The growth restriction effect of TiCN nanoparticles on Al-Cu-Zr alloys via ultrasonic treatment

Yiwang Jia\textsuperscript{a,\*}, Dongfu Song\textsuperscript{a,\*}, Nan Zhou\textsuperscript{a}, Kaihong Zheng\textsuperscript{a}, Yanan Fu\textsuperscript{c}, Da Shu\textsuperscript{d}

\textsuperscript{a} Guangdong Provincial Key Laboratory of Metal Toughening Technology and Application, Institute of New Materials, Guangdong Academy of Sciences, Guangzhou 510650, China
\textsuperscript{b} National Engineering Research Center of Near-net-shape Forming for Metallic Materials, South China University of Technology, Guangzhou 510641, China
\textsuperscript{c} Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, CAS, Shanghai 201204, China
\textsuperscript{d} Shanghai Key Lab of Advanced High-temperature Materials and Precision Forming, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

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\textbf{A B S T R A C T}

Ex situ and in situ synchrotron X-radiography study on Al-Cu-Zr alloys with addition of Al-5Ti-1B and TiCN nanoparticles (TiCN\textsubscript{np}) were carried out at different cooling rates. Al-Zr alloy can be effectively refined by TiCN\textsubscript{np} via Ultrasonic treatment as compared with Al-5Ti-1B which has Zr poisoning effect. The influence of cooling rate on the nucleation and growth of grains have been studied quantitatively. The results show that the grain size was decreased and the growth rate was increased with the increasing of cooling rate. At the same cooling rate, the grain size with addition of 0.5\% TiCN\textsubscript{np} was smaller than that with the same addition of Al-5Ti-1B. The blocking factor \( f \) of TiCN\textsubscript{np} decreases with increasing cooling rate. Based on the free growth model, a new numerical model considering the growth restriction effect of nanoparticles was established. The growth of grain was inhibited by the combining effect of solute and nanoparticles. The growth rate of grain is reduced due to part of the solid/liquid interface coated by nanoparticles. The blocking factor \( f \) is linearly decreased with the coverage ratio \( \omega \) which is proportional to the critical grain radius. The grain size decreases with increasing cooling rate and decreasing \( f \). This study is especially beneficial for Al alloys that have poisoning phenomenon inoculated by traditional refiner.

\section{1. Introduction}

High-strength aluminum alloys containing trace amounts of Zr element are widely used in the aerospace field [1]. The addition of Zr element can form a fine and dispersed Al\textsubscript{3}Zr phase [2], which can reduce the quenching sensitivity of the Al alloy, inhibit recrystallization during heat treatment, increase the dislocation density, and improve the mechanical properties of the Al alloy [3]. The Zr-containing aluminum alloy can also effectively retain the small-angle grain boundaries obtained by processing deformation and improve the stress corrosion resistance of the Al alloy [4]. Therefore, adding a small amount of Zr element can comprehensively improve the strength, toughness and corrosion resistance of the Al alloy [5].

However, traditional grain refiners such as Al-Ti-B [6] or Al-Ti-C [7] have poisoning phenomenon when refining Zr-containing aluminum alloys [8]. At present, The Zr poisoning theory is divided into two categories. One is that Zr deteriorates the nucleation potency of the nucleation sites [6]. The other is that Zr depletes the alloying elements reducing the restriction effect of grain growth [9,10]. The Synchrotron radiation X-radiography research [11] found that the degree of nucleation undercooling and the grain growth velocity increased with addition of Zr. Zr poisoning is caused by the simultaneous increase in solute suppression and the average interparticle spacing of the most potent TiB\textsubscript{2} particles. Thus it is necessary to find a new refinement method for Zr-containing Al alloy.

