

Effects of Ni on the microstructure, hot tear and mechanical properties of AlZnMgCu alloys under as-cast condition

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Abstract

The effects of Ni on the phases, microstructural evolution, hot tear susceptibility and mechanical properties of Al₆Zn-1.4Mg-1.2Cu alloys fabricated by gravity casting were investigated using X-ray diffraction (XRD), scanning electronic microscopy (SEM), optical microscopy, the N-Tec Hot tear and tensile test. The calculation of phase diagrams (CALPHAD) modelling was also conducted to understand the phase formation of the experimental alloys. The results showed that the secondary phases (including h-MgZn₂, SeAl₂CuMg and Al₃Ni) are mainly distributed at grain boundary, while round SeAl₂CuMg particles are also found in a-Al matrix. Ni only exists as Al₃Ni with different morphologies and its number density ascends with the increase of Ni content in alloys, which also significantly improves the hot tear resistance. As a result, the increased Ni in the alloys remarkably improves the ultimate tensile and yield strength, while the elongation increases when Ni < 0.6 wt% followed by decreases when Ni > 0.6 wt%. © 2019 Elsevier B.V. All rights reserved.

1. Introduction

The development in aerospace and automobile industry demands the continuous improvement of aluminum alloys for better mechanical performance [1e5]. AlZnMgCu (7xxxx) alloys have been widely used in wrought products [4,5] to offer high specific strength in light weight structure. In recent years, the interests in developing castable AlZnMgCu alloys for shaped casting is increased [6e10], targeting to reduce the manufacturing cost but maintain the high-strength in components. However, one of the problems is the high tendency to form hot tear during solidification [9e11]. Once hot tear occurs, the casting components should be repaired or even discarded, which significantly limits the application of AlZnMgCu alloys in the manufacturing of shaped castings.

In order to overcome the hot tear problem and tailor the mechanical properties of AlZnMgCu cast alloys, the efforts have mainly focused on using special casting techniques [12e22] and developing novel aluminum alloys [23e29]. The special casting techniques including powder metallurgy [12], semi-solid metal processing [13e16], rapid solidification [17], spray deposition [18e20] and electromagnetic casting [21,22], have been

used to achieve the near-net shape casting of AlZnMgCu alloys. However, these casting techniques are only effective in specific components, but not very applicable in massive manufacturing of components with complex shapes, in particular when combining the consideration of manufacturing cost.

In reality, the development through modifying the elemental constituents is a cost-effective, simple and proved approach in application. It is easy to apply in conventional foundry practice without significant changes in processing equipment and procedures. Previous studies confirmed that the modification of main alloying elements and their contents had complex and/or even contradictory effects on the hot tear tendency of AlZnMgCu alloys [11,23,24]. Krajewski [25] and S. Shin et al. [26] pointed that extra high Zn level (>20 wt%) could effectively suppress the formation of hot tear during solidification, however, the high density induced by high Zn is not favoured for light-weight requirement. On the other side, grain refinement using AlTi or AlTiB master alloys has been extensively studied to reduce hot tear and simultaneously increase the strength and elongation of cast aluminium alloys [27e29]. J. Shin et al. [29] found that the addition of Ti have a positive effect on the reduction of hot tear susceptibility. However, Warrington et al. [24] found that the addition of excessive grain refiner lead to the increase of hot tear susceptibility because of the

Table 1

Chemical compositions of AlZnMgCu-xNi alloys analyzed by OES (wt.%).

Alloy^a Zn Mg Cu Ni Ti Fe Others Al

AlZnMgCuNi 6 ± 0.11 1.4 ± 0.06 1.2 ± 0.05 Varied 0.02 ± 0.01 0.08 ± 0.01 <0.05 Bal.

^a Actual Ni contents were measured to be 0.03, 0.34, 0.63, 0.94, 1.25, 1.67, 2.68, 3.69 and 4.71, respectively.

formation of equiaxed-cellular grains in alloys. Moreover, in order to decrease the hot tear susceptibility of cast AlZn alloys, other elements were also studied [29]. J. Shin et al. [29] claimed that Si could eliminate the hot tear when Si content is up to 3 wt% in the as-cast Al6Zn1Mg3Si-0.1Zr-0.1Ti alloy. Unfortunately, the addition of Si remarkably worsen the elongation. Therefore, an applicable solution to decrease the hot tear tendency and maintain or improve the mechanical properties of AlZn based alloys is urgently needed. Recently, Ni was found as a potential element capable of achieving these goals. The addition of Ni in Al alloys can increase the strength at room or elevated temperatures [30e36], which have been widely confirmed in Al-Si [30e33], AlMgSiMn [34], Al-Si-Cu-Mg [35] and AlZnMgCu [36] alloys. Meanwhile, Belov et al. [37e39] analyzed the equilibrium phase diagram of AlZnMg-(Cu)eNi alloys using Thermal-Calo software, and found that Ni only exists in the form of Al β Al3Ni eutectics. Generally, the increase of eutectics is helpful to suppress the formation of hot tear in cast alloys. It is speculated that the Ni addition can further increase the effectiveness of strengthening in AlZn based alloys when the hot tear resistance was improved. However, there is no experimental evidence supporting these expectations up to now.

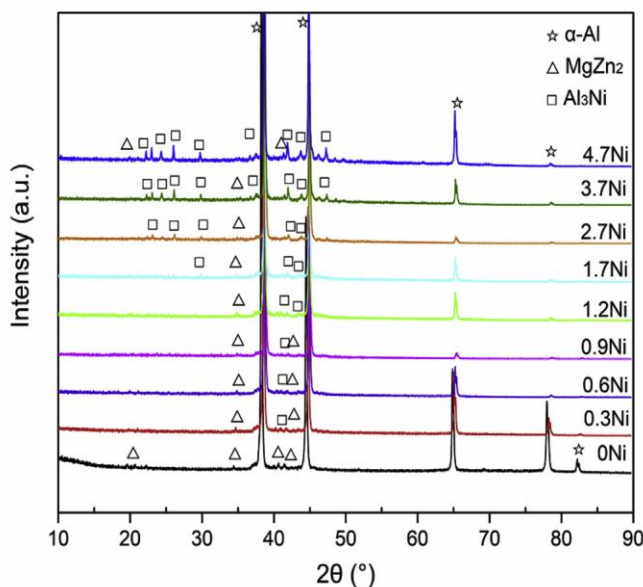


Fig.1. XRD patterns of the AlZnMgCuNi alloys under as-cast condition.

Therefore, in this paper, it is aimed to study the effect of Ni on the microstructure, hot tear and mechanical properties of AlZnMgCu alloys. A series of AlZnMgCu alloys with different Ni contents were prepared by gravity casting. The hot tear susceptibility was measured, and the phase formation and microstructure were analyzed in association with the mechanical properties. The phase formation was also studied through the calculation of phase diagrams (CALPHAD) modelling of multi-component AlZnMgCuNi system. The mechanism of improving the hot tear resistance was analyzed by the theoretical calculation of solid fractions and surface morphology. The relationship between microstructure and mechanical properties is also discussed in the experimental alloys.

