Temperature Gradient Field Theory of Nucleation

S. Das[1], W.Q.Ain[2], A.Azhari[2], A.K. Prasada Rao[2*]

[1] Department of Metallurgical and Materials Engg., National Institute of Technology, Raipur, INDIA.

[2] Faculty of Manufacturing Engineering, Universiti Malaysia Pahang, MALAYSIA

*Corresponding author: akprasada@yahoo.com

Abstract. According to the proposed theory, ceramic particles present in molten metal, lose heat at a slower rate than the metallic liquid during cooling. Such condition results in the formation of a spherical thermal gradient field (TGF) around each particle. Hence, the interstitials (low temperature) of such TGFs are the regions to reach the nucleation temperature first, owing to low energy barrier than the liquid-particle interface (higher temperature). Analytics also indicate that the nucleation rate is higher at the TGF interstitials, than at the liquid-particle interface. Such TGF network results in simultaneous nucleation throughout the system, resulting in grain refinement.

Keywords: Grain Refinement; Solidification; Nucleation; Wetting; Heat-transfer

1. Introduction

Heterogeneous nucleation and the solidification science of metals are being studied for past many decades. Heterogeneous nucleation happens by the catalysis on impurities or grain refiners, present within or added in the parent liquid. According to Turnbull et al. (1949), the nucleation process is aided by a catalyst surface (nucleating substrate) which reduces the magnitude of the energy barrier. However, there are considerable limitations with this theory, particularly when the catalytic efficiency is high. Cantor (2003) reported that heterogeneous nucleation occurs by dynamic atom by atom adsorption process. A relation between the undercooling and melting points of catalyst and liquid was introduced to understand its effect on nucleation. Theory of nucleation by adsorption satisfactorily explains how primary Al nucleates by the adsorption of excess Ti onto the TiB2 particle surfaces to form a catalytic Al3Ti layer (Cantor (2003)). In a different investigation, Li et al (2011) and Zuo et al. (2011) reported that intensive melt shearing in liquid aluminium, disperses the oxide particles (γ-Al2O3), which result in grain refinement. Although the surface energy of γ-Al2O3 is significantly high [5] to nucleate α-Al by adsorption theory, remarkable grain refinement was reported by Li et al (2011), comparable with that obtained by TiB2 particles whose surface energy is lower than that of γ-Al2O3. All the theories (Turnbull (1949), Cantor (2003), Li et al (2011), Zuo et al (2011), Hunt et al. (2011), Murty et al (2002) and Quian et al (2005)) which try to explain the heterogeneous nucleation mechanism consider that the temperature of the substrate to be lower than the melting point of the liquid, or the occurrence of an interface reaction between the particle and the liquid. Therefore these particle substrates act as potent nuclei for the liquid liquid-solid transformation. However, earlier theories did not consider the heat-transfer aspect across the liquid-particle interface. According to the

proposed theory, the temperature of the ceramic particle substrates is higher than the melting point of the liquid. Hence, the heterogeneous nucleation is much more complex phenomenon as the temperature distribution in the solidifying liquid plays a vital role.

This paper discusses the role of the ceramic particles (grain refiners) on the temperature distribution in the solidifying liquid and hence affecting the nucleation behaviour, and more viable theory is proposed herein. The primary considerations of this theory are (i) no chemical interaction takes place across the liquid/ceramic-particle interface; (ii) temperature of the ceramic particle and the liquid is same, initially; and (iii) Heat is continuously lost by the system to the surroundings.

2.   Nucleation Mechanism

Present theory is focused on the nucleation mechanism in a liquid metal containing ceramic particles of uniform size with spherical morphology, dispersed uniformly in the liquid. It is known that ceramic particles do not wet liquid metal completely. In other words, there exists some un-wetted surface area of the particle.
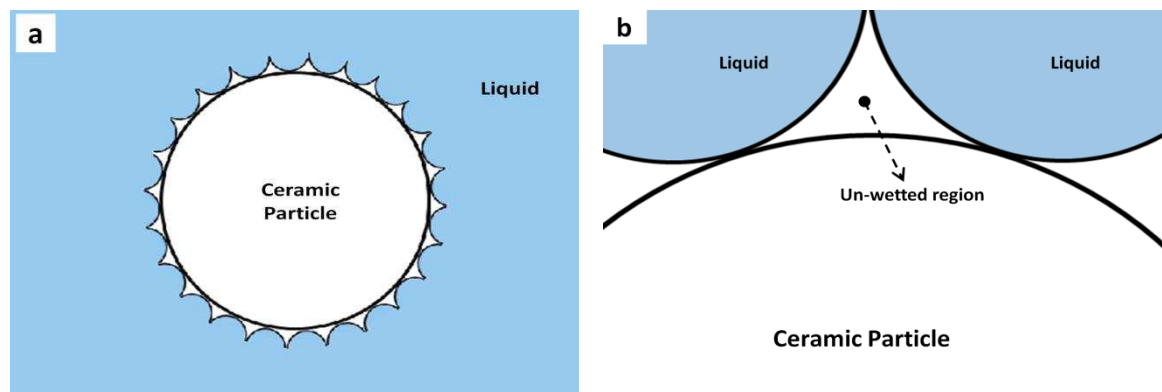