Recent studies have shown that commercial purity aluminum (CPAl) [12], Al-Cu [13] and Al-Si alloys [14–16] can be effectively refined by a small amount of TiCN nanoparticles (TiCN\textsubscript{np}) which were dispersed into the matrix by high-energy ultrasound treatment. Chen et al. [17] added TiC\textsubscript{0.2}N\textsubscript{0.8} nanoparticles with a volume fraction of 2\% to the Al-20Bi alloy which were dispersed in the matrix after ultrasonic treatment. As a result, the size of the Bi phase was reduced from 821 \( \mu \text{m} \) to 7.5 \( \mu \text{m} \). Levi et al. [18] found that TiCN\textsubscript{np} can refine the Mg\textsubscript{3}Si phase in Al-Mg-Si alloy...
alloys and proposed an irreversible adsorption model. Adding 2% volume fraction of TiCN nanoparticles can refine the grain size of CPAl to 138 μm [19], and the hardness, strength and plasticity of the material have been greatly improved [20].

The effects of TiCN nanoparticles added to Al melts have opened a new field of grain refinement. On the one hand, TiCN nanoparticles are a potency nucleation site for α-Al which has an orientation relationship of (111)Al // (111)NP, (001)Al // (001)NP analyzed by high resolution transmission electron microscopy [12]. On the other hand, nanoparticles are attached to the surface of the crystal grains in a very short time [17], which hinders the migration of solute elements at the interface. As the crystal grows, the nanoparticles are moved and accumulated on the solid/liquid (S/L) interface, reducing the growth of crystal grains. This allows the melt to form a large degree of undercooling, thereby inducing more nucleation behavior.

However, the hypothesis that TiCN nanoparticles wrap the surface of crystal grains to inhibit growth is only an post-mortem research. There is a lack of real-time solidification process research, and the accuracy of the theoretical model needs to be further verified. The in situ synchrotron radiation observation of the solidification of metals has a history of more than 20 years [22–24]. With the increase of the energy of the light source and the advancement of the equipment, it has better spatial and temporal resolution. At the same time, image processing methods for imaging experimental data are also advancing with the times [25], which can quantitatively calculate nucleation rate [26,27], nucleation undercooling [28], solute concentration [29], solid phase thickness [30] and nanoparticles on dendritic grain growth [31,32]. Al-Cu alloys added with TiC nanoparticles were investigated by in situ X-radiography [33] which found that the TiC nanoparticles promoted heterogeneous nucleation of α-Al. The machine learning algorithm is applied to the processing of experimental data, which can fully track the nucleation and growth process of all crystal grains [34].

As Al alloy containing Zr cannot be refined by traditional grain refiner, the aim is to find a new refinement method by nanoparticles and reveal the mechanism. In the current study, ex situ and in situ synchrotron X-ray radiography technique were adopted to research the growth restriction effect of TiCN nanoparticles on Al-Zr alloys. The influence of cooling rate on the nucleation and growth of grains of Al-Cu-Zr alloys with addition of Al-Ti-B and TiCN nanoparticles have been quantitatively studied. With the blocking factor f obtained from the in situ experiments, a new numerical model considering the growth restriction effect of nanoparticle has been established based on free growth model.

2. Experimental procedure

2.1. Raw materials

The raw materials are CPAl (99.6%, all compositions are in weight percent unless specified), high purity Cu (99.9%), Al-10Zr (99.5%) master alloy and TiC0.5N0.5 nanoparticles (99%). The size distribution of TiCN nanoparticles was determined from image analysis of scanning electron micrographs. More than 4000 TiCN nanoparticles were measured for obtaining the size distribution [35]. It was well fitted by a lognormal function as shown in Fig. 1(a).

\[ N(d) = \frac{N_0 \cdot \Delta d}{\sigma d \sqrt{2\pi}} \exp \left( -\frac{(\ln(d) - \ln(d_0))^2}{2\sigma^2} \right) \]  

Where \( N(d) \) is the number of nanoparticles with a diameter between \( d \) and \( d + \Delta d \). \( N_0 \) is the total number of TiCN nanoparticles \( d_0 \) is the geometric mean value of the distribution, which is 78.2 nm, and \( \sigma \) is the geometric standard deviation, which is 0.444.