2. Experimental

The alloys with a nominal composition of Al₆Zn-1.4Mg-1.2Cu_xNi (x = 0, 0.3, 0.6, 0.9, 1.2, 1.7, 2.7, 3.7 and 4.7, hereafter denoted AlZnMgCu-xNi) were prepared by melting pure Al, Zn, Mg, Cu, and Al-20 wt% Ni master alloy (all compositions reported in this paper are in wt.% unless otherwise clarified). During alloy preparation, firstly, the pure Al and Cu, Al-20 wt% Ni master alloy were melted in a 12-kg clay-graphite crucible coated with boron nitride using an electric resistance furnace at 780 ± 5 °C. Secondly, pure Zn and Mg were added into the melt, followed by gentle stirring the melt, Zn and Mg was over added by 5 wt% respectively for compensating the burning lost during melting. After 30 min of homogenization at 750 °C, the melt was degassed using high purity argon input through a rotary impeller at a speed of 300 rpm for 6 min. After degassing, 0.1 wt% Al₅Ti₁B master alloy was added into the melt for grain refinement, and then the melt was held at 720 °C for 30 min before casting. During casting, a metal mold to make two tensile samples was used, which is made according to ASTM Be108 for the details of gating system and casting structure [40,41]. The mold was coated with boron nitride and preheated up to 400 °C. The pouring temperature was controlled at 720 °C. All casting samples were kept under ambient condition for 3 days before the tensile testing.

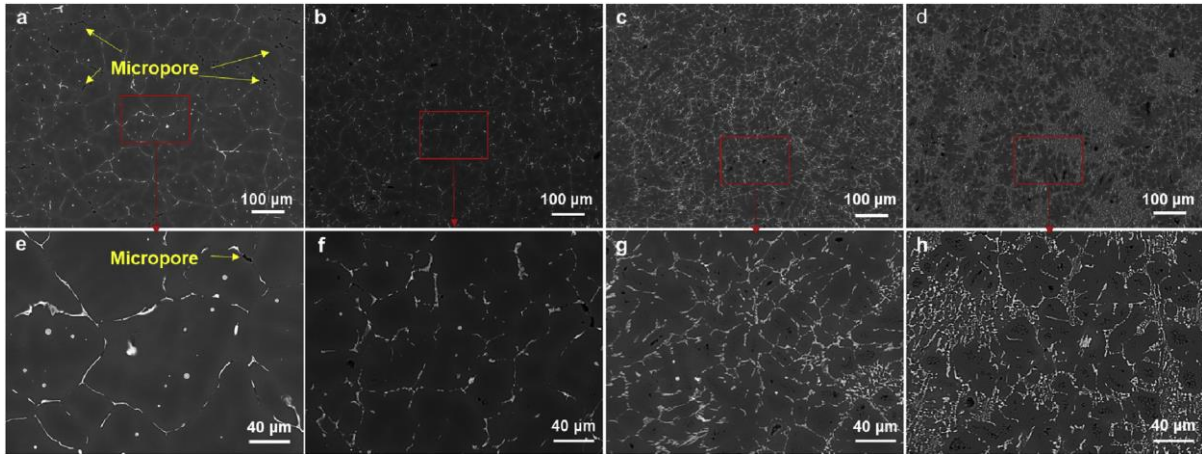


Fig. 2. Backscattered SEM images showing the as-cast microstructure of AlZnMgCuNi alloys, (a,e) 0Ni, (b,f) 0.6Ni, (c,g)2.7Ni and (d,h) 4.7Ni.

The mushroom samples for the composition analysis were obtained by pouring the melt into a permanent mold preheated at 200 °C 3 mm thick of materials at the bottom of the mushroom samples were machined off before applying the composition analysis. The chemical compositions were measured using Foundry-Master Pro optical emission spectrometer (OES) with testing five sparks. The average value was taken as the results, listed in Table 1.

The hot tear susceptibility (HTS) was measured by using an N-Tec Hot tear test mold [42,43], which consists of five ‘dog bone’ sections with different lengths, constrained at each end with a hot spot along their length. The HTS test mold was coated with boron nitride and preheated to 250 °C. HTS values were calculated using equation (1). Where L_i is the length indexing of the dog bone where the crack appeared and C_i is the severity indexing of the crack, and their indexing values can be found in Refs. [42,43].

Tensile testing was performed at room temperature (25 °C) according to ASTM B557 M standard using an Instron 5500 Universal Electromechanical Testing Systems equipped with Bluehill software and a ± 50 kN load cell. The elongation of samples was measured using an extensometer with the gauge length of 50 mm, and the ramp rate was selected as 1 mm/min during tensile tests. At least five samples were measured to obtain the average value of ultimate tensile strength (UTS), yield strength (YS) and elongation (El).

The X-ray diffraction (XRD) patterns of the samples were examined using the D8 Advance X-Ray Diffractometer equipped with Cu Ka radiation in the range of 10° to 90° at a scanning speed of $1^\circ/\text{min}$. The specimens for microstructural characterization were cut from the middle of F10 mm round tensile bars and prepared using a standard procedure [44]. The Keller agent (1 vol% HF, 1.5 vol % HCl, 2.5 vol% HNO₃ and 95 vol% H₂O) was used for chemical

etching. The microstructure was examined utilizing a LEO 1455VP or Zeiss SUPRA 35VP field emission scanning electron microscope

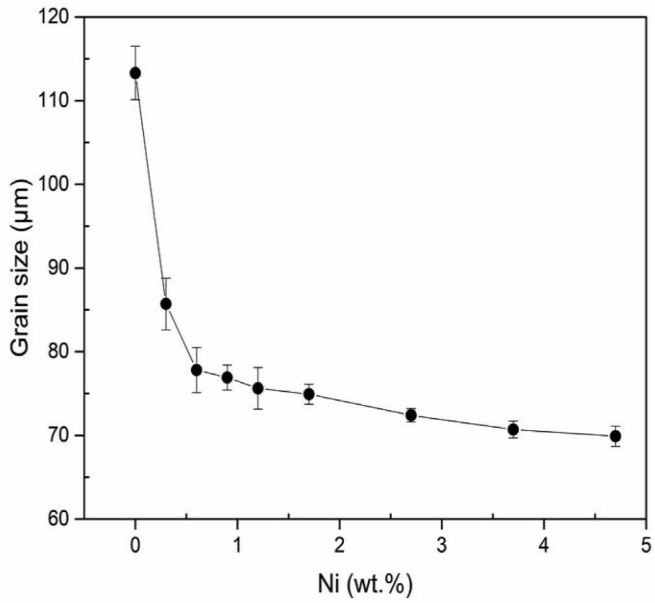


Fig.4.EffectofNicontentonthesizeof α -Algrainsintheas-castAl-Zn-Mg-Cu-Nialloys.