Fig. 1 Schematic illustration of a ceramic particle in liquid **(a)** with poor wetting and **(b)** un-wetted area at liquid-particle interface

Figure 1(a) and (b) depict the schematic of a ceramic particle in liquid, with poor wettability (Rhee et al. (1970)). Hence the effective area of wetting (A_e) is less than the geometric surface area of the particles present in the liquid. In addition to the poor wetting area, these ceramic particles possess lower thermal conductivity (Powell et al. (1966)) than the liquid metal surrounding them. Therefore, these ceramic particles which are at same temperature as the liquid (initially) lose heat at a lower rate than the liquid following the Newton's Law of cooling as in Eq.1 (considering simple mode of heat transfer, ignoring Brownian motion of the particles and liquid flow):

$$Q_{cv} = hA_e\bigl(T_p - T_i\bigr) \qquad (1)$$

It is obvious from Eq.1 that the heat dissipation from the particle to the surrounding liquid depends on the effective area wetted (A_e). Since the heat dissipation from the ceramic particle is relatively slower than from the liquid, a spherical temperature gradient field (TGF) is formed around each particle as shown in Fig.2.

Nomenclature

Q_{cv}	Convective heat transfer (Watt)
h	heat transfer coefficient (Watt $m^{-2}K^{-1}$)
T_p	Temperature at the liquid-particle interface (K)
T_i	Temperature of the liquid at the interstitials of TGF (K)
A_e	Effective area of heat transfer (area of the particle wetted by the liquid) (m^2)
T_g	Growth temperature (K)
T_n	Nucleation temperature (K)
ΔG^*	Energy barrier for nucleation
k	Boltzmann's constant
ΔG	Solid-liquid interface energy
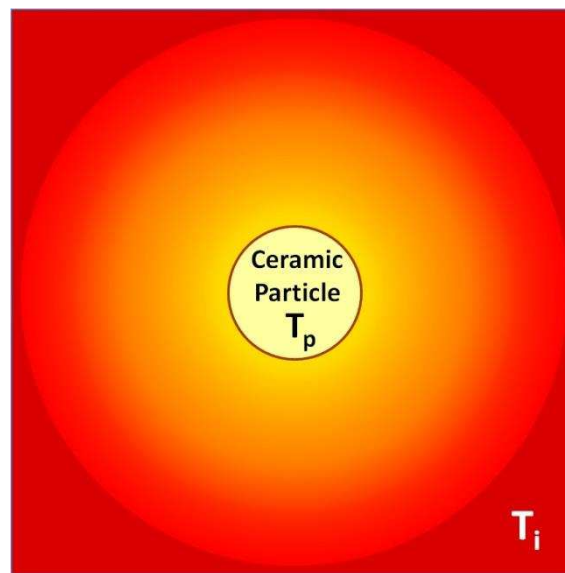
Fig. 2 Temperature gradient field (TGF)

The diameter of the TGF depends on the wettability and thermal conductivity of the particle in the liquid metal. For example in liquid aluminium, TiB_2 forms a smaller TGF than Al_2O_3; as the former has better wettability and hence, the better thermal conductivity than the later. The diameter of the TGF depends on the spacing between the ceramic particles. In other words, the size of the TGF depends on the volume fraction of the suspended ceramic particles, which are hot spots. The system containing several such particles forms a network of TGFs during the process of cooling, as illustrated in Fig. 3(a). Influence of the TGF network on the nucleation mechanism can be analysed as follows:

The temperature-distance curve shown in Fig. 3(a) indicates the nature of temperature field in the stages (I to IV). Each of the points on the curve represents the average temperature (T_j) in the corresponding stage, as usually measured by a thermo-couple. The temperature T_j is given by the Eq.2.

