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The effect of introducing the Al–Ni eutectic composition into Al–Zr–V alloys on microstructure and tensile properties

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article info

ABSTRACT

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1. Introduction

It has been widely reported that by employing a very fast cooling rate; such as in direct chill casting, the transition metals Sc, Zr, and V may dissolve in aluminum to from supersaturated solid solutions in which the concentration of the transition metal is significantly higher than the maximum solubility indicated by the equilibrium phase diagram $[1-4]$ $[1-4]$. Proper aging of these super saturated solid solutions results in the formation of precipitate particles with a chemical composition that corresponds to the general stoichiometric formulae $Al₃TM$, where TM ≡transition metal. These precipitates, i.e., Al₃Sc, Al₃Zr, and also Al₃(Zr_x,V_{1-x}), may have an ordered $L1₂$ crystal structure, and therefore they have the potential to be excellent inducers of precipitation hardening in creep-resistant thermally stable aluminum alloys. Fan and Makh-louf [\[5\]](#page--1-0) have shown that $\text{Al}_3(\text{Zr}_x,\text{V}_{1-x})$ precipitate particles are significantly more thermally stable than $Al₃Zr$ and $Al₃V$ particles due to their low lattice mismatch with the aluminum matrix; and they are also more thermally stable than $A₁₃$ Sc particles because scandium diffuses more readily in aluminum than zirconium and vanadium (at 400 °C $D_{sc} = 1.98 \times 10^{-17} \text{ m}^2\text{/s}$ $[6]$, $D_{Zr} = 1.2 \times 10^{-20} \text{ m}^2/\text{s}$ [\[7\]](#page--1-0), and $D_V = 4.85 \times 10^{-24} \text{ m}^2/\text{s}$ [\[8\]\)](#page--1-0). However, in order for the Al–Zr–V system to fulfill its potential in being the basis of aluminum casting alloys that are useful at elevated temperatures, several major issues have to be resolved. These are: (1) its poor castability, including its insufficient fluidity and its

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<http://dx.doi.org/10.1016/j.msea.2015.12.044> 0921-5093/© 2015 Published by Elsevier B.V. The effect that the Al–Ni eutectic composition has on the microstructure and tensile properties of Al–Zr– V alloys is discussed. It is found that the change in the alloy's solidification behavior brought about by the presence of the eutectic composition mitigates segregation of the zirconium and vanadium atoms, and by doing so it enhances the precipitation hardening characteristics of the alloy and improves its yield strength.

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high tendency to hot tear during solidification, (2) the relatively low solubility of zirconium and vanadium in aluminum (the maximum solubility of Zr in aluminum, $C_{\alpha p-Zr} \cong 0.28$ wt% [\[9\]](#page--1-0), the maximum solubility of V in aluminum, $C_{\alpha p-V} \cong 0.56$ wt% [\[10\]\)](#page--1-0), which limits the volume fraction of the precipitate phase that forms upon aging, and (3) the rather large equilibrium partition coefficient of the binary aluminum–zirconium and aluminum– vanadium systems ($k_{e(A1-Zr)} \cong 4$ [\[9\],](#page--1-0) $k_{e(A1-V)} \cong 2.5$ [\[10\]\)](#page--1-0), which contributes to excessive microsegregation of zirconium and vanadium atoms in the dendritic structure of the as-cast alloy $[1,11]$ $[1,11]$. This latter issue is exacerbated by the inability to homogenize these alloys without inducing incipient melting of the cast component. A possible way of addressing these issues involves introducing a proper eutectic into the Al–Zr–V alloy. Solidification of a eutectic composition does not result in a dendritic structure since it solidifies like a pure metal; i.e., it solidifies at a single temperature – as opposed to solidifying over a temperature range. Moreover, the fluidity of a eutectic composition is superior to that of other compositions since the eutectic composition tends to solidify with a plane front that originates at the walls of the mold and progresses towards its center. Consequently, the stream of molten metal can continue to flow until the freezing fronts meet and close the flow channel $[12]$. In contrast, compositions that are far from the eutectic tend to form dendrites during solidification. The dendrites, which originate at the walls of the mold and grow inwards towards its center may be fragmented by the flow of the molten metal, and the stream develops as a slurry of tumbling dendritic crystals [\[12\].](#page--1-0) Eventually, the dendrites interlock, and the flow of molten metal stops. Also, a eutectic composition has a comparatively longer time during solidification that is available for

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stress relief; i.e., it exhibits a longer time at which mass feeding can occur. Consequently, eutectic compositions are more resistant to hot tearing than other compositions [\[13\]](#page--1-0). Alas, not all aluminum-based eutectic systems are capable of addressing the abovementioned issues. Eutectic systems that are appropriate for addition to Al–TM alloys must fulfill three general requirements. (1) Their eutectic temperature should be higher (or at least not much lower) than the peritectic temperature of the Al–TM system; otherwise the eutectic reaction may not occur preferentially to the peritectic reaction. (2) The eutectic structure should enhance the strength of the alloy both at room temperature and at elevated temperatures in order to compensate for the small strengthening increment provided by the $Al₃TM$ phase (low strengthening increment because of its relatively low volume fraction). (3) The eutectic structure should be thermally stable.