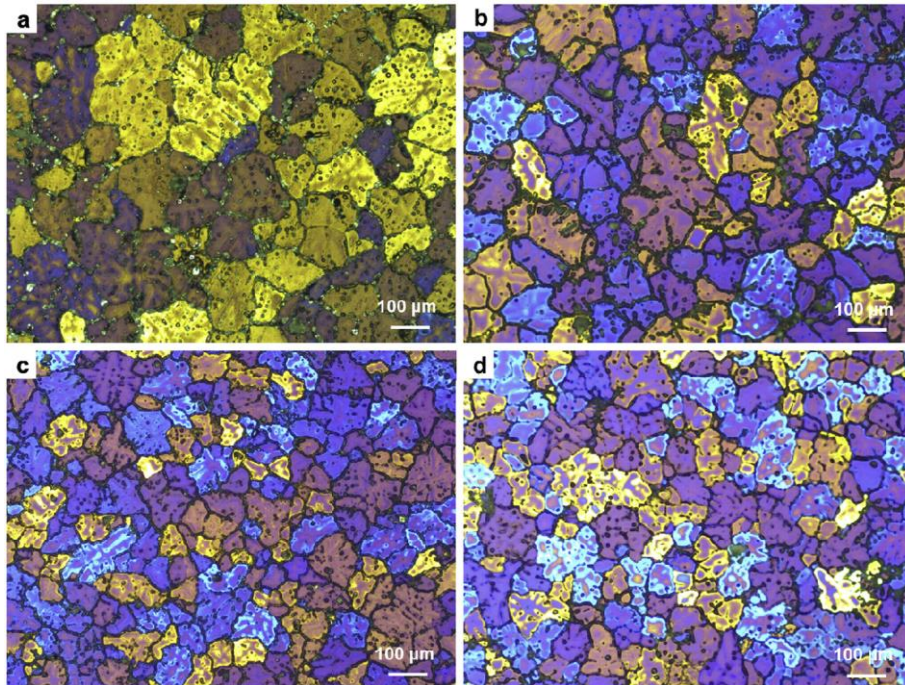


Fig. 3. Polarized images showing the as-cast microstructure of AlZnMgCuNi alloys, (a) 0Ni, (b) 0.3Ni, (c) 0.6Ni and (d) 0.9Ni.

(SEM) equipped with energy dispersive X-ray spectroscopy (EDS) working at an accelerating voltage of 20 kV. The microstructure of hot tear and tensile fracture surface was probed instantaneously by SEM operated at the secondary electron (SE) mode and backscatter electron mode (BSE). The calculation of the average grain size was conducted using Image-J software after anodized the polished surface of each sample in Barker reagent (3 vol% HBF₄ aqueous solution) operated at 20 V for 90s.

3. Results

3.1. Phase formation and microstructural evolution

Fig. 1 shows the XRD patterns of the as-cast AlZnMgCu-xNi alloys (denoted as xNi hereafter). The peaks of α -Al and MgZn₂ phases were always obvious in the samples. The Al₃Ni phase was also observed in the Ni-containing alloys and the peak intensity were increased when Ni content was increased, indicating that the amount of Al₃Ni phase was increased.

To understand the phases and microstructure of AlZnMgCu-xNi alloys, the representative backscattered SEM images showing the as-cast microstructure of AlZnMgCuNi alloys are shown in Fig. 2. All the experimental alloys included gray primary α -Al grains with equiaxed morphology and bright inter-metallic phases with different shapes including

rod-like, round and agglomerated particles. It was also noticed that the Ni-containing alloys had a much smaller α -Al grain size. The polarized images showing the microstructure of as-cast AlZnMgCuNi alloys are shown in Fig. 3 and the average size of α -Al grain are depicted in Fig. 4 as a function of Ni content. Clearly, when the Ni content was increased, the average size of α -Al grains was reduced from 113 μm (0Ni) to 77 μm (0.6Ni), and gradually stabilised at 70 μm for the increased Ni content.

The intermetallic phases and the corresponding EDS analysis results are shown in Fig. 5. It is seen that the alloy without Ni consisted of α -Al phase, η -MgZn₂ phase and S-Al₂CuMg phase under as-cast condition. From the EDS analysis, the primary α -Al phase was enriched by 2.29 at.% Zn, 2.11 at.% Mg and 0.67 at.% Cu, which is agreed with others' results [6,7,23]. The irregular η -MgZn₂ phase was distributed at grain boundaries. The round S-Al₂CuMg phase was distributed mainly in the α -Al matrix from the alloy containing increased Ni content. The EDS results shown in Fig. 5 indicated that S-Al₂CuMg phase (marked at C) contained much higher Zn (8.71 at.%) than Al matrix (2.29 at.%) had. When Ni was increased in the alloys, Al₃Ni phase was formed while other phases had no obvious change. When Ni content was less than 0.6 wt%, Al₃Ni had a morphology of fine dots or irregular strips, which were usually associated with irregular η -MgZn₂ phase in the eutectic areas, as shown in Figs. 5b and 6a. The EDS results shown in Fig. 5 confirmed that Al₃Ni phase did not contain other elements.

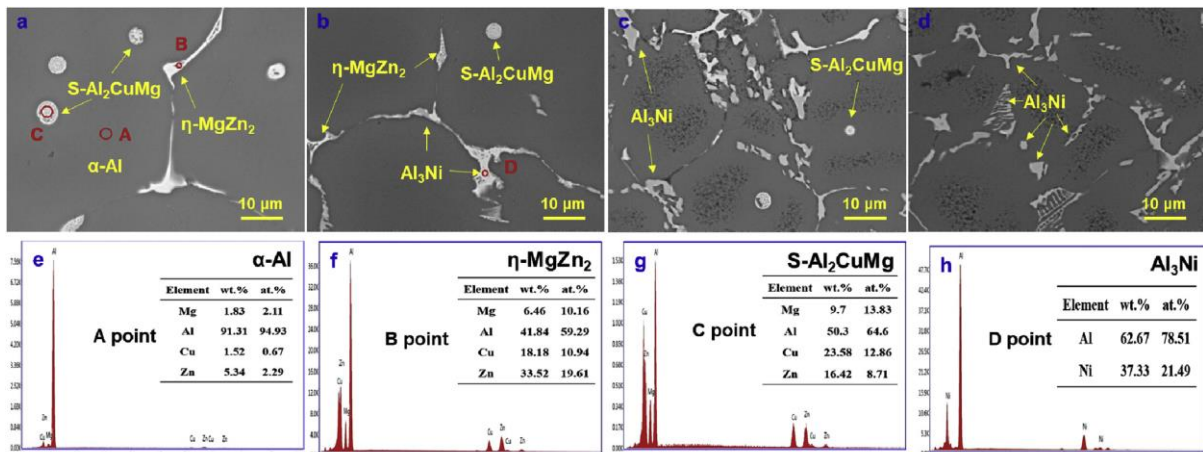


Fig. 5. Representative backscattered SEM images and the corresponding EDS analysis of different phases in the as-cast AlZnMgCuNi alloys, (a) 0Ni, (b) 0.6Ni, (c) 2.7Ni, (d) 4.7Ni, (e)A point, (f)B point, (g)C point and (h)D point.

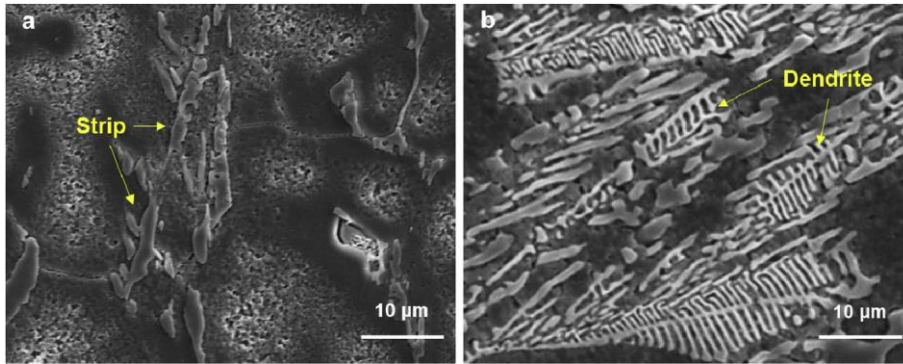


Fig. 6. Typical morphologies of eutectic Al₃Ni phase, (a) strip and (b) dendrite.