2.2. Grain refinement tests

Grain refinement experiments were carried out on Al-0.2Zr alloy with addition of 0.2% Al-Ti-B master alloy (99.5%) and 0.5% TiCN nanoparticles using the Reynolds standard golf T-mold method [35]. CPAl and Al-Zr alloy which placed in an alumina crucible melted in a resistance furnace, while Ar gas is introduced into the crucible to reduce oxidation. After holding at 750 °C for 10 min, TiCN nanoparticles were preheated at 300 °C for 2 h and wrapped in Al foil was added into the melt. The ultrasonic treatment promotes the dispersion of TiCN nanoparticles as shown in Fig. 1(c). The ultrasonic frequency is 20KHz, power is 1500 W, and the time is 5 min. The melt was cast into a Reynolds standard golf T-mold after ultrasonic treatment.

After the sample was polished and corroded by Keller reagent, the microstructure of the sample was observed by high resolution transmission electron microscopy (HRTEM) and energy dispersive spectrometry (EDS) to observe the microstructure of the sample.
The setup of X-radiography experiment.

Table 1

| Energy (keV) | Pixel size (μm) | Temporal resolution (Hz) | FOV (mm²) |
|--------------|-----------------|--------------------------|-----------|
| 18           | 3.25            | 1                        | 4.225 × 4.225 |

Fig. 1. (a) Size distribution of TiCN\textsubscript{np}; (b) SEM microstructure of TiCN\textsubscript{np}; (c) The illustration of ultrasonic treatment.

Fig. 2(c) and 2(d). More than 10 microstructure pictures are measured by equivalent area diameter method to obtain the average grain size of each sample. The average grain size of Al-0.22Zr alloy is 682 μm with addition of 0.5% Al-5Ti-1B and 97 μm with addition of 0.5% TiCN\textsubscript{np}. This suggests that TiCN\textsubscript{np} can effectively overcome the effect of Zr poisoning.

The SEM results of Al-0.2Zr alloy with addition of 0.5% TiCN\textsubscript{np} show a high solute concentration appears in red. As the cooling rate increases, more solute is expelled into the liquid phase. Thus the liquid phase with a high solute concentration appears in red. As the cooling rate increases, more grains appear in the FOV. The grains number in the FOV is 174, 339, 282, 258, 240 and 218 μm respectively.

3.2. X-radiography results

Fig. 4 shows the image sequences of in situ X-radiography experiments of Al-13Cu-0.22Zr alloys with addition of 0.5% Al-Ti-B at different cooling rates (0.2, 0.3, 0.5, 1 and 1.5 K/s). The origin time set to be the first appearance of the grain. 

Where V is the volume of the FOV, and N is the total grains in the FOV.

In order to investigate the effect of TiCN\textsubscript{np} on the growth of grains, two grains were chosen from each X-radiography experiments for analysis. The criteria for selection were that the grain was stationary in favor of statistics and initially isolated from the surrounding grains. In
addition, the influence of gravity can be ignored. The grain growth is nearly spherical as shown in Fig. 4 and Fig. 5. Thus the grain growth rate can be calculated by the variation in the radius with time. The time evolution of radii with addition of Al-5Ti-1B and TiCN_{np} at different cooling rates is shown in Fig. 6. Due to the spatial resolution limitation, the grains had grown to about 20 μm in diameter by the time they

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**Fig. 2.** Macrographs and optical microstructures of Al-0.2Zr alloy solidified in the T-mold. (a)&(c) Addition of 0.5% Al-5Ti-1B; (b)&(d) Addition of 0.5% TiCN_{np}.

**Fig. 3.** (a)&(d) SEM micrographs of Al-0.2Zr refined by 0.5% TiCN_{np}; (b) Al mapping; (c) Ti mapping; (e) Spectrum 1; (f) Atomic percent of spectrum 1.
became measurable and the error was about ± 10 μm.