$$T_j = \frac{1}{k}\sum_{k=1}^{p} T_k \qquad (2)$$

The solidification process undergoes various stages as illustrated in the Fig. 3(a). Initially, the particles are dispersed uniformly in the liquid as shown in stage-I (Fig.3a). The temperature at stage-I is above the melting point (T_m) and the difference between the temperatures of the particle and the liquid is insignificant. As the heat is extracted from the system continuously, several TGFs are formed as a network is formed (stage-II), as explained above in Fig.2. The overall temperature read by a thermocouple at stage-II varies from melting point (T_m) to nucleation temperature (T_n). However, in

reality the temperature T_j may vary from T_p to T_n as shown in stage-II (Fig. 3a). At stage-III, the temperature, T_j varies from T_p to T_n. Since the interstitial temperature T_i at stage-III is greater than or equal to the growth temperature (T_g); it is here, in the interstitial of the TGF network, the nucleation initiates as shown in Fig. 3(b), followed by growth process.
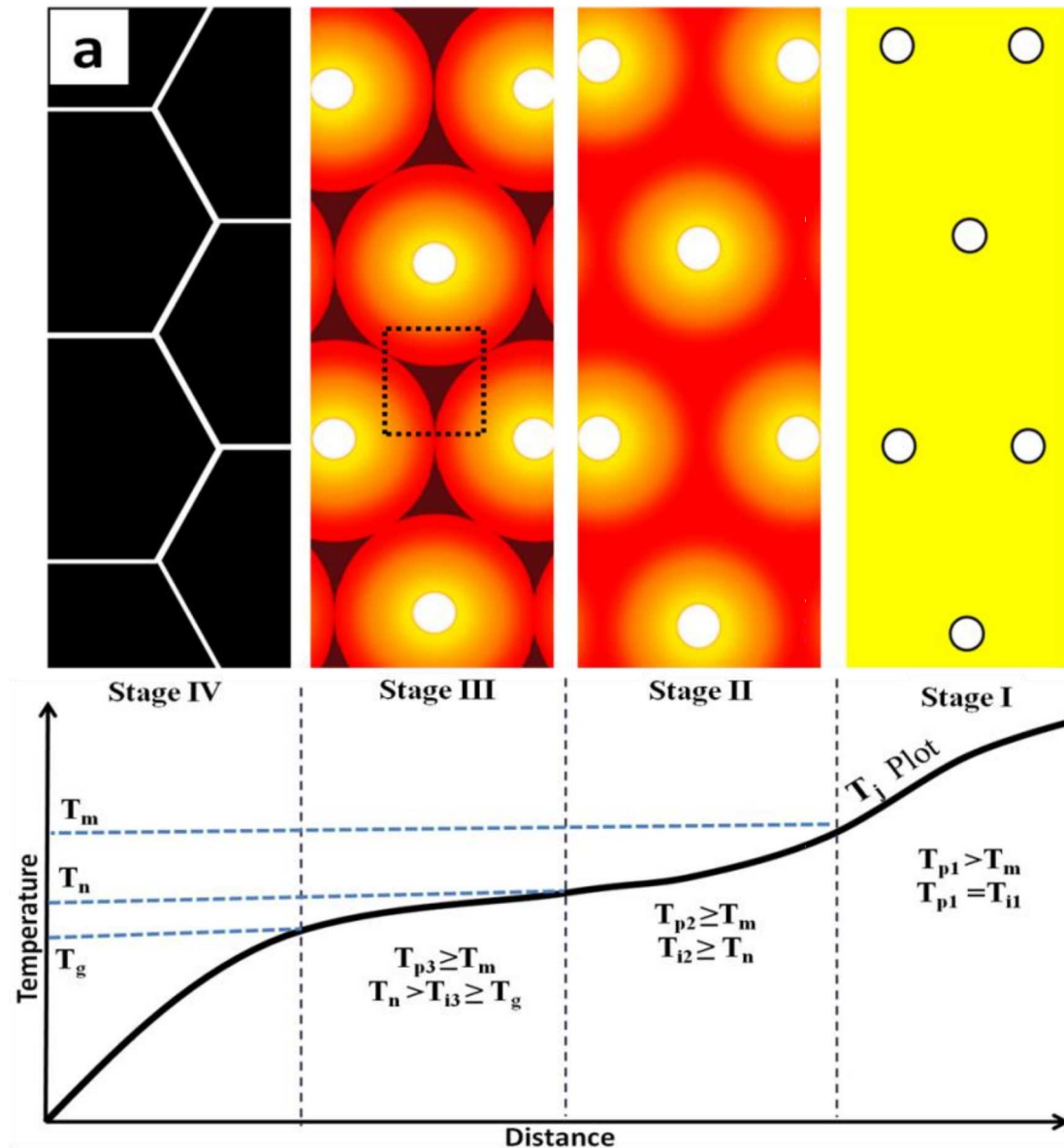

