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Grain Refinement of Al-Si Alloys: Scientific and Industrial Aspects

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Abstract

Casting of aluminum alloys is a common industrial practice and widely used in automotive industry in the entire world. This practice is used to promote the formation of a fine, uniform and equiaxed grain structure. To understand the mechanism of grain refinement is very important since a refined microstructure lead to improve uniform mechanical properties and reduced hot tearing tendency of the alloy by improving feeding ability of liquid metal. Sufficient amount of liquid fraction at last stage of solidification ensure the less shrinkage porosity, and finer distribution of second phases. Nowadays in casting industry, finer grain structure is achieved by addition of grain refiner in the melt. The most commonly used inoculants are Al-Ti, Al–Ti–B, and Al-Ti-C master alloys. Usually Al–5Ti–1B is added to molten aluminum at a typical level of .01 to .05 by weight of titanium. After addition of grain refiner, the number of active nucleation sites during solidification start to dispersed in the melt and nucleate solid particles. There are two mechanism of grain refinement; (i) Nucleant effect: it promotes suitable sites for heterogeneous nucleation of grains, and (ii) Solute effect: it restricts the growth of grains through segregation of solute elements. It has been seen that $TiAl_3$ and TiB_2 particles are the maximum common heterogeneous nucleation particles for aluminium crystals. The required driving force for grain refinement during solidification is provided by cooling rates in the form of constitutional undercooling. Many researcher has given a great contribute to understand the mechanism of grain refinement in melt. However, the exact mechanisms by which grain refinement occurs using the grain refiner have not been fully understood yet. Experimental and theoretical studies on the mechanisms have mainly focused on (a) the role of the titanium solute causing a growth restriction effect, (b) the thermodynamics of Al–Ti-based alloy systems, and (c) the heterogeneous nuclei of $TiAl_3$ and TiB_2 particles. In the present paper, a review is given of the studies of grain refinement taking into consideration of both the industrial practice and scientific aspects of grain refinement. The paper will be useful in understanding the performance of grain refiners for the scientific and industrial community.

Keywords: *Aluminum alloys, constitutional undercooling, grain refinement, heterogeneous nucleation, solute effect.*

INTRODUCTION

Grain refinement is a suppression of columnar grains and produce fine equiaxed grains by the addition of grain refiners to the molten metal. Grain refinement process decide the enhancement in metallurgical characteristics of aluminum alloys [1–4]. Fine equiaxed grains confirm uniform and improved machinability, better feeding to eliminate shrinkage porosity, better surface finishes improved resistance to hot tearing, better strength, toughness, fatigue life and corrosion resistance [2, 3, 5, 6]. Titanium shows the tendency of higher grain refinement effect in aluminium, especially in the presence of Boron or Carbon in 1950 [7], and widely accepted in industry for microstructure control of aluminium-silicon alloys. It was already known in the 1920s and 1930s [8] that grain refinement of aluminium and its alloys could be achieved by addition of small amount of elements such as titanium, niobium, boron and zirconium as fluxes. The classic work of Cibula in the late 1940s early 1950s [9] has found that combinations of Ti and B were the most effective means of refining aluminium and its alloys. The first commercial exploitation of Cibula's finding was the introduction into the aluminium industry of "salt tablets" containing mixture of potassium titanium fluoride and potassium borofluoride [10]. These tablets were plunged into molten Al to release Ti and B, and subsequently form in situ Ti boride, believed to be the nucleating particles. As late as 1967 Van Lancker [11] stated that KBF_4 salts were preferable to BAl or TiBAl due to the presence of hard particles. A major step forward in the technique of grain refining with TiBAl was the move in the late 1960 early 1970s from its use as waffle plate and ingots as a melting or holding furnace addition to rod automatically fed into the metal stream in the launder [12]. Continuous grain refinement with rod is more efficient and more precise than furnace grain refinement. It allows much lower addition rates, eliminates the risk of Ti boride sludge build up in the furnace and ensures a constant level of grain refinement during the whole casting cycle. In the late 1970s/early 1980s, driven by industry's need to produce thinner and thinner sheet and foil products of increasingly high quality, attention was switched to the production of even cleaner TiBAl rod [13]. Cleaner TiBAl rod means a product substantially free from oxides and with Ti boride particles below a certain maximum allowable size, usually determined by the particular field of application.