Therefore, Ni did not form phases with Zn, Mg and Cu. When Ni content was more than 0.9 wt%, the Al₃Ni phase became coarse but still showed a strip-like morphology. However, the Al₃Ni phase showed a long dendritic morphology (Fig. 6b) with a length of about 35 µm in the alloy containing 4.7 wt% Ni. This morphology has not been reported in literatures. However, the widely reported rod-like morphology of Al₃Ni phase was also not observed in the present work [45,46].

3.2. Hot tear susceptibility

Fig. 7 shows the calculated HTS indexes according to equation (1) and the castings for testing hot tear before demolding. It is clear that the HTS values were decreased as the Ni content was raised. The alloy without Ni had the highest HTS value of 17.36 and three dog bones were observed with cracks. When the Ni content was increased, the HTS values were gradually decreased from 12.37 in the alloy with 0.3 wt%Ni to 9.23 in the alloy with 0.6 wt%Ni and 5.44 in the alloy with 0.9 wt%Ni. When the Ni content was greater than 1.2 wt%, the HTS values were dropped to 0, meaning that there was no tendency to hot tear. The results clearly confirmed that Ni could effectively eliminate the formation of hot tear in the experimental AlZnMgCuNi alloys.

3.3. Mechanical properties under as-cast condition

Fig. 8 depicts the mechanical properties of the as-cast AlZnMgCuNi alloys at room temperature. It is seen three different changes for the ultimate tensile strength (UTS), yield strength (YS) and elongation (El). When Ni was added at a level from 0 to 0.6 wt%, the yield strength was increased from 201.3 MPa to 221.7 MPa, and the elongation was also increased from 0.99% to 1.86%. When Ni was increased from 0.6 to 0.9 wt%, the yield strength was increased to 231.3 MPa, but the elongation was decreased to 1.49%. When Ni content was further increased from 0.9 wt% to 3.7 wt%, the yield strength was slightly increased to 240.1 MPa, while the elongation was further reduced to 1.01%. Further increasing the Ni content to 4.7 wt%, the yield strength was increased to 262.8 MPa, while the elongation was maintained

at similar level of 1.03%.

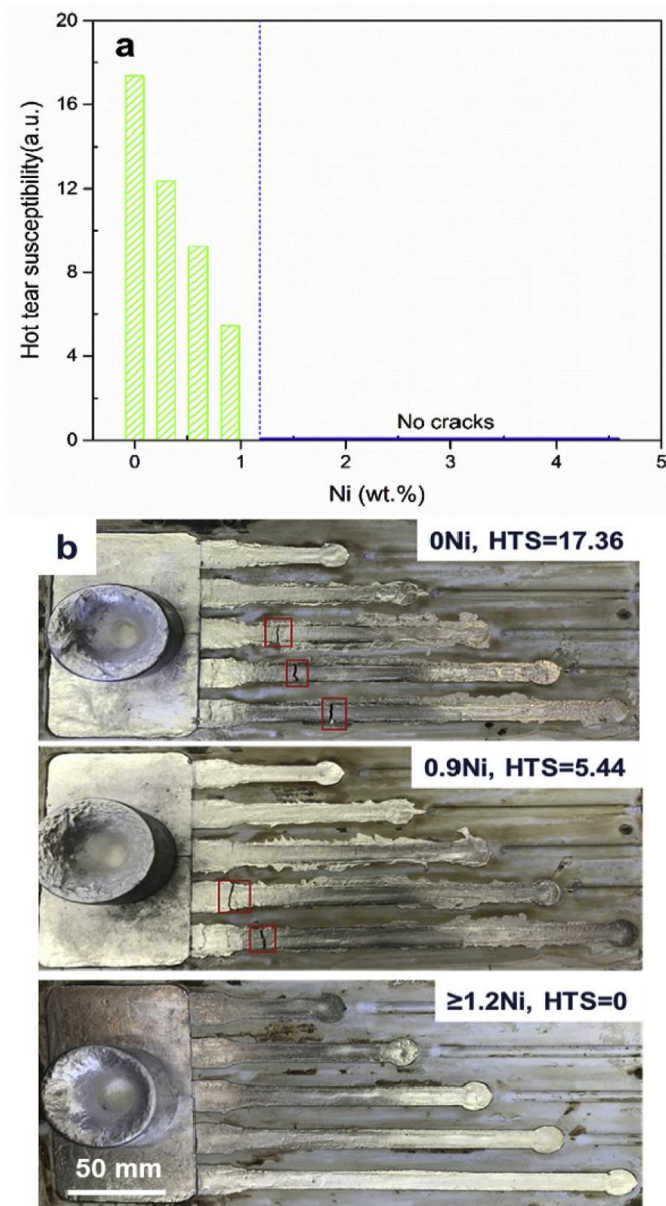


Fig.7.(a)Hottearsusceptibilityand(b)castingsfortestinghottearbefore demoldingas a function of Ni content in the Al-Zn-Mg-Cu-Ni alloy evaluated by the N-Tec Hottear test mold.

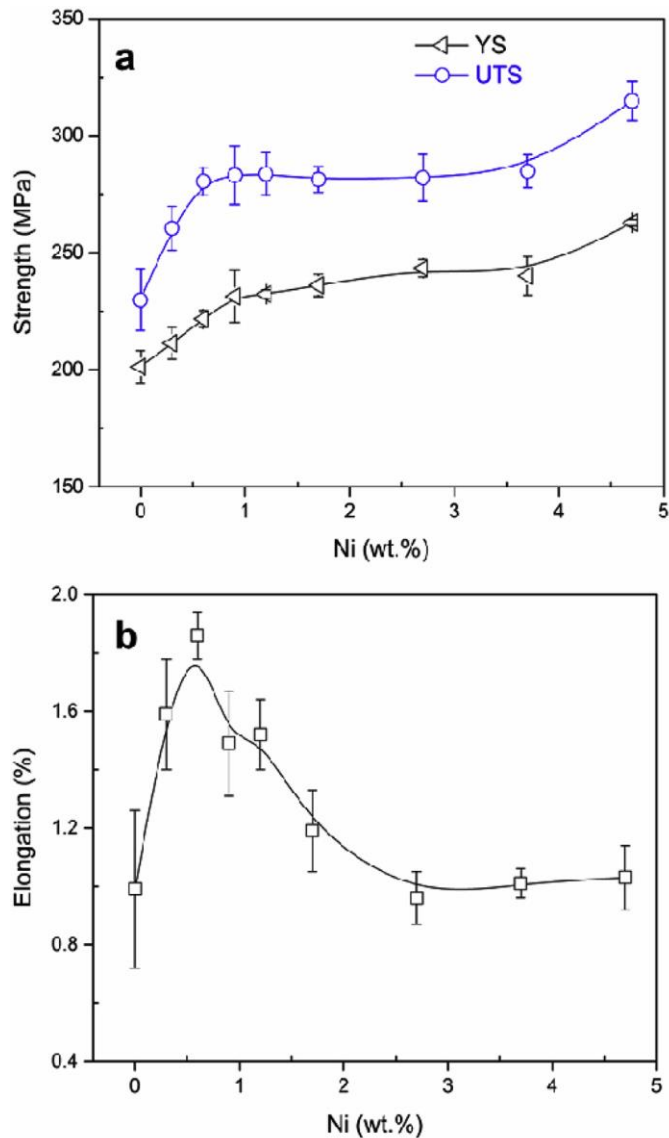


Fig.8.Mechanical properties of the as-cast Al-Zn-Mg-Cu-Ni alloys at room temperature, (a) ultimate tensile strength and yield strength, (b) elongation