The aluminum–nickel system has a eutectic composition that meets these requirements. Nickel forms with aluminum a series of nickel aluminides, one of them is Al₃Ni. Aluminum forms a eutectic with $Al₃Ni$ at 6.1 wt% nickel. The melting point of the Al–Al₃Ni eutectic is 640 °C and the volume of Al₃Ni in the eutectic structure is relatively large (9.7 vol%); consequently, the Al–Al3Ni eutectic composition has very good fluidity, and castings made of this material have a low tendency to hot tear $[14]$. Moreover, the two eutectic phases in this structure (namely, α-Al and Al_3Ni) are in chemical equilibrium with one another so they are not prone to chemical degradation, and the interface between them has a low energy structure that ensures the thermal stability of the material [\[15\]](#page--1-0). Moreover, the two eutectic phases share a strong interfacial bond with one another, which allows efficient load transfer between them. Examination of the portion of the equilibrium diagram that pertains to the eutectic reaction: $L \leftrightarrow Al + Al₃Ni$, shows that nickel has only very limited solubility in aluminum (about 0.05 wt% at 640 °C, and less than 0.005 wt% at 450 °C) [\[16\].](#page--1-0) Table 1 shows various characteristics of the binary intermetallic compound Al₃Ni which, together with α-Al, are the two phases in this eutectic structure.

In this publication, we discuss the effect that the Al–Ni eutectic composition has on the microstructure and tensile properties of Al–Zr–V alloys.

2. Materials and procedures

Al–0.4Zr–0.4V and Al–6Ni–0.4Zr–0.4V alloys¹ were constituted from pure aluminum ingots (99.999% purity), Al–20Ni, Al–15Zr, and Al–65V master alloys. The alloys were melted in an induction furnace in clean silicon carbide crucibles coated with boron nitride. The melts were degassed with high purity argon gas by means of a rotating impeller degasser for 30 minutes, and they were poured at approximately 800 °C into a water-chilled copper mold. The water-chilled copper mold produces ASTM standard sub size tensile specimens with a uniform solidification cooling rate of about 120 \degree C/s. The specimens, in their as-cast condition, were aged in an electric furnace and then cooled from the aging temperature to room temperature in air. Although precipitation

Table 1 Characteristics of Al3Ni.

Stoichiometric composition 0.25 at% Ni Degree of order Melting type incongruent Strukturbericht symbol $D0_{20}$ Al_3Ni Prototype Pearson symbol oP16 Space group Pnma	

hardenable aluminum casting alloys are solution heat treated and quenched before they are artificially aged, the Al–0.4Zr–0.4V and Al–6Ni–0.4Zr–0.4V alloys of this study were aged without solutionizing and quenching. This deviation from the norm is dictated by the fact that these alloys are based on peritectic systems wherein a solutionizing heat treatment is not possible without causing incipient melting of the cast part. For these alloys, it is submitted that the liquid is homogenized during melting and the fast cooling rate during solidification replaces the quenching step and preserves the homogeneous super saturated solid solution. As seen in [Fig. 1,](#page--1-0) microstructure analysis shows that this statement is true for the Al–6Ni–0.4Zr–0.4V alloy, but not necessarily for the Al–0.4Zr–0.4V alloy.

Samples from both alloys were prepared for scanning electron microscopy (SEM) by grinding and polishing according to standard metallographic methods. Samples used for transmission electron microscopy (TEM) were produced by thinning foils of the alloys to perforation by means of a twinjet electro-polisher (Fischione Instruments, model 120) operating at 12 V and utilizing a solution of 10 vol% perchloric acid in methanol that is maintained at -20 °C. A JOEL-7000F scanning electron microscope operating at 200 kV and a JOEL-2010F transmission electron microscope were used for microstructure analyses.

Room temperature tensile properties of the alloys were measured by means of a Universal Testing machine (Instron model 5500R) at an extension rate of 0.05 in./min. A 1-inch gage length extensometer (MTS model 634.25E-24) was used to measure extension. At least 5 specimens were used in each measurement and the results were averaged and the standard deviations were calculated. Fracture of all specimens occurred within the gage length and specimens with severe porosity and/or oxides that would affect the results were excluded.

3. Results

3.1. Microstructure of the as-cast specimens

[Fig. 1](#page--1-0) shows SEM photomicrographs and EDS spectra of the ascast Al–0.4Zr–0.4V and Al–6Ni–0.4Zr–0.4V alloys. The Al–0.4Zr– 0.4V specimen was etched with Keller's reagent in order to reveal its dendritic structure. The average secondary dendrite arm spacing was measured and it was found to be 10 μ m. At the fast cooling rate employed (120 °C/s), the Al–0.4Zr–0.4V alloy is an α -Al solid solution in which formation of primary Al_3Zr and Al_3V phases is completely suppressed. The Al–6Ni–0.4Zr–0.4 V alloy exhibits a eutectic microstructure in which rods of eutectic Al₃Ni are dispersed in α -aluminum. Similar to the Al-0.4Zr-0.4V alloy, the fast cooling rate employed in casting the Al–6Ni–0.4Zr–0.4V alloy suppresses formation of primary $Al₃Zr$ and $Al₃V$ phases in this specimen. EDS line scanning was performed along the black lines indicated in the photomicrographs in order to detected segregation of zirconium and vanadium atoms. Although EDS results are not very precise, they are accurate enough to indicate the presence of concentration fluctuations, and as such, they have been widely used to detect microsegregation in metallic alloys (e.g., $[2,11]$). Results of the EDS measurements are shown in [Fig. 1](#page--1-0) (d) – (f) . Fig. $1(d)$ shows that the concentration of zirconium and vanadium atoms near the outer periphery of the secondary dendrite arms is significantly lower than that near the dendrite's core. The standard deviations of the measured zirconium and vanadium atom concentrations across a typical secondary dendrite arm are respectively \pm 0.24 and \pm 0.20. Similar behavior has been

 $¹$ All compositions are in weight percent unless it is stated otherwise.</sup>

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