Titanium based master alloys containing soluble $TiAl_3$ and insoluble TiB_2 particles which have been dominant in Al-Si industry for 30 years. They are used in a wide range of chemical composition such as Al-3Ti, Al-5Ti-1B, Al-3Ti-1B, Al-5Ti-1C and Al-0.45Ti-1C and many more [14]. Many theories have been published till now but there is no such theory which exactly explain that how Al-Ti and Al-Ti-B grain refiners work. It is known that when refiners are added to Al-alloy melts, the aluminum matrix dissolves and releases intermetallic particles ($TiAl_3$, TiB_2 and AlB_2) into the melt. Many researchers published that TiB_2 particles are more stable than $TiAl_3$ particles which means that TiB_2 particles have high nucleating potency. However, exactly which particles have more nucleating potency and their subsequent reaction with the melt are still debatable [15]. Several mechanisms have been postulated, but no clear consensus has emerged as yet.

Nucleant Paradigm

The phenomenon of grain refinement can be understood directly by the studying nucleation and growth process of grains. In heterogeneous nucleation, the critical nucleus size is

$$r^{*}_{\text{heterogeneous}} = \frac{-2Y_{sL}}{\Delta G_{v}} \qquad (1)$$

the free energy barrier is

$$\Delta G^{*}_{\text{heterogenoous}} = \frac{16tY_{sL^3}}{3Lt_{v^2}} f(\theta) \qquad (2)$$

Where, f(θ) is a function of the contact angle, θ on the substrate on which nucleation takes place. Fig. 1(a) displays the solid nucleating on a substrate in a liquid. Fig. 1(b) displays the variation of f(θ) with θ and since f(θ) is always ≤ =1, the critical free energy for heterogeneous nucleation is always less than or equal to that for homogeneous nucleation. [16]

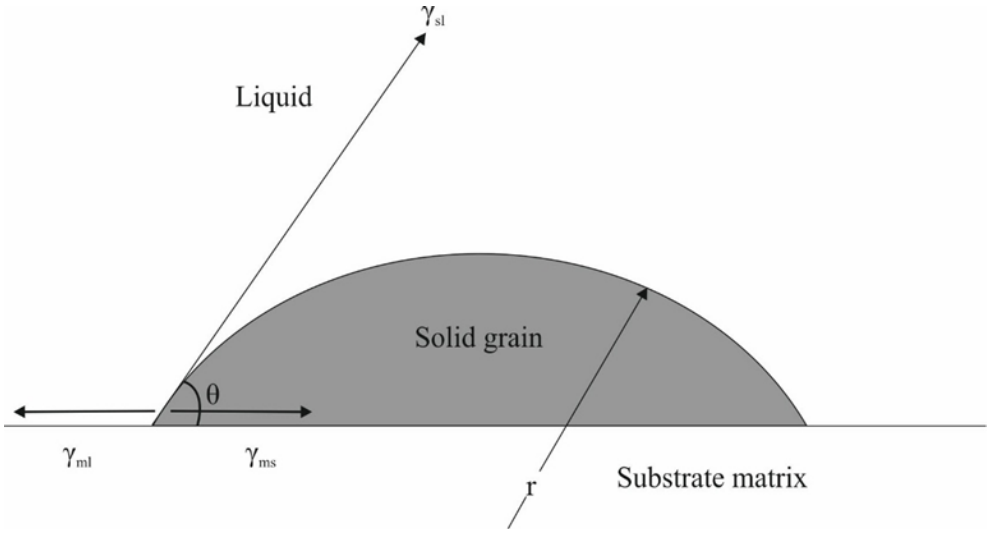


Figure 1: *Schematic representation showing the formation of spherical cap of solid on a substrate, contact angle and surface tension forces.*

