. % Cu content) results in an equilibrium melting reaction around 550°C, below the normal preheat temperature of ~560°C.[32]

Lithium

Because control of recrystallization is important in the Al-Li alloys the use of zirconium or scandium can be a desirable strategy. A copper-scandium interaction may occur in alloys such as 1420 and 2020, and the higher copper alloy, 2195. Addition of scandium exceeding ~0.1 wt.% to alloys with copper exceeding ~3.5 wt.% is not recommended due the interaction with copper. In the low, or copper free alloys containing lithium and/or magnesium where the metastable δ' ($L1_2$) phase forms, several investigators report the co-operative precipitation of δ' on Al_3Sc.[33,34] Because the diffusivity of scandium in Al is much lower than Li, the ternary Al-Li-Sc alloys more effectively respond to a two step aging practice where a high temperature(~400°C) is used to precipitate the Al_3Sc and a lower temperature (~200°C) to precipitate the δ'. The misfit of δ' is of the opposite sign of that of Al_3Sc. The combined effects of use of higher aging temperature to precipitate the Sc $L1_2$ phase and misfit different leads to marked co-precipitation of δ' on Al_3Sc. Scandium is reported to slow the kinetics of δ' precipitation.[35,36] No further interaction is noted.

Zinc

There appears to be no interaction of scandium and zinc in aluminum alloys, although the phase relationships are not very well examined. Several studies indicate the use of scandium in Al-Zn-Mg ternary alloys significantly improves mechanical and stress corrosion properties. A Russian alloy, 01975 (~0.2 wt. % Cu), of composition similar to 7021 but with small amounts of both scandium and zirconium (0.03 wt. % and 0.07 wt. %, respectively) reports yield strength of ~525 MPa, with "improved fracture toughness and LCF performance" comparable to 7475 and 7050.[37] Russian alloy 01987 with both 0.1-0.15 wt. % scandium + zirconium addition, is reported to exhibit excellent superplastic behavior with an m-value of ~0.4, three times that observed in the same alloy with only scandium addition. The ingot alloy structure of the alloy is reported to be "equiaxed or non-dendritic."[6] The latter work notes that the hot-rolled alloy with only scandium was recrystallized, especially along the centerline, but the alloy with both zirconium and scandium was unrecrystallized. These were small ingots and no information is provided on preheating practice.

The Effect of Secondary Alloy Additions - Dispersoids and Constituents

Manganese and Silicon

There is no reported interaction of scandium with manganese.[38] Binary dispersoids (Al_6Mn), should form independently of Sc. There is confusing work on the possible interaction of scandium and silicon. Tyvanchuk, et al. Examined the Al-rich region of the Al-Mn-Si diagram using non-preheated chill cast ingots. At low silicon content aluminum-rich alloys could be in either the α-Al/Al_3Sc/$AlSi_2Sc_2$, or α-Al/Si/ $AlSi_2Sc_2$ phase fields. [39] A later study of a Al-10 wt.% Si- 0.5 wt. % Sc alloy reports silicon suppresses the $L1_2$ phase and an Al-Si-Sc "V-phase" of reported stoichiometry $AlSi_2Sc_2$ forms.[40] However, the conclusion of these authors that this is a "metastable" ternary phase ($AlSi_2Sc_2$) needs clarification. A lack of interaction with the silicon may offer an opportunity for use in alloys with moderate silicon content where zirconium is not used due to a zirconium -silicon interaction that promotes the formation of an incoherent tetragonal phase.[41] In light of the conflicting reports, the possible interaction of scandium with silicon should be carefully evaluated.

Al-Cu-X

It is clear that at least one ternary Al-Sc-Cu constituent forms, the W-phase. There are several Al-Cu-X constituents, e.g., the Q-phase in Al-Mg-Cu alloys.[41] Therefore, the possible interaction of scandium in combination with copper to form a complex constituent, or dispersoid cannot be excluded.

Zirconium

Recent work in Al-Zn-Mg and Al-Mg alloys with either scandium, zirconium, or scandium+zirconium shows a significant change in grain structure when both zirconium and scandium are present. The recrystallization resistance and m-value of alloys with scandium+zirconium is much greater compared to alloys with either scandium or zirconium, and the nature of recrystallization is distinctly different.[6,26].

