# Effect of Zirconium on Liquidus and Hardening of AI–6%Ni Casting Alloy

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#### Abstract

The effect of pouring and heat treatment temperatures on the structure and mechanical properties of the casting Al–6 wt.%Ni–Zr alloys was studied. It was shown that at 0.5 wt.% Zr the primary crystals of the Al<sub>3</sub>Zr phase form at a temperature lower than 770–780 °C. The optimal combination of strength and ductility corresponds to a structure consisting of a dispersion-strengthened (by Al<sub>3</sub>Zr dispersoids) aluminium matrix and submicron-size globular particles of Al<sub>3</sub>Ni. This structure can be obtained by annealing at 350-450 °C.

## 1. Introduction

The eutectic alloy AI-6 wt.% Ni has been studied many times, mainly as a model alloy, due to a possibility to obtain a structure consisting of the ductile aluminium matrix and the hardening component as the phase Al<sub>3</sub>Ni [1–5]. This structure is typical of many composite materials, which are of great interest at present. In particular, the eutectic Al-Al<sub>3</sub>Ni was often considered as a base for natural, directly solidified composites. An advantage of this eutectic over other Al-based eutectics is its fine structure, which enables a higher ductility. However, the absolute values of the strength properties in castings are too low (UTS < 150 MPa) for this alloy to be used commercially, which is due to the low solubility of nickel in aluminium. Additional alloying is required to significantly strengthen the aluminium matrix and preserve the fine structure of Al-Ni eutectic. Traditional alloying elements for commercial aluminium alloys (Cu, Mg, Zn and Si) sharply increase the solidification range of this eutectic, which leads to its coarsening and strongly decreases its casting properties. The most expedient approach is to alloy the aluminium matrix with transition metals, in particular, scandium and zirconium. Even at low concentrations, these transition metals yield a significant effect of dispersion hardening due to the secondary precipitates with crystalline structure  $Ll_2$  (Al<sub>3</sub>Sc and Al<sub>3</sub>Zr) [6–8].

The scandium cannot be applied due to the high coast of it, that is why only zirconium as alloying element often used in rapidly solidified aluminium alloys (RS/PM technologies). The composite alloying only with transition metals enhance mechanical properties at room and elevated temperatures as compared with commercial aluminium alloys obtained by conventional proccesses [9]. In particular, according to [10], the AlNiZr composition enables UTS > 800 MPa. However, the use of RS/PM technology strongly increases the cost of the final product, which restricts the range of its applications. On the other hand, as

shown in [6–7], conventional casting into metal molds can form oversaturated solid solutions containing up to 0.8 wt.% Zr, in addition to 6 wt.% Ni. This significantly increases the strength properties (up to 50%). A fine structure of the Al–Ni eutectic is preserved; in annealing this feature produces submicron-size globular particles of nickel aluminide. This can ensure a relatively high ductility. As addition of 0.8 wt.% Zr requires the melt to be strongly overheated (not lower than 900 °C), a low concentration of this element make it possible to decrease the temperature range to a commercially acceptable level. The aim of this work is:

- (1) to construct the liquidus line in the Al–6 wt.% Ni–Zr section and to find the optimal concentration of zirconium and the pouring temperature;
- (2) to study the effect of heat treatment on the structure and mechanical properties of an optimal-composition alloy.

## 2. Experimental

The alloys containing 6 wt.% Ni and from 0.2 to 1 wt.% Zr were prepared in an electric furnace using 99.99 % pure aluminium and Al–20 wt.% Ni and Al–3.5 wt.% Zr master alloys. The chemical composition of alloys was accurate within 5 rel. %. Ingots were cast in a graphite mould with internal dimensions of  $15 \times 30 \times 180$  mm (cooling rate being about 10 K/s). Alloy preparation and pouring temperature was 900–950 °C, which at a zirconium concentration of up to 0.8 wt.% enabled the complete presence of this element into the aluminium solid solution - (Al).