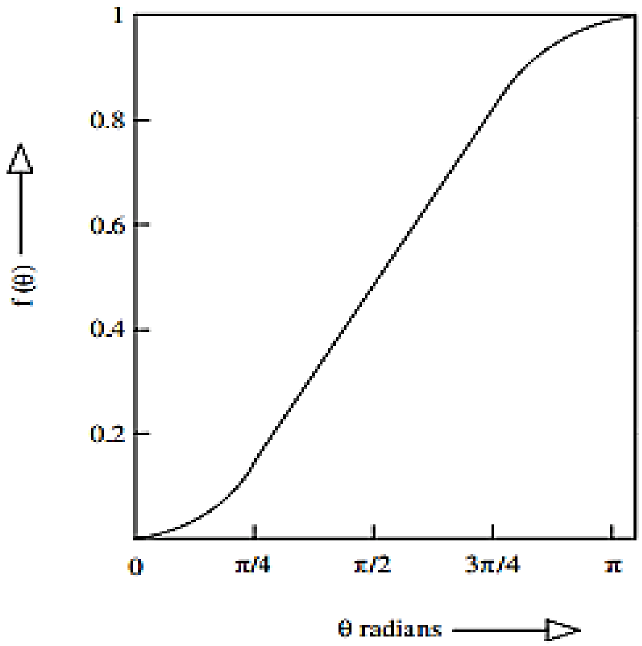
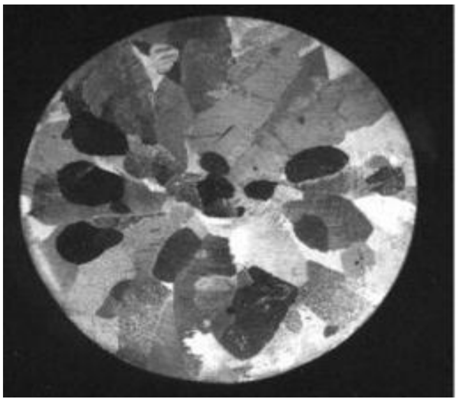


Figure 2: *Variation of f(θ) with θ where f(θ) is equal to (2-3 cos θ + cos^3 θ).*

The values of undercooling, ΔT is of the order 1–2 K for observable nucleation rates in commercial aluminum alloys with addition of grain refiners. Therefore, clearly heterogeneous nucleation is taking place. The well-known constitutional super cooling occurs as solute is rejected at the interface and the criterion is given by [17]:

$$\frac{G_L}{R} \geq \frac{-m_L C_0 (1-k)}{k D_L} \tag{3}$$

Where, G_L is the temperature gradient in the liquid (K/m). R the growth rate of phase diagram (K/wt%), C_0 the bulk alloy composition in the liquid (wt%), k the partition coefficient between solid and liquid, and D_L the diffusion coefficient of the solute in the liquid (m^2/s). Generally, a casting exhibit columnar to equiaxed grains as reach to central portion of crystals. The columnar dendrites grow in directions in the cubic system and growth direction is opposite to the heat flow direction. The equiaxed dendrites grow in the same direction of heat flow, i.e., radially outward. The formation of equiaxed crystals is due to dendrite arm melt off [11], which provides nuclei for equiaxed crystals. The Fig. 3(a) and (b) are shown below without grain refinement and with grain refinement [18].



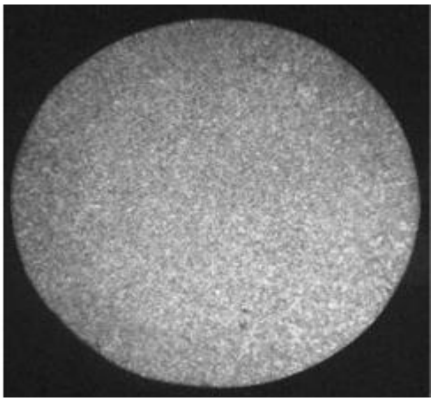


Figure 3(a): *1.5x; 99.9% aluminum ungrain refined.*

Figure 3(b): *99.9% aluminum grain refined with 0.008% titanium added as Al-5%Ti-1%B rod.*

Principles of Grain Refinement

The basic requirements which must be fulfilled in order to obtain a good grain refining in aluminum alloys are as follows [7, 9, 19, 20]:

(i) To promote the formation of crystals on a nucleant, the interface between the nucleants and the liquid should be of higher energy than the nucleant and the crystal solid (lattice compatibility). One way of maximizing this condition is to provide a nucleant-crystal relationship that is associated with a good crystallographic match between the respective crystal lattices and nucleant when closed packed planes of the two crystals can have a one-to–one correspondence of atoms at the interface.