The main purpose of this paper is to study the blocking effect of nanoparticle. At the same cooling rate, the rate of heat released to the outside is the same. As the DSC curve shown in Fig. 7, the temperature at the beginning of the solidification of Al-13Cu-0.2Zr alloy with addition of Al-5Ti-1B and TiCN$_{np}$ is 622.89°C and 623.02°C respectively. The difference is only 0.13°C. Thus we assume the driving force for the grain growth is the same with addition of Al-5Ti-1B and TiCN$_{np}$. As the free Ti in the melt is only 0.014 wt% with addition of 0.5% Al-5Ti-1B.

Comparing with the $Q$ of Cu which is 38 K, the $Q$ of Ti is less than 1 K. So we assume the growth restriction effect by the solute is the same with addition of Al-5Ti-1B and TiCN$_{np}$. With addition of 0.5 wt% Al-5Ti-1B, the volume percent of TiB$_2$ in the melt is less than 0.01%. As a comparison, the volume percent of TiCN$_{np}$ is 0.164%. Thus the blocking of S/L interface growth by TiB$_2$ can be ignored. The main difference is the presence of nanoparticles ahead the S/L interface with addition of TiCN$_{np}$.

So the blocking factor $f$ by TiCN$_{np}$ can be defined by the growth rate
$v_{np}$ with addition of TiCN$_{np}$ dividing the growth rate $v_{gr}$ with addition of Al-5Ti-1B, i.e., $f = v_{np}/v_{gr}$. As shown in Table 2, the average growth rates of radius at cooling rates of 0.2, 0.3, 0.5, 1, 1.5 K/s are 8.3, 11.03, 13.78, 15.44, 17.41 μm/s with addition of Al-Ti-B and 4.55, 6.79, 9.05, 11.07, 13.2 μm/s with addition of TiCN$_{np}$ respectively (Table 2). Thus, $f$ is 0.547, 0.615, 0.657, 0.717 and 0.758 at cooling rates of 0.2, 0.3, 0.5, 1 and 1.5 K/s respectively. This indicates that the blocking factor of TiCN$_{np}$ decreases with increasing of cooling rate.

4. Modeling of growth restriction effect of nanoparticle

Wang et al. [12] studied the Al/TiCN$_{np}$ interface using HRTEM. There had good lattice matching between Al matrix and TiCN$_{np}$. The orientation relationship is (TT1)$_{Al}$[0 1 1]$_{Al}$//(TT1)$_{np}$[0 1 1]$_{np}$ with a lattice misfit of 5.5%. If the misfit is less than 10%, an orientation relationship exists according to the edge to edge model [39]. This indicates that TiCN$_{np}$ is high potency nucleation sites for Al. The adsorption model
may be appropriate with such potent nucleation\cite{40}. So we assume that the free growth condition determines the nucleation of Al on TiCN$_{np}$\cite{41}. The nucleation undercooling $\Delta T_{fg}$ on a TiCN nanoparticle with diameter $d$ is:

$$\Delta T_{fg} = \frac{4\sigma}{\Delta S_v d}$$

Where $\sigma = 158 \times 10^{-3}$ J/m$^2$ is the S/L interfacial energy, and $\Delta S_v = 1.112 \times 10^6$ J/(Km$^3$) \cite{41} is the entropy of fusion per unit volume. We assume that the melt is spatially isothermal for this small amount of alloy.

Growth restriction factor $Q$ by the solute is defined by:

$$Q = mC_0(k - 1)$$

Where $m$ is the liquidus slope, $k$ is the equilibrium partition coefficient, $C_0$ is the solute concentration. \cite{42} Those parameters of Cu are listed in Table 3, so the $Q$ is 38 K in this study. The influence of Zr to $Q$ is neglected. The free Ti in the melt is only 0.014 wt% with addition of

![Fig. 6. Time evolution of the radius of grains at different cooling rates.](image)
The parameters of Cu used in the calculation

| Element | m (K wt.%)^3[43] | k [43] | C_0 (wt.%) | Q (K) |
|---------|-----------------|--------|------------|-------|
| Cu      | -3.4            | 0.14   | 13         | 38    |

Table 3

0.5% Al-5Ti-1B. Thus the growth restriction factor Q and the influence to solute diffusion coefficient D_s by Ti can be neglected.