To plot the liquidus line in the cross-section of Al-6 wt.% Ni-Zr, 15-g samples were cut from the ingots and placed in alumina crucibles into a furnace at a temperature of 700 up to 900 °C. After 1 hour of holding, the crucibles with the melt were cooled in cold water. Then the structure of the rapidly cooled ingots was studied along the entire height, first of all close to the bottom, because the primary crystals of the Al<sub>3</sub>Zr phase concentrated due to their higher density as compared with the liquid phase. The presence or absence of these primary crystals enabled a conclusion in which phase region the alloy was at the holding temperature (Figure 1). The other experiments were carried out on an AI-6 wt.% Ni-0.5 wt.% Zr alloy, a 30-kg sample of which was melted in an induction furnace at a melting temperature of 900–950 °C. Then 1-kg portions of the melt were transferred into a ladle and cooled to temperatures within the range of 700-900 °C. After that the melt was poured into a metal mold to produce a cast shape. Specimens cut from this casting (Figure 2a) were used for microstructure analyze (Figure 2b,c) and determine the hardness (Figure 3). The effect of the annealing temperature on the structure and mechanical properties were studied on the ingots ( $15 \times 30 \times 180$  mm) obtained by pouring from 850 °C.

Ingots were annealed in an electric furnace at 350-600 °C. The structure was examined in light (Neophot 30), scanning electron (JSM-35CF) and transmission electron (JEM 2000EX) microscopes. Samples for LM and SEM were polished in a perchloric acid–ethanol electrolyte. The electron microprobe analysis (EMPA) of primary crystals (Al<sub>3</sub>Zr) was performed in the JSM-35CF microscope equipped with a four-crystal wave spectrometer. Foils for TEM were thinned in a perchloric acid–ethanol solution and examined at a voltage of 120 kV. Identification of precipitations (Al<sub>3</sub>Zr) was done by analyzing selected-areas electron diffraction patterns. Hardness (HB) and tensile properties (UTS, YS and El) were measured using standard techniques. Tensile tests were performed at a tensile rate of 4 mm/min using cylindric samples (5 mm gauge diameter).



Figure 1: Experimental line of liquidus in Al-6 wt.% Ni-Zr section and typical microstructures in as-quenched state.



Figure 2: Microstructure of experimental alloy Al-6 wt% Ni-0,5 wt.% Zr from shaped castings (a) poured from 750  $^{\circ}$ C (b) and 800  $^{\circ}$ C (c), SEM.



Figure 3: Effect of pouring temperature (T) on the hardness (HB) of Al-6 wt.% Ni-0.5 wt.% Zr alloy in as-cast (F) and annealed (400  $^{0}$  C, 20 h) states.

#### 3. Results and Discussion

As follows from Figure 1, zirconium sharply increases the liquidus temperature, which at 1 wt.% exceeds 900°C. If the temperature of the melt before pouring is below the liquidus, primary crystals of Al<sub>3</sub>Zr inevitably appear in the structure even at rapid solidification, as they are already present in the melt. Given the maximal pouring temperature for commercial aluminium alloys (800–810 °C, hypereutectic Al–Si alloys of the AA393.0 type), additions of zirconium in amounts larger than 0.5–0.6 wt.% are not expedient. On

the other hand, the concentration of about 0.5 wt.% should be considered optimal, if one takes into account that the strengthening of castings due to the formation of  $AI_3Zr$  dispersoids in annealing is not high at a Zr content of less than 0.4–0.5 wt.% [6].