(ii) Minimizing the atomic mismatch will promote a low surface energy (lattice disregistry less than 10-12%). For the inoculation particles to have a high potential of nucleation the energy of the newly formed interface should be low. Thus for this both the phases that of the nucleant particle and that of nucleating face must be coherent, i.e., they must have an orientational relation between the crystals[15, 21, 22], which reduces the discrepancy. A large difference will introduce a considerable strain and potential energy to the interface, in contrast to a similar structure, allowing for close-to relaxed, fully or partially coherent interface.

(iii) In addition to lowering the contact angle by good lattice matching, a successful nucleating agent should be stable in the molten metal and possess a large surface area and roughness.

(iv) A high enough growth restriction factor (GRF) [12, 23, 24].

(v) Grain refiners must be effective in small amounts and they should not impart any deleterious effect to the alloy being refined.

A low interfacial interface requires to coherent or partially coherent phases, which have a certain orientation relationship. An orientational relationship expectations on a low discrepancy between atomic distances over the liquid solid interface. Several model can predict inoculation properties based on the crystallographic discrepancy of two phases or of two closed-packed planes. However, the interatomic spacing for different relative directions for two phases, produces different interplanar distances between the atom rows. Edge-To-Edge Matching minimize both the interatomic mismatch in an closed packed set of directions, and the corresponding interplanar mismatch between the line-ups of atom planes [13]. Fig. 4 illustrates the basis for the edge-to-edge matching model, where the edges of consecutive atoms row across an interface is the close-packed directions. In order to minimize strain energy over the interface, the stacks of planes for the two phases should have similar interplanar spacing. The misfit threshold of the former is usually said to be 10 % to be considered an orientational relationship [24, 25, 26].

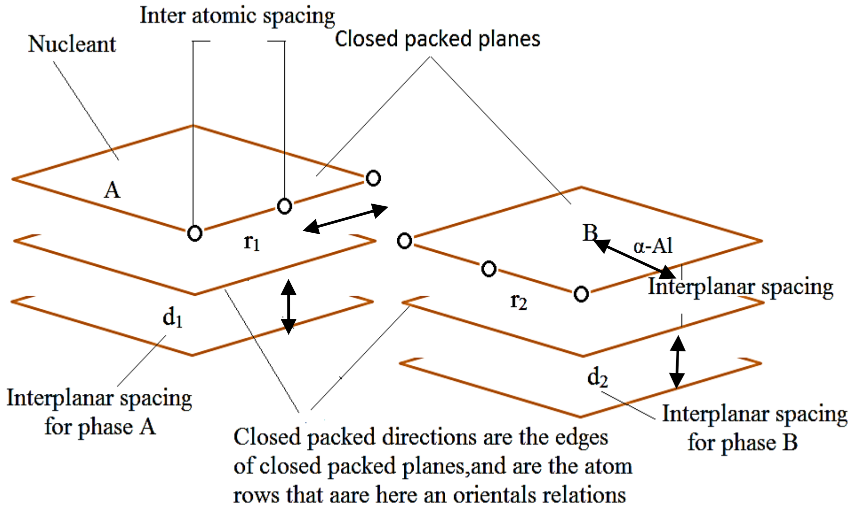


***Figure 4:** Edge-To-Edge mismatch model evaluates both the interatomic mismatch over an interfaces, and the interplanar mismatch of the consecutive atom rows.*

For the latter a mismatch of more than 6% may force the phase to adjust its projected interplanar distance by rotating a few degrees and is considered as a threshold.
The interatomic mismatch, f_r and the interplanar mismatch, f_d over the semi-or-coherent interface is given by:

$$f_r = \frac{r_1 - r_2}{r_1} \quad (4)$$

And;

$$f_d = \frac{d_1 - d_2}{d_1} \quad (5)$$

Where $\frac{r_1}{d_1}$ and $\frac{r_2}{d_2}$ is the interatomic/ interplanar spacing for the two phases, A and B, and the mismatch is calculated with respect to the former.

IMPORTANT GRAIN REFINERS THEORIES

1. Nucleation theory
2. Solute theory

The Nucleant Paradigm

Boride/Carbide Theory

In this theory nucleation occurs on borides or carbides, It is suggested that Ti as a powerful segregant restricts growth of grains, nucleation events.

Phase Diagram Theory

This is via peritectic reaction and Ti is present to form $TiAl_3$, which act as a nuecleant.