The growth rate of a spherical grain can be obtained by differentiating Eq. [6] with respect to time:

\[
\frac{dr}{dt} = \frac{2r^2}{3} D_s
\]

The spherical radius r has the following relationship with the time t in isothermal melt [45,46]:

\[
r = \lambda_s (D_t t)^{1/2}
\]

Where D_s = 4.65 \times 10^{-9} \text{ m}^2/\text{s} is the solute diffusion coefficient of Cu in the Aluminum melt [41]. \lambda_s can be obtained by:

\[
\lambda_s = \left( \frac{-S}{2k} \right) + \left( \frac{S^2}{4k} - S \right)^{1/2}
\]

S is given by [47]:

\[
S = \frac{2\Delta T_s}{(k-1)\Delta T_f + Q}
\]

The growth rate \(v_p\) of a spherical grain can be obtained by differentiating Eq. [6] with respect to time:

\[
v_p = \frac{dr}{dt} = \frac{2r^2}{3} D_s
\]

In the conventional grain refinement, the growth restriction is only by solute. However, the growth of grain is also restricted by the nanoparticles after the addition of TiCN_{np}. As there have nanoparticles in the melt, the interface migration could be pinned by TiCN_{np}. So we should consider the blocking factor \(f\) by TiCN_{np}. The blocking factor \(f\) defined by:

\[
f = \frac{v_p}{v_p^*}
\]

Where \(v_p\) is the growth rate of grain with addition of TiCN_{np} and \(v_p^*\) is that without TiCN_{np}. \(f\) at different cooling rates had been obtained from in situ X-radiography experiments as shown in Table 2.

Thus the growth rate \(v_p\) with addition of TiCN_{np} can be obtained by:

\[
v_p = v_p^* f = \frac{1}{2} \sqrt{\frac{2}{\pi}} \frac{D_s}{r}
\]

The numerical calculation is performed by dividing time into a series of steps. The cooling rate is \(R\), the time step duration \(\Delta t\) is set to be 0.001 s. Before the beginning of solidification:

\[
T_{n-1} = T_n - R^* \Delta t
\]

As the temperature decreases, nucleation begins on the largest TiCN_{np} participating in nucleation decreases from \(d_n\) to \(d_{n+1}\). The number \(N_i\) of nanoparticles participating in nucleation in the nth time interval is:

\[
N_i = N_i^* \left( d_n - d_{n+1} \right)
\]

When one grain which is nucleated in the nth time interval grows to the nth time interval, the radius \(r_{(n)}\) is obtained by:

\[
r_{(n+1)} = r_{(n)} + v_{np}(n-1) A \Delta t (1 \leq i \leq n)
\]

In the nth time increment, the latent heat \(q_{(n)}\) which is released by the grains nucleated in the nth increment is:

\[
q_{(n)} = N_i^* 4\pi r_{(n-1)}^2 \left[ r_{(n)} - r_{(n-1)} \right] \Delta H_f (1 \leq i \leq n)
\]

where \(\Delta H_f = 9.5 \times 10^8 \text{ J/m}^3\) is the latent heat of solidification per unit volume. [41]

The whole latent heat \(Q_f\) which is released in the nth time increment is:

\[
Q_f = \sum_{i=1}^{N_i} q_{(i)}
\]

The melt temperature in the next time increment is then given by:

\[
T_{n+1} = T_n - R^* \Delta t + \frac{Q_f}{C_{p_f}}
\]

where \(C_{p_f} = 2.58 \times 10^6 \text{ J/(Km}^3)\) is the specific heat of the melt per unit volume.[41]