To support this conclusion, we studied the microstructure and hardness of Al-6 wt.% Ni-0.5 wt.% Zr specimens cut from cast shapes (Figure 2a), depending on the pouring temperature (T<sub>p</sub>) within the range of 900 to 700 °C. The microstructural analysis of the casting (Figure 2b, c) showed that primary crystals of Al<sub>3</sub>Zr phase were found only at  $T_p$  < 770-780 °C. The microstructural analysis data agrees with the hardness test results. Figure 3 shows that in as-cast state the effect of T<sub>p</sub> is almost nil, as the solid-solution strengthening due to zirconium addition is small, but after a heat treatment the increase of  $T_p$  from 700 up to 800°C significantly increases HB, and a further increase of  $T_p$  fails to lead to any strengthening. It is evident that the formation of primary crystals of the Al<sub>3</sub>Zr phase leads to a decrease of the concentration of zirconium in (AI) in as-cast state, which reduces the amount of dispersoids formed in annealing. Respectively, the effect of strengthening also decreases. Thus, the AI-6 wt.% Ni-0.5 wt.% Zr alloy makes it possible to produce thin-walled castings of complex shape (~5 K/s) using an acceptable casting temperature, ensuring a significant strengthening during annealing (ageing). We should note a high quality of castings at all pouring temperatures, whereas Al-Si-Cu alloys (for instance, of the AA355 type) in the same casting (Figure 2a) tend to form hot cracks under similar conditions.

As shown in [5–8], two major processes can occur in annealing of Al–Ni–Zr alloys: (a) morphological change of eutectic crystals of the Al<sub>3</sub>Ni phase (fragmentation, spheroidization and coarsening), which leads to softening; (b) decomposition of oversaturated Zr-containing (Al), which can strengthen the alloy if the heating temperature does not exceed 450 °C. To optimize the heat treatment of the Al–6 wt.% Ni–0.5 wt.% Zr alloy, we selected the five regimes which enable the formation of various types of microstructure: A1 – as-cast; A2 – 350 °C, 3 h + 400 °C, 3 h; A3 – 350 °C, 3 h + 450 °C, 3 h; A4 – 350 °C, 3 h + 500 °C, 3 h; A5 – 350 °C, 3 h + 600 °C, 3 h. We should note that light microscopy (even at a maximal magnification) does not reveal the inner structure of the Al–Ni eutectic, because it is distinguished by a fine structure, which is significantly finer as compared with the Al–Si eutectic obtained in the same castings.

Regime A1 characterizes the initial state when the eutectic (AI)+Al<sub>3</sub>Ni is not fragmented (Figure 4a) and zirconium is completely soluble in (AI). Regime A2 corresponds to the preservation of the eutectic morphology (Figure 4b), which is revealed most reliably by TEM (Figure 4c), and a maximal strengthening of the aluminium matrix due to Al<sub>3</sub>Zr dispersoids (Figure 4 d). This structure was assumed to ensure the greatest strength of the alloy. The choice of regime A3 was determined by the wish to achieve complete fragmentation in order to obtain more or less compact inclusions of the Al<sub>3</sub>Ni phase of a minimal size (Figure 4e) with the maximal strengthening of the aluminium matrix preserved, because the size of Al<sub>3</sub>Zr dispersoids did not exceed 20 nm. Just this structure was assumed to enable the best combination of strength and ductility. Heat treatment by regime A4 leads to the total spheroidization and an increase of size of Al<sub>3</sub>Zr dispersoids increases, but the stable phase is not formed yet. Finally, regime A5 corresponds to a strong coarsening of both the inclusions of the Al<sub>3</sub>Ni phase (Figure 4g) and Al<sub>3</sub>Zr dispersoids which, in contrast with A1–A3, are a stable phase.

The tensile test results given in Table 1 show the different effects of the heat treatment regime on various characteristics. The largest values of UTS and YS are achieved in state

A2, and the lowest in A5, in which the ductility is maximal. In state A2 the value of El is, in contrast, minimal. It should be noted that the absolute values of El for the as-cast state of the alloy under study are sufficiently high as compared with those for the eutectic Al–Si alloys, which is probably due to the increased dispersity of the eutectic [5].