Fig. 3(a) Schematic showing formation of TGF network followed by nucleation and solidification

John Hunt et al. (2011) proposed that the nucleation occurs at a temperature T_n, which is lower than the liquidus. In the present case, the lowest temperature (T_i) prevails in the interstitial regions of these TGFs, as depicted in the Fig.1 (b) and (c); where the free energy is minimum. On the other hand, the free energy at the particle-liquid interface is higher than at the interstitial, as discussed above. Hence, there is a greater possibility of nucleation in these interstitial regions as soon as 'T_i' approaches the nucleation temperature, 'T_n', followed by growth process. During the growth process, the ceramic particles are pushed away by the solidifying front, until the completion of solidification; and this could be the reason for finding these particles in the grain boundaries, often (Murty et al. (2002), Jones et al. (1976)).
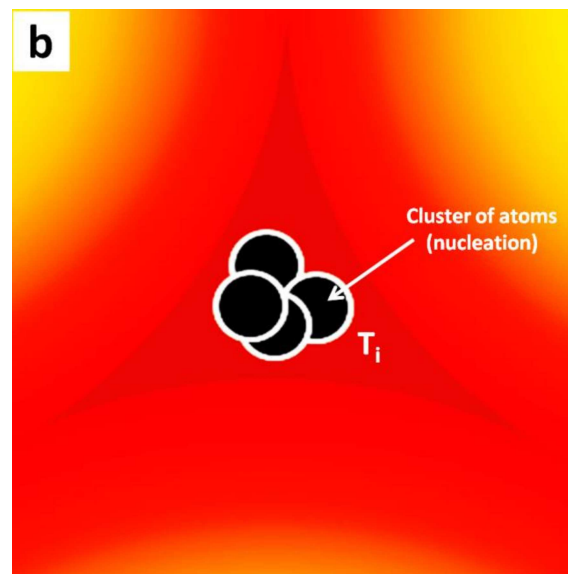
Fig. 3(b) nucleation in the interstitial regions of TGF indicated in the marquee region (stage-III)

On the other hand, some researchers investigated the ceramic particle-matrix interface; eg., interface between TiB_2 and Al matrix and shown a mono-layer of Al_3Ti at the interface. It was reported that this Al_3Ti layer was formed due to partial diffusion across the $TiB_2 - Al$ interface, which aids in the nucleation of primary Al on TiB_2 particle (Mohanty et al. (1995)). In contrast, present theory believes that Al_3Ti mono-layer forms during the last stages of the solidification; as the solute titanium present in the liquid is pushed towards the grain boundaries along with the TiB_2 particles; eventually forming an interface between Al and TiB_2. Similarly, present theory also believes that the grain refinement achieved by the intensive melt shearing (Li et al. (2011) and Zuo et al (2011)), is due to the uniform distribution ceramic oxide particles, thereby the TGFs formed by the Al_2O_3 particles, where the nucleation occurs at the TGF interstitials. Similarly in aluminium melts with TiB_2 particles in it, the fading phenomenon which occurs when the particles settle-down is due to the localized agglomeration of these TGFs. Hence un-even dissipation of the heat and coarser grain structure results.

On the other hand, some researchers investigated the ceramic particle-matrix interface; eg., interface between TiB_2 and Al matrix and shown a mono-layer of Al_3Ti at the interface. It was reported that this Al_3Ti layer was formed due to partial diffusion across the $TiB_2 - Al$ interface, which aids in the nucleation of primary Al on TiB_2 particle (Mohanty et al. (1995)). In contrast, present theory believes that Al_3Ti mono-layer forms during the last stages of the solidification; as the solute titanium present in the liquid is pushed towards the grain boundaries along with the TiB_2 particles; eventually forming an interface between Al and TiB_2. Similarly, present theory also believes that the grain refinement achieved by the intensive melt shearing (Li et al. (2011) and Zuo et al (2011)), is due to the uniform distribution ceramic oxide particles, thereby the TGFs formed by the Al_2O_3 particles, where the nucleation occurs at the TGF interstitials. Similarly in aluminium melts with TiB_2 particles in it, the fading phenomenon which occurs when the particles settle-down is due to the localized agglomeration of these TGFs. Hence un-even dissipation of the