When the latent heat released equals to the external heat extraction, the melt temperature stops decreasing and further grain nucleation is stifled. Then no new nanoparticles participate in nucleation and the calculation is over. The total number \(N\) of grains is all of the nanoparticles participating in the nucleation.[48]

\[
N = \sum_{i=1}^{N_i} N_i
\]

The average diameter \(d\) of grains can be calculated by:

\[
d = \frac{0.5}{N} \sqrt{\frac{V}{N_i}}
\]

The calculations were implemented in Matlab. The grain size at different cooling rates was plotted in Fig. 8. The calculation considering blocking factor \(f\) by TiCN_{np} is well consistent with the experimental results. Without considering the blocking factor \(f\), the calculated grain sizes are larger than the experimental results. The growth rate of the grain will be faster without the blocking of TiCN_{np}. This results in the faster releasing of latent heat and lower undercooling at recalescence.
Thus less nucleation has been activated and the grain size will be coarser.

5. Discussion

Engulfment of TiCN\textsubscript{np} by S/L interface happens above a critical interface velocity that is inversely proportional to particle diameter\cite{49}. The critical velocity would be $1.4 \times 10^3$ m/s for the TiCN\textsubscript{np} diameter of 78.2 nm in this work. As shown in our in situ X-radiography results, the S/L interface velocity is $\sim 10 \times 10^{-6}$ m/s, which is four orders of magnitude lower than the critical velocity. This indicates that the TiCN\textsubscript{np} would be pushed by the interface. As analyzed by Greer\cite{21}, Brownian motion of TiCN\textsubscript{np} is not significant in bring them to the S/L interface in the Al melt. The nanoparticles cannot be spontaneously absorbed by the interface. So we also assume that the nanoparticles are pushed by the growing grain and accumulate at the interface when they meet as shown in Fig. 9. Part of the interface may be coated by nanoparticles, but not the entire interface is wrapped with a layer of nanoparticles. The advancing speed of S/L interface would be retarded by nanoparticles, but not the entire interface is wrapped with a layer of nanoparticles. The coverage ratio $\omega$ of TiCN\textsubscript{np} on the growing grains surface can be calculated by:

$$\omega = \frac{\pi r_g^2 \rho \omega (\frac{1}{2})^2}{4 \pi r_g^2} = \frac{r_g^* P_v}{2d}$$

Where $r_g$ is the radius of growing grain, $P_v$ is the volume percent and $d$ is the average diameter of TiCN\textsubscript{np}. As $P_v$ and $d$ are constant at the same addition level of TiCN\textsubscript{np}, the coverage ratio $\omega$ is proportional to the critical grain radius. The critical grain radius is the radius when recalescence happened. After recalescence, the melt temperature stops decreasing. There is no new nucleation occurred in the melt and the number density of the grains will not increase.

Taking the weight percent of Ti is 0.26% analyzed by ICP in this study and the density of TiC\textsubscript{np} to be 4775 kg/m\textsuperscript{3}, we calculate that the weight percent of TiC\textsubscript{0.5N0.5} is 0.33 wt% and the volume percent $P_v$ is 0.164 vol%. The average diameter of TiCN\textsubscript{np} is 78.2 nm in this study. Thus:

$$\omega = \frac{r_g^* P_v}{2d} = 1.05% \times r_g(\mu\text{m})$$

At different cooling rates, the critical radius can be calculated from the model as the red line shown in Fig. 10. Then we can determine the coverage ratio of TiCN\textsubscript{np} at different cooling rates from Eq. [20]. At high cooling rate, there are more grains resulting in smaller critical radius. So the coverage ratio $\omega$ of TiCN\textsubscript{np} decreases with cooling rate. The coverage ratio $\omega$ and blocking factor $f$ of TiCN\textsubscript{np} are well fitted by a linear relationship as shown in Fig. 11(a).