4. Discussion

4.1. Solidification of Al-Zn-Mg-Cu-Ni alloys

In order to understand the effect of Ni on solidification and microstructural evolution, CALPHAD modelling of the experimental Al-Zn-Mg-Cu-Ni alloys was conducted using Pandat software. The Ti and other minor elements were not taken into account in calculation. The calculated equilibrium phase diagram of Al-Zn-Mg-Cu-Ni system on the cross section of the Al-6 wt.%Zn-1.4 wt%Mg-1.2 wt% Cu is shown in Fig. 9. Meanwhile, to have a better understanding of the solidification process of the experimental alloys, the phase fraction versus temperature of several typical experimental alloys was also calculated and shown in Fig. 10a.

According to Fig. 9, the calculated equilibrium phase can be divided into several regions according to different solidification behaviour with different Ni contents. The phase formation via liquid-solid reactions in the alloys are as follow:

- (1) when $Ni < 0.18$ wt%, only one liquid-solid reaction $L/L\beta$ -AlP occurred.
- (2) when 0.18 wt% $< Ni$ content < 4.34 wt%, $L/L\beta$ -AlP/aAlP β (a-Al β Al₃Ni)E.
- (3) when $Ni > 4.34$ wt%, $L/L\beta$ Al₃NiP/Al₃NiP β (a-Al β Al₃Ni)E with prior Al₃Ni phase.

The subscript P referred to the primary phase and E referred to the eutectics. After the liquid-solid reactions, the Al₂CuMg phase, MgZn₂ phase and Al₃Cu₅Zn₂ phase are sequentially precipitated in all the experimental alloys via solid-solid reactions. And it is also noted that the initial formation temperatures of the intermetallic phases including Al₃Ni, Al₂CuMg, MgZn₂ and Al₃Cu₅Zn₂ have a small increase with increasing the Ni content (shown in Figs. 9 and 10a).

According to Fig. 10a, it is found that although the mole fraction of MgZn₂, Al₂CuMg and Al₃Cu₅Zn₂ phases are different during solidification, but they are very close at 100 °C. While, the Al₃Ni phase fractions of different alloys always have a significant difference during the solidification process. The strengthening effect of different phases is closely related with that are from the final phase fractions in solidified alloys. There, the phase fraction (at 100 °C) in the all experimental Al-6 wt.%Zn-1.4 wt%Mg-1.2 wt% Cu alloys with different Ni contents is calculated and illustrated in Fig. 10b. It is found that the addition of Ni only increases the mole fraction of Al₃Ni phase but almost has no obvious influence on the mole fractions of MgZn₂, Al₂CuMg and Al₃Cu₅Zn₂ phase. According to the CALPHAD results in Fig. 10b, the phase fractions of Al₂CuMg and Al₃Cu₅Zn₂ are only 0.8 mol.% and 0.6 mol.%, respectively. Therefore, their effect on strengthening is limited at such a low fraction. The main strengthening phase is MgZn₂, and its phase fraction has a very small increase with the increase of Ni content, which changes from 4.02 mol.% in the Ni-free alloy to 4.16 mol.% in the alloy with

4.7 wt%Ni. Meanwhile, as the Ni content increases from 0 to 4.7 wt %, the phase fraction of Al₃Ni can reach 9.9 mol.%. As such, Al₃Ni becomes the dominant strengthening phase, resulting in a great influence on the mechanical properties of the experimental alloys.

However, it needs to emphasize that the equilibrium Al₃Cu₅Zn₂ phase was not observed in the as-cast microstructures of the experimental Al₂ZnMgCu-xNi alloys, and also the equilibrium primary Al₃Ni phase was rarely identified in the alloy containing

4.7 wt% Ni. The differences can be attributed to several factors including the variation of the actual non-equilibrium solidification in gravity casting process and the accuracy of the database used in the equilibrium phase diagram calculation. It was also reported previously that Al₃Cu₅Zn₂ was not identified in Al₂ZnMgCu based alloys for its very low fraction

and also it may be mixed with other intermetallic phases [27e30].

One interesting phenomenon was also noticed in the present work. According to the phase diagram, both the h-MgZn₂ and SeAl₂CuMg phases precipitated by solid-solid reactions from Al matrix. While, from Figs. 2 and 3, the irregular h-MgZn₂ phase was

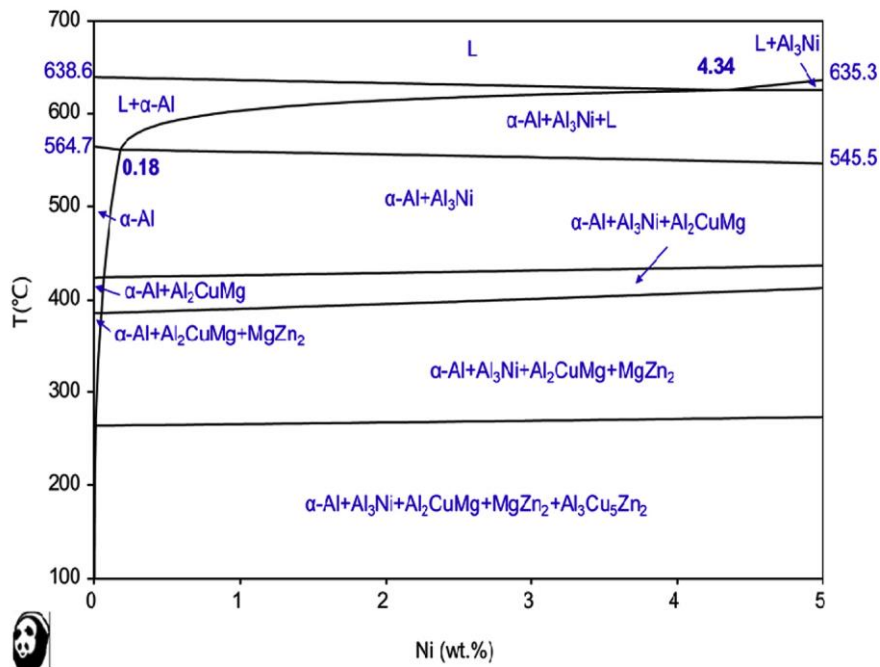


Fig. 9. The equilibrium phase diagram of AlZnMgCuNi system on the cross section of the Al-6 wt.%Zn-1.4 wt%Mg-1.2 wt% Cu calculated using Pandat software.