Peritectic Hulk Theory

In this theory, peritectic reaction occurs in a Ti-rich boride shell via the peritectic reaction. Ti is present to form Ti Al_3, which acts as a nucleant. Ti is present in boride shell after Ti Al_3 dissolution at the peritectic concentration.

Hyper nucleation Theory

On borides, Ti segregates down an activity gradient to the boride to provide a suitable interface for nucleation of α-Al.

Duplex Nucleation Theory

$TiAl_3$, which is formed on the surface of TiB_2 particles, Ti is present segregate to TiB_2 down an activity gradient to form Ti Al_3 on the surface, which then nucleates Al.

Solute Paradigm

The paradigm shift was given in 1993 by Jhonsson, [8] who proposed that addition of nucleant particles is important in grain refinement. Furthermore, he found that the amount of segregating elements also, quantified by the growth restriction factor in grain refinement. There have been others [3, 53] who have also found that solutes as growth-restricting important elements. And they accepted that titanium act as a powerful segregant in grain refinement [1]. Both the existence of nucleant particles and the amount of segregating elements play an essential role in the grain refining process [2, 7, 15]. This segregating power of elements is quantified by the growth restricting factor (GRF) [16].

Despite the earlier perception, Johnsson et al., [8, 24, 5] disputed that borides are poor nucleants. He found borides in the centre of grains at hypoperitectic additions of Al-5Ti-1B master alloys. Even at concentrations below the stoichiometric ratio of Ti:B, where no grain refinement was observed, Johnsson found borides at the grain centres [24]. It was observed that that there is a small disregistry of 4.30 percent between the α-Al and the TiB_2 for (111)Al|(001)TiB_2, [110]Al||[110]TiB_2. Therefore, TiB_2 should be a noble nucleant efficiency, though not as noble as $TiAl_3$ particles. Johnsson, et al. [5] proposed that in the presence of solute elements such as titanium and silicon sufficient amount of the undercooling is provided for TiB_2 to be a good nucleant. If there is no solute element than borides do not nucleate aluminum. Furthermore, AlB_2 particles also grain refine to aluminum alloy to some extent at concentrations above the Al-B eutectic, i.e., 0.022 pct B,[3, 27, 4] and Tondel [5] searched AlB_2 particles have(111) Al |(001)TiB_2,[110] Al ||[110] TiB2 orientation relationship between the AlB_2 particles, with a low disregistry of 3.5 pct. Generally disregistry should be very low (less than 5.00 pct.). Marcantonio and Mondolfo [27] found that the lattice parameters of the mixed borides varied almost linearly with composition and therefore borides are good nucleants.

The concept of GRF is needed to quantify the segregating behaviour of elements upon solidification. The GRF is a measure of the growth-restricting effect of solute elements on the growth of the solid-liquid interface of new grains as they grow into a melt. It is defined as $mC_0(k - 1)$, where m is the gradient of the c, usually approximated to a straight line, C_0 is the concentration of the solute in the alloy, and k is the partition coefficient between the equilibrium concentrations of the solid and liquid at the growing interface (*i.e.*, $k = c_s/c_l$ at the interface temperature). The GRF for an alloy with multiple solute elements is $\Sigma mC_0(k - 1)$. The solute element decides the dendrite growth by building up a constitutionally undercooled zone in front of the interface. This is a process which provides nucleation and the new grain does the same to the next grain. Undercooling-driven mechanism, borides /or other particles. Solute affects the dendrite growth and builds up. This undercooled zone facilitates nucleation and the new grain does the same to the next grain.

FADING MECHANISM

Fading mechanism can be quantified by the larger grains in the casting [27]. From the Fig. 5, it is clear that maximum grain refinement is achieved with 10 min of holding time of grain refiner in the melt. When holding time is increased up to 60 minute no further refinement is achieved. However, 120 minute of holding time show coarser grains as compared to 10 minute of holding time. So, there are no benefits for holding the grain refiner in the melt for more than 10 minutes.