Figure 4: SEM (a,b,e-g) and TEM (c,d) structures of an Al–6 wt.%Ni–0.5 wt.%Zr alloy:a) as-cast; b-d) 350 °C, 3 h + 400 °C, 3 h; e) 350 °C, 3 h + 450 °C, 3 h; f) 350 °C, 3 h + 500 °C, 3 h; g) 350 °C, 3 h + 600 °C, 3 h.

The fracture features were studied by examining the fractures of ruptured specimens, in particular, those corresponding to states A2 and A4 (Figure 5). Both fractograms show the features characteristic of ductile failure (ridges, small dimples, absence of plane regions), the difference between them is revealed only at a sufficiently high magnification. The structure corresponding to the non-fragmented eutectic is the cellular structure (Figure 5a), when a considerable part of the fracture face has broken Al<sub>3</sub>Ni eutectic dendrite branches. In the second case, the dimples are clearly seen (Figure 5b), with globular particles of Al<sub>3</sub>Ni inside them. The depth of the dimples is significantly larger than the size of the particles, which implies a considerable plastic deformation.



Figure 5: Fracture surface of a tensile samples of Al-6 wt.%Ni-0,5 wt.%Zr alloy, SEM:a) 350  $^{\circ}$ C, 3 h + 400  $^{\circ}$ C, 3 h; b) 350  $^{\circ}$ C, 3 h + 500  $^{\circ}$ C, 3 h.

The properties of the Al–6 wt.% Ni–0.5 wt.% Zr alloy are more expediently compared with those of the heat-treated alloy AA356, which has approximately the same casting and strength characteristics. The main advantages of the experimental alloy are that, first, the structure is stable at prolonged heating, at least up to 350 °C inclusive (for AA356, the temperature of 250 °C is already inadmissibly high), and second, its heat treatment is simpler as compared with T6. Addition of 0.5 wt.% Zr is approximately equivalent by its strengthening effect to an addition of scandium at about 0.2–0.3 wt.%, which corresponds

to a typical concentration of this element in new aluminium alloys [8]. As scandium is a very expensive metal, the practical use of alloys, in particular, casting alloys, with increased zirconium content appears to be a promising trend.

Temper		Tensile properties		
		UTS, MPa	YS, MPa	EI,%
A1	as-cast	180	125	19
A2	350 °C, 3 h + 400 °C, 3 h	245	185	7
A3	350 °C, 3 h + 450 °C, 3 h	235	165	11
A4	350 °C, 3 h + 500 °C, 3 h	165	100	18
A5	350 °C, 3 h + 600 °C, 3 h	120	80	34

Table 1: Tensile properties of Al-6 wt.% Ni-0.5 wt.% Zr alloy.

## 4. Conclusions

1. The liquidus line in the Al–6 wt.% Ni–Zr diagram cross-section was plotted by quenching the melt from temperatures of 700–900°C. It was shown that at 0.5 wt.% Zr the primary crystals of the Al<sub>3</sub>Zr phase are formed at a temperature lower than 770–780 °C. This enables a significant decrease of the casting temperature, thus preserving the possibility of a considerable strengthening during annealing due to the precipitation of dispersoids of the metastable phase Al<sub>3</sub>Zr.

2. The effect of heat treatment on the structure and mechanical properties of the Al–6 wt.% Ni–0.5 wt.% Zr alloy was studied. It was shown that the optimal combination of strength and ductility corresponded to a structure consisting of a dispersion-strengthened aluminium matrix and submicron-size globular particles of Al<sub>3</sub>Ni. This structure can be obtained by annealing, in particular, according to the regime 350 °C, 3 h + 450 °C, 3 h. 3. It was shown that the optimal structure of the Al–6 wt.% Ni–0.5 wt.% Zr alloy can be realized in complex-shape thin-walled pouring at a casting temperature of about 800 °C, which enables the use of a process acceptable for commercial casting aluminium alloys.

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