$$f = a + b \times \omega$$

Where $a$ and $b$ are constant related to the experimental condition, which are 1.3 and $-0.038$ in this study. When more nanoparticles accumulate at the S/L interface (larger $\omega$), the blocking effect is better (smaller $f$). So the blocking effect of TiCN\textsubscript{np} is linearly increased with the coverage ratio on the surface of the growing grain. As predicted by Greer\cite{21}, the growth inhibiting effect of nanoparticles is weakened at higher cooling rates in the same addition level. One reason is that faster migration of S/L interface favors the engulfment of nanoparticles. Another more important reason is that the smaller critical radius at higher solidification rate results in fewer TiCN\textsubscript{np} accumulating at the S/L interface. The effect of cooling rate and blocking factor $f$ on grain size shows in Fig. 11(b). Generally, the grain size decreases with increasing of cooling rate and decreasing off. More nanoparticles wrapped on the surface of the growing grains and faster cooling rates will result in finer grain size.

The ultrafine grain structure will exhibit extraordinary properties.
With high volume fraction of nanoparticles, the coverage ratio \( \omega \) is linearly increasing from Eq. 20. The growth restriction effect by nanoparticles would be especially remarkable. Our calculation shows that the grain size can be refined to tens of microns by combining effect of solute and nanoparticles under the slow cooling rate (less than 3.5 K/s). As reported by Cao et al.\(^\text{[50]}\), metal grains size can be refined to nanoscale by high volume percent nanoparticles dispersion in bulk via special method during slow cooling. As shown in Fig. 2, Al-Zr alloy can be obviously refined by TiCN\(_{np}\) without poisoning. This is especially beneficial for Aluminum alloys that have poisoning effect inoculated by traditional refiner such as Al-Zr\(^\text{[6]}\), Al-Si\(^\text{[51]}\) and Al-Sc\(^\text{[52]}\).

6. Conclusions

In order to overcome the poisoning effect of Al-Cu-Zr alloy inoculated by Al-5Ti-1B, TiCN nanoparticles were used as grain refiner. In situ X-radiography observation and numerical modeling were adopted to investigate the refinement mechanism of TiCN\(_{np}\). The obtained conclusions are as follows:

1. Al-Zr alloys with addition of Al-Ti-B and TiCN\(_{np}\) were studied. The grain size can be effectively refined by TiCN\(_{np}\) via ultrasonic treatment as compared with Al-5Ti-1B which has poisoning phenomenon. A small number of TiCN\(_{np}\) was dispersed inside the grain and a majority of TiCN\(_{np}\) was agglomerated along the grain boundaries.

2. The effect of Al-Ti-B and TiCN\(_{np}\) on Al-Cu-Zr alloy were investigated by in situ synchrotron X-radiography at different cooling rates. The grain size was decreased and the growth rate was increased with the increasing of cooling rate. At the same cooling rate, the grain size with addition of 0.5% TiCN\(_{np}\) was smaller than the addition of 0.5% Al-5Ti-1B. The blocking factor \( f \) of TiCN\(_{np}\) decreases with increasing cooling rate.

3. A new model considering the growth restriction effect of nanoparticles was established. The growth of grain was restricted by the combining effect of solute and nanoparticles. Nanoparticles accumulated at the S/L interface when they met. The blocking factor \( f \) of nanoparticles is linearly decreased with coverage ratio \( \omega \) which is proportional to the critical grain radius. The grain size decreases with increasing cooling rate and decreasing \( f \).

**CRediT authorship contribution statement**

**Yiwang Jia:** Methodology, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

**Dongfu Song:** Data curation, Formal analysis.

**Nan Zhou:** Project administration, Resources.

**Kaihong Zheng:** Supervision, Validation.

**Yanan Fu:** Resources, Software.

**Da Shu:** Funding acquisition, Investigation.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at [https://doi.org/10.1016/j.ultsonch.2021.105829](https://doi.org/10.1016/j.ultsonch.2021.105829).

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