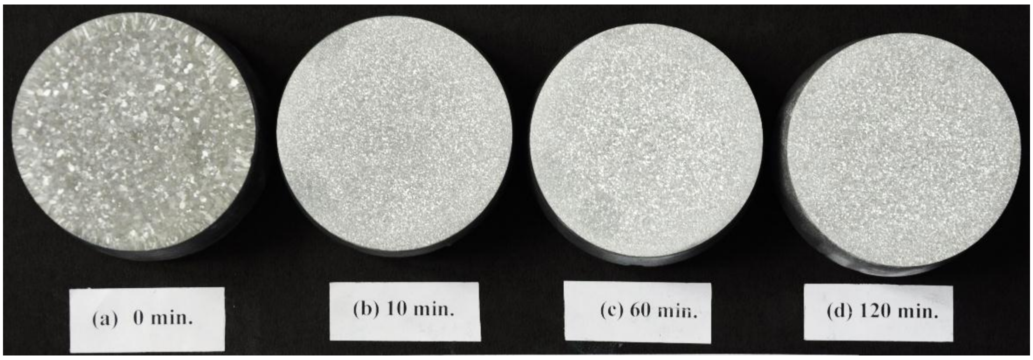


Figure 5: *The samples of Al-7Si alloy show the grain refinement effect and fading with holding time.*

CONCLUSION

The future of the grain refiner supply industry will continue to be inextricably linked to the aluminium industry. The aims of the grain refiner suppliers will be to continue and extend a policy of cooperation and collaboration with the aluminium producers, which goes back to early days of DC casting in the 1940s. Continuing efforts will be made to provide the industry with cleaner and more effective grain refiners, possibly based on carbon. Progress has been made in understanding several aspects of the inoculation of aluminium melts by Al-Ti-B and Al-Ti-C refiners. Fading of grain refinement can be varied with type of grain refiners.

REFERENCES

1. Hamadellah A, Bouayad A. (2017), "Study of hot tear of AlCu5MgTi by restraining casting shrinkage in green-sand mold", Volume 8, pp. 3099–3105.
2. Wang HJ, Xu J, Kang YL, Tang MO, Zhang ZF. (2014), "Effect of Al-5Ti-1B-1Re on the Microstructure and Hot Crack of As-Cast Al-Zn-Mg-Cu Alloy.

J Mater Eng Perform, Volume 23, pp. 1165–1172. doi:10.1007/s11665-013-0860-0.

3. Huang H, Fu P, Wang Y, Peng L, Jiang H. (2014), "Effect of pouring and mold temperatures on hot tearing susceptibility of AZ91D and Mg − 3Nd − 0. 2Zn − Zr Mg alloys", Volume 24, pp. 922–929. doi:10.1016/S1003-6326(14)63144-7.
4. Samuel AM, Doty HW, Gallardo SV, Samuel FH. (2016), "The effect of Bi-Sr and Ca-Sr interactions on the microstructure and tensile properties of Al-Si-based alloys", *Materials (Basel)*, Volume 9. doi:10.3390/ma9030126.
5. Jarry P, Rappaz M. (2006), "A granular model of equiaxed mushy zones : Formation of a coherent solid and localization of feeding", Volume 54, pp. 4023–4034. doi:10.1016/j.actamat.2006.04.035.
6. Rathi SK, Sharma A, Sabatino M Di. (2017), "Influence of Annealing of Al-5Ti-1B Master Alloy on Hot Tearing of Cast Al-7Si-3Cu Alloy", Volume 737, pp. 27–31. doi:10.4028/www.scientific.net/KEM. 737.27.
7. Elsayed A, Ravindran C. (2011), "Effect Of Aluminum-Titanium-Boron Based Grain Refiners On Az91e Magnesium Alloy Grain Size And Microstructure", pp. 29–41.
8. Khushboo Gupta, Dr. Sachin Rathi. (2019), "Modeling of Wireless Sensor Networks in an Energy-Efficient Manner Using Quantum Physics", *Journal of Computer Science Engineering and Software Testing*, Volume 5, Issue 1, pp. 20–29. http://doi.org/10.5281/zenodo.2592994
9. Pattnaik AB, Das S, Jha BB, Prasanth N. (2014), "Effect of Al-5Ti-1B grain refiner on the microstructure, mechanical properties and acoustic emission characteristics of Al5052 aluminium alloy", *J Mater Res Technol*, Volume 4, pp. 171–179. doi:10.1016/j.jmrt.2014.10.017.
10. Khushboo Gupta, K. P. Yadav (2015), “Data Collection Method to Improve Energy Efficiency in Wireless Sensor Network”, *International Conference of Advance Research and Innovation (ICARI - 2015),*
11. M van Lancker. (1967), “Metallurgy of Aluminium Alloys”, *Chapman Hall Ltd*, London.
12. A. Agarwal, K. Gupta, K. P. Yadav (2016), "A novel energy efficiency protocol for WSN based on optimal chain routing", *2016 3rd International Conference on Computing for Sustainable Global Development (INDIACom)*, New Delhi, pp. 368–373.
13. Kumar S, Ashok R, Marisa S, Sabatino D. (2017), "Performance of Al – 5Ti – 1B Master Alloy After Ball Milling on Minimizing Hot Tearing in Al – 7Si – 3Cu Alloy. *Trans Indian Inst Met*, Volume 70, pp. 827–831. doi:10.1007/s12666-017-1065-2.
14. Kumar S, Sharma A, Di M. (2017), "Effect of mould temperature, grain refinement and modification on hot tearing test in Al-7Si-3Cu alloy", Volume 79, pp. 592–605. doi:10.1016/j.engfailanal.2017.04.037.
15. Khushboo Jain, Dr Anoop Bhola. (2018), “Data Aggregation Design Goals for Monitoring Data in Wireless Sensor Networks”, *Journal of Network Security Computer Networks*, Volume 4, Issue 3, pp. 1–9. http://doi.org/10.5281/zenodo.1464554 .
16. Society TR, Transactions P, Sciences E. inoculation of melts (2013), Volume 361, pp. 479–495.
17. Li JG, Huang M, Ma M, Ye W, Liu DY, Song DM, et al. (2006), "Performance comparison of AlTiC and AlTiB master alloys in grain refinement of commercial and high