Both zirconium and lithium form a metastable $L1_2$ phase. both the zirconium and scandium $L1_2$ phase, are nucleation sites for the lithium $L1_2$ phase, δ'.[33,34,42] Furthermore, a metastable $L1_2$ phase may exist in the Al-Mg system. On first consideration, it may be suspected that zirconium, or even magnesium, may show an interaction forming a ternary phase. Such a zirconium interaction is reported as well as some indication of a measurable solubility of scandium and zirconium in the respective $L1_2$ phases.[43,44] If the zirconium and scandium occupy the same lattice sites in a disordered manner, one would form an $L1_2$ phase of stoichiometry $Al_3(Zr_{1-x}Sc_x)$. TEM examination of Al-Li-Cu-Mg-Zr-Sc alloys found no evidence of zirconium in the $L1_2$ scandium-containing dispersoid.[33]

It is possible that the presence of scandium and zirconium leads only to a modified dispersoid distribution of individual $L1_2$ phases rather than a ternary phase. Al-rich Al-Zr alloys solidify via a peritectic reaction and Al-rich Al-Sc alloys solidify via a eutectic reaction; therefore, segregation of scandium and zirconium in the cast structure should be opposite one from the other and an interaction is suspect. The reported increase in volume fraction of $Al_3(Zr_{1-x}Sc_x)$ may be a consequence of the more uniform distribution of total dispersoid binary phases rather than a solute interaction leading to one ternary phase. There us no conclusive evidence to support the claim of a chemical interaction between zirconium and scandium in the Al_3Sc phase. However, this possible interaction of $L1_2$ phase formers, merits some additional study.

Other transition metals

Scandium has been examined as a possible additive to aluminide structural intermetallic compounds. Scandium is reported to be soluble in Ti_3Al up to 6.4 at. % without change in crystal structure.[45,46] Other studies indicate possible ternary interaction in the iron-rich Fe-Ti-Sc region, of stoichiometry $Fe_{1.95}Ti_xSc_{1-x}$ ($x=0.6$-0.85).[47] Little information exists on interaction with other transition metals.

Effects of Scandium on Solidification Microstructure and Welding

Scandium is reported to be an effective grain refiner. With low solubility in aluminum and low diffusivity, scandium-containing alloys show metastable increase in supersaturation of scandium and displacement of the eutectic at solidification rates of 100K/s or higher.[48] As much as 1 wt.% scandium has been retained in solution under chill casting conditions.[49] However, casting alloys with such high level of scandium present challenges.[16,17] Frequently researchers have directly processed such alloys. without initial preheating as is given conventional alloys.[11] Alloys containing scandium do typically exhibit a smaller and more equiaxed as-cast grain structure. The maximum effect of refinement in cast grain size is reported to occur at near the equilibrium eutectic composition.[48,50]

The major aluminum alloys with reasonable welding character are the magnesium-free 2XXX alloys, the 5XXX alloys and several copper free 7XXX alloys. Improved welding characteristics are mentioned in connection with alloys of high scandium content, for example, weldable 2XXX alloys containing greater than 1 wt.% Sc are reported.[1] Copper-free 7XXX alloys containing 0.2 wt.% Sc and Al-Li-Mg alloys with scandium+zirconium addition with good weldability are reported. [37,51] The effect of scandium on welding could arise from the presence of eutectic, or primary Al_3Sc phase present in the melt which refines cast grain size and reduced scale of segregation. However, the specific shape of liquidus and solidus boundary is also very important in determining positive weld characteristics.[52,53] The shape of the hypoeutectic liquidus and solidus of the aluminum-scandium system should not improve weld cracking resistance.

Conclusions

The most important benefit of scandium in aluminum alloys is to inhibit recrystallization, especially in combination with zirconium. This improves all properties related to preserving an unrecrystallized microstructure, yielding up to a 10% increase in strength. Scandium stabilizes an equiaxed, fine recrystallized grain size after recrystallization, allowing superplastic behavior. Recrystallization with superplasticity causes lower creep resistance and lower elevated temperature strength. The phase relationships of constituent and dispersoid formers in scandium containing systems are very important. There are conflicting reports on interaction of scandium with zirconium and silicon. Up to ~0.13 wt. % Sc is soluble in Al-Cu alloys at 548°C, the eutectic temperature of Al_2Cu.[29] Eutectic melting reactions of and Al_2CuMg (S-phase) also occurs at relatively low temperatures compared to the solvus temperature of Al_3Sc. Increasing the amount of scandium over ~0.1 wt.% should lead to W-phase formation, or complex Al-Cu-X constituents, and eutectic melting in most practical Al-Cu and Al-Cu-Mg alloys, with the possible exception of an alloy such as 2618 which has reduced copper. Al-Mg-Cu alloys also will require careful design to avoid equilibrium melting at typical Al-Mg ingot preheating temperatures. Scandium can provide meaningful improvement in properties in 5XXX, 6XXX and 7XXX alloys where copper levels are suitably controlled. If the cleanliness of the alloy is controlled in 5XXX, 6XXX and 7XXX alloys, the refined ultrafine grain size should lead to improved toughness, and high cycle fatigue resistance. The effect of ultrafine, equiaxed grain size is detrimental to fatigue crack growth under many loading conditions, however. Additional alloy design strategies will be required to improve this situation.[54]

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