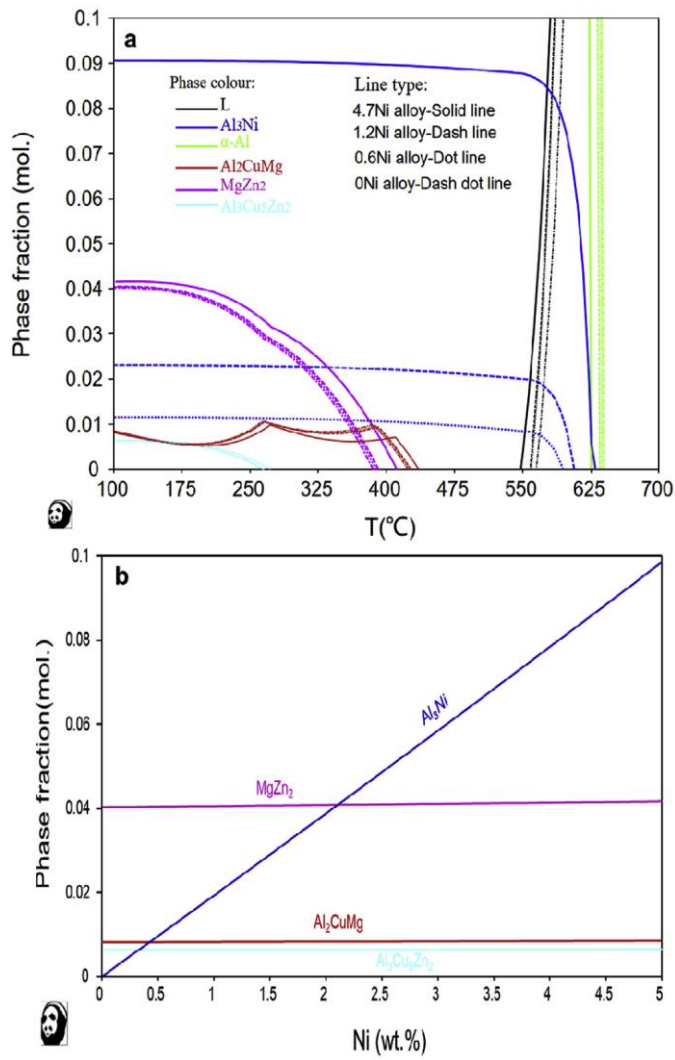


Fig. 10. Phase fraction versus temperature (100 to 700°C) (a) and (b) phase fraction (at 1000°C) of the Al-6wt.% Zn-1.4wt% Mg-1.2wt% Cu with different Ni contents calculated using Pandat software.

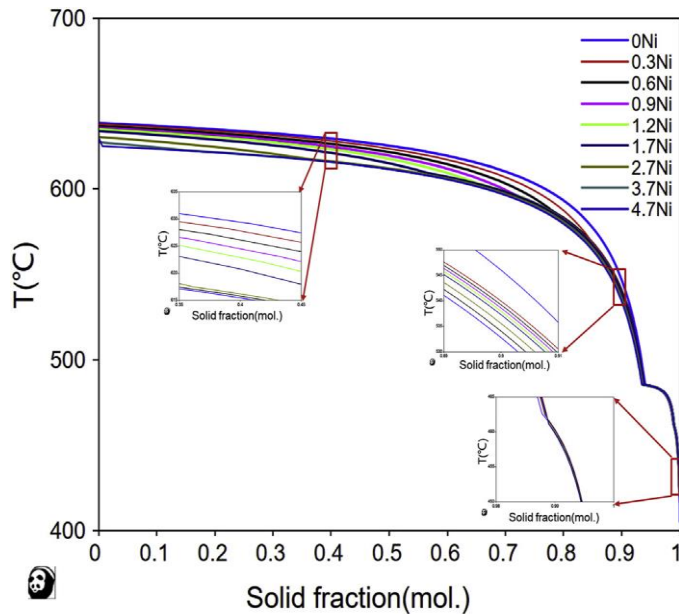


Fig.11. Calculated temperature at different solid fractions for Al-6Zn-1.4Mg-1.2Cu-xNi alloys using gPandat software.

mainly distributed at the grain boundary, but SeAl_2CuMg phase formed in the α -Al grains and had a round shape as shown in Fig. 5. Considering all atoms forming h-MgZn_2 and SeAl_2CuMg phases are from Al solid solution, the interesting difference in distribution locations of these two phases should be determined by the different mobility of solute atoms in α -Al matrix. While, a further study is still needed to describe the details. It has been reported that the diffusion coefficient of Zn, Mg and Cu in Al matrix are $4.9 \times 10^{-12} \text{ m}^2/\text{s}$, $6.2 \times 10^{-12} \text{ m}^2/\text{s}$ and $1.8 \times 10^{-12} \text{ m}^2/\text{s}$, respectively [47]. Therefore, it can be concluded that Cu hindered the long-range diffusion of precursor of SeAl_2CuMg phase and forced it precipitate in Al matrix. While, a further study is still needed to describe the detail. As for Al_3Ni phase, it precipitated from melt directly according to the phase diagram, thus would be pushed to the grain boundary areas during the following solidification process.

4.2. The mechanism of improving hot tear resistance

To understand the hot tear behaviour, experimental methods combined with hot tear criteria would be a suitable approach. Initially, the freezing range (FR) is used to evaluate the tendency to hot tear. Usually, the wider FR is, the higher tendency to hot tear is. However, many researchers have reported that this criterion is not well consistent with the actual hot tear experimental results [23,28,29,48e50]. Therefore, researchers have adopted other criteria to evaluate the HTS index. Clyne and Davies developed a HTS index based on the concept of vulnerable time period versus the time available for accommodation [48]. The HTS index was named as the cracking susceptibility coefficient (CSC) as follow:

$$\text{CSC} = \frac{1}{4} \frac{tV}{tR} \quad (2)$$

Where t_V is the time during solidification in which the casting is vulnerable to cracking, usually $t_V \propto (t_{0.99}-t_{0.9})$, and t_R is the time available for the stress relief process, usually $t_R \propto (t_{0.9}-t_{0.4})$.

Generally, there is no tendency to hot tear when the solid fraction is at 0.4-0.9, while the hot tear would occur if the solidification time is too long when the solid fraction is increased from 0.90 to 0.99. And when the solid fraction is above 0.99, the alloys will be too strong to hot tear. For the convenience of calculation, the time can be replaced by the temperature at the corresponding solid fraction [49,50] based on the consideration of the same average cooling rate, and so the TV and $CSC^* \propto (T_{0.9}-T_{0.99})/(T_{0.4}-T_{0.9})$ are usually used to evaluate the tendency to hot tear.

In order to analyze the mechanism of improving hot tear resistance of AlZnMgCu alloys with different Ni contents, the theoretical calculation of temperature at different solid fractions for all the experimental alloys was calculated, and the results are listed in Fig. 11 and Table 2. It is found that the finishing temperatures of solidification (solid fraction \propto 0.99) of all the experimental alloys are almost the same, but the temperatures with solid fraction of 0.4 and 0.9 are obviously different. It is seen that the TV and CSC^* values are gradually reduced with increasing the Ni content, which is well agreed with the experimental results. Therefore, the CSC model can well describe the effect of Ni content on the HTS of the experimental AlZnMgCuNi alloys.