purity aluminum", *Trans Nonferrous Met Soc China*, English Ed, Volume 16, pp. 242–253. doi:10.1016/S1003-6326(06)60042-3.
18. Ma XL, Wang X, Li XL, Yang L. (2010), "Effect of Al5Ti1B master alloy on microstructures and properties of AZ61 alloys", *Trans Nonferrous Met Soc China*, English Ed, Volume 20, pp. 1–5. doi:10.1016/S1003-6326(10)60505-5.
19. Markushev M V (2009), "On the Principles of the Deformation Methods of Aluminum-Alloys Grain Refinement to Ultrafine Size : I", *Fine-Grained Alloys*, Volume 108, pp. 43–49. doi:10.1134/S0031918X09070060.
20. Estrin Y, Vinogradov A. (2013), "Extreme grain refinement by severe plastic deformation: A wealth of challenging science", *Acta Mater*, Volume 61, pp. 782–817. doi:10.1016/j.actamat.2012.10.038.
21. Zhang M, Kelly PM. (2005), "Edge-to-edge matching model for predicting orientation relationships and habit planes — the improvements", Volume 52, pp. 963–968. doi:10.1016/j.scriptamat.2005.01.040.
22. Zhang MX, Kelly PM. (2005), "Edge-to-edge matching and its applications: Part I. Application to the simple HCP/BCC system", *Acta Mater*, Volume 53, pp. 1073–1084. doi:10.1016/j.actamat.2004.11.007.
23. Dissertation A. (2010), "Hot Tearing inCast Aluminum Alloys",
24. Khushboo Gupta and Vaishali Sikka (February 2015), "Design Issues and Challenges in Wireless Sensor Networks", *International Journal of Computer Applications*, Volume 112, Issue 4, pp. 26–32.
25. Yang J, Wang JL, Wu YM, Wang LM, Zhang HJ. (2007), "Extended application of edge-to-edge matching model to HCP/HCP (α-Mg/MgZn2) system in magnesium alloys", *Mater Sci Eng A*, pp. 460–461, 296–300. doi:10.1016/j.msea..01.097.
26. Zeng Y, Jiang B, Li R, Yin H, Al-Ezzi S (2017), "Grain Refinement Mechanism of the As-Cast and As-Extruded Mg–14Li Alloys with Al or Sn Addition", *Metals (Basel)*, Volume 7, Issue 172. doi:10.3390/met7050172.
27. Hassanbeygi V, Shafyei A (2014), "Investigation on Microstructure and Grain Refining Performance of a New Type of Al-3Ti-1C Master Alloy", pp. 49–55.

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