To further understand the improvement in hot tear resistance, the fracture was examined in the failure alloy and the results are depicted in Figs. 12 and 13, respectively. It can be seen that the alloy without Ni had a relatively flat fracture surface (Fig. 12), and smooth α -Al grains and several dot-like intermetallics were observed. Several ruptured liquid films were also clearly observed on the fractured surface. During solidification, α -Al dendrites are usually formed as prior phase and the interconnected network is

Table 2

Calculated temperature at different solid fractions with Scheil model for Al6Zn-1.4Mg-1.2Cu-xNi alloys using Pandat software.

Ni content (wt.%)	Tl ($^{\circ}$ C)	Ts ($^{\circ}$ C)	FR ($^{\circ}$ C)	T0.4 ($^{\circ}$ C)	T0.9 ($^{\circ}$ C)	T0.99 ($^{\circ}$ C)	TV ($^{\circ}$ C)	CSC*
0	638.62	564.66	73.96	629.43	546.08	460.02	86.06	1.033
0.3	637.65	559.63	78.02	627.6	539.94	460.4	79.54	0.907
0.6	636.7	557.95	78.75	626.34	539.19	460.35	78.84	0.904
1.	635.74	556.57	79.17	625.5	538.57	460.32	78.25	0.900
2.	634.79	555.45	79.34	624.89	537.94	460.27	77.67	0.893

1. 633.53 553.85 79.68 624.57 537.27 459.69 77.58 0.889
2. 630.38 548.54 81.84 622.17 535.57 460.05 75.52 0.872
3. 627.21 544.99 82.22 620.76 534.05 459.87 74.18 0.855
4. 629.4 542.46 86.94 618.43 532.55 459.72 72.83 0.848

Note: T_l is liquidus temperature, T_s is solidus temperature, FR is freezing range, $FR \approx \frac{T_l - T_s}{T_l}$, $TV \approx \frac{T_{0.9} - T_{0.99}}{T_{0.4} - T_{0.9}}$, $CSC \approx \frac{T_{0.9} - T_{0.99}}{T_{0.4} - T_{0.9}}$ [49,50].

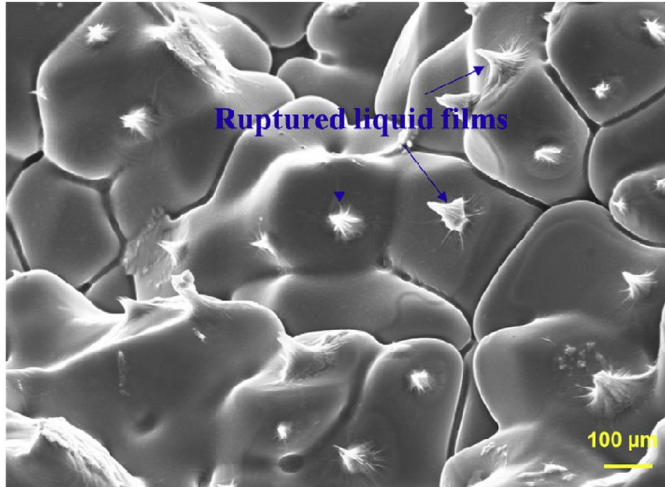


Fig.12.SEM images showing the ruptured liquid films of the hot tears surface in alloy without Ni.

formed after growth. In the same time, a small amount of liquid is still existed in the form of film in the small gap among the arm space of solid α -Al dendrites. Meanwhile, the thermal strain and $T_{0.4}, T_{0.9}$ and $T_{0.99}$ are the temperature of 0.4, 0.9 and 0.99 solid fraction, respectively, stress formed during solidification also accumulated and played on the liquid film, making the liquid film become thinner and thinner.

Once the thermal stress is larger than the strength of remaining liquid film, the liquid film is ruptured and hot tear is initiated. From the diagram shown in Fig. 9, all the melt is precipitated as primary α -Al phase. In other words, there was no eutectic melt exist between α -Al phase therefore can't refill the initial cracks. As the result, the initial tear would propagate quickly and induced the hot tear finally.

From Fig. 13, it can be found that the Ni-containing alloys possessed a bumpy fractured surface with numerous bright dendritic intermetallic phases among the primary α -Al dendrites (Fig. 13 b, c, d), which were identified as the Al_3Ni phase. When the Ni content is climbed from 0.3 wt% to 0.9 wt%, the mole fraction of eutectic Al_3Ni phase is obviously increased. According to the CALPHAD results, Al_3Ni is formed via a eutectic reaction $L/(\alpha-Al + Al_3Ni)_E$ at the last stage of solidification after the precipitation of primary α -Al via the reaction $L/L + \alpha-Al$. Therefore, the increased Al_3Ni phase on the fractured surface means that

the remnant liquid among the solid primary α -Al dendrites becomes more and more. In this case, the initial tears would be refilled by the sufficient remaining eutectic liquid. Thus, the HTS significantly is reduced with further increasing Ni content due to the increment in the amount of eutectic liquid. In other words, the higher the content of remaining liquid, the less likely the hot tear is initiated, due to large amount of liquid available to block the propagation of the crack.

Therefore, the decrease of TV and CSC*, and the increase of eutectic Al_3Ni phase content are the main reasons for the improvement in the hot tear resistance of the experimental alloys.

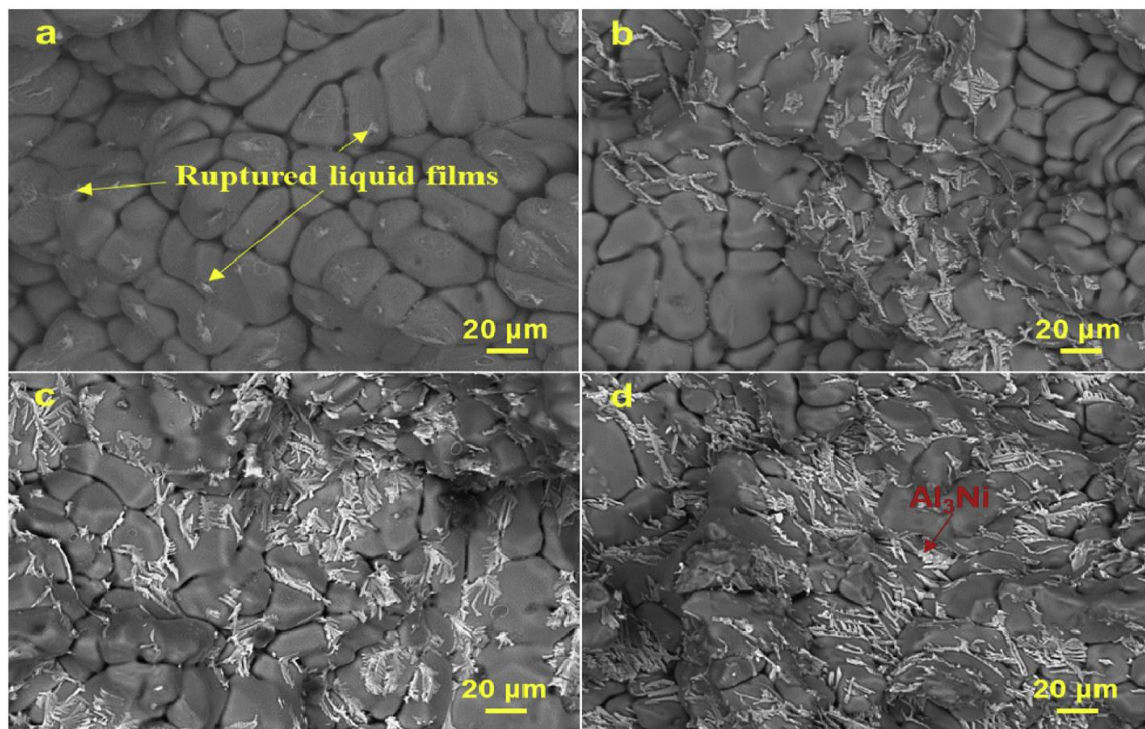


Fig. 13. Backscatter SEM fractography images showing the hot tear surface of AlZnMgCuNi alloys, (a) 0Ni, (b) 0.3Ni, (c) 0.6Ni and (d) 0.9Ni.

4.3. Fractured surface and the microstructure-properties relationship

The mechanical properties of the experimental alloys are closely related to their as-cast microstructures, including matrix, strengthening phases as well as defects. To further investigate the underlying mechanism of the mechanical properties variation in experimental alloys, the fractured surfaces after tensile testing at room temperature were analyzed and the results are exhibited in Fig. 14.

From Fig. 14 a and b, it is found that many separated α -Al grain boundaries appeared on the fractured surface of the Ni-free alloy. It means that there exists a lots of initial shrinkage

porosities between α -Al grains, which can be also observed from Fig. 2. As discussed above, the shrinkage porosity is induced by the sufficient remaining eutectic liquid, and then results in a high hot tear tendency. For the mechanical properties, the shrinkage porosity also plays a negative role. During tensile test, the porosities would be the initial part of crack and result in low strength and elongation simultaneously. From Fig. 14b, it can be found the dimples on the fracture surface of the Ni-free alloy is small and shadow, which is the feature of unfavored ductility.

In the Ni-containing alloys, Al₃Ni phase is formed and acted as strengthening phase due to its high values of Young's modulus (116e152 GPa), hardness (HV0.01 $\frac{1}{4}$ 5130 MPa) and tensile strength (2160 MPa) [35,36], while the rigid Al₃Ni compound is substantially inert in the alloy and acts as hard pinning points restraining dislocation motion which can affect the strength and elongation of Al alloys. Meanwhile, according to the discussion above, the amount of eutectic melt would increase, thus the initial shrinkage porosity can be refilled and healed. Therefore, the amount of shrinkage porosities in castings decreased obviously. As the result, the separated α -Al grain boundaries on the fractured surface of Ni-containing alloys become less and are even disappeared, as shown in Fig. 14 c-h. On the other hand, Ni addition (0e0.6 wt%) also refines α -Al grains continually (Fig. 4). The improvements on shrinkage defects and grain size could increase both the strength and the elongation simultaneously. It should be mentioned that although the strengthening phase Al₃Ni has a deleterious effect on elongation, the elongation increment from the defect improvement and refinement is more obvious, therefore both the elongation and strength could be improved as Ni content is increased from 0 to 0.6 wt%, as shown in Fig. 8.

As Ni content further increased from 0.6 wt% to 2.7 wt%, it still has a small grain refinement (Figs. 3 and 4), and the hard Al₃Ni phase content is increased continually. The combined effect of refinement and Al₃Ni phase hardening result in the improvement of strength and the decrease of elongation. And when the Ni content changed from 2.7 wt% to 4.7 wt%, the elongation is kept at the same level with the increment of strength, which may be caused by the shape variation and aggregation of the strengthening Al₃Ni phase (shown in Figs. 2e5), and it needs to point out that the dendritic Al₃Ni phases can link together to form integral hard points leading to great improvement in strength of the alloy with wt%Ni.

Conclusions

In the present paper, the effects of Ni content on the phase formation, microstructural evolution, hot tear susceptibility and mechanical properties of the Al-6 wt.% Zn-1.4 wt%Mg-1.2 wt%Cu alloy produced by gravity casting were investigated, and the main results

were concluded as follows:

(1) In the experimental AlZnMgCuNi alloys under as-cast condition, there are four phases including α -Al matrix, hMgZn₂, SeAl₂CuMg and Al₃Ni phases. The round SeAl₂CuMg phase is distributed in α -Al matrix, and the other intermetallic phases are mainly at grain boundaries. The addition of Ni increases the phase fraction of Al₃Ni but has no effect on the phase formation of h-MgZn₂ and SeAl₂CuMg.

(2) The addition of Ni decreases TV and CSC*. Therefore, it is favorable for the improvement in hot tear resistance. When Ni content is greater than 1.2 wt%, the experimental alloys have no tendency to hot tear.

(3) The strength and elongation of experimental AlZnMgCuNi alloys are improved simultaneously when Ni addition is less than 0.6 wt% due to the effects of Ni on healing initial tears, refinement, forming Al₃Ni phase for strengthening. While, when Ni content is more than 0.6 wt%, the strength is increased but the elongation is decreased.

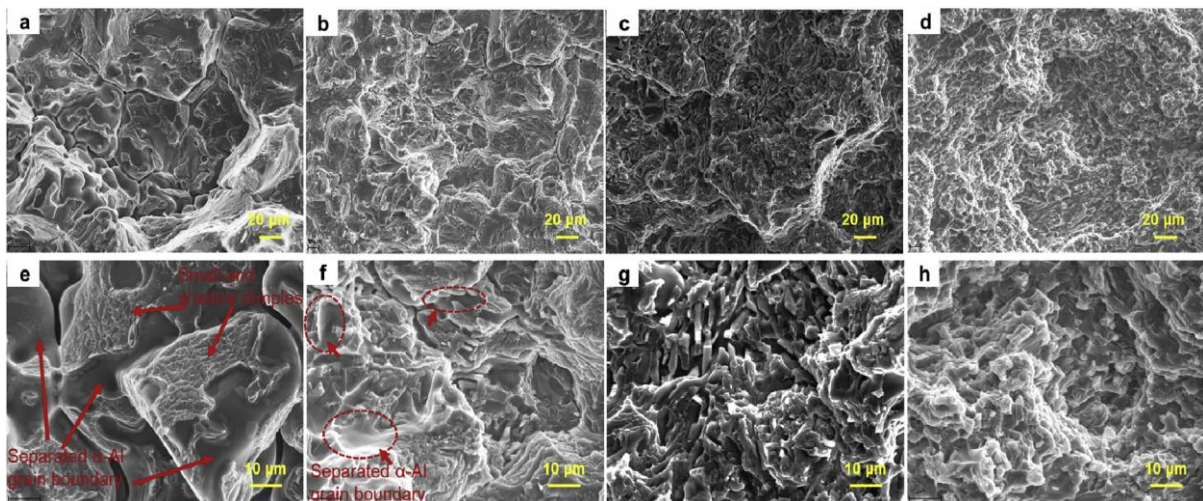


Fig. 14. Typical SEM images showing fractured surface of the as-cast AlZnMgCuNi alloys after tensile test, (a,e)0Ni, (b,f)0.6Ni, (c,g)1.7Ni and (d,h)4.7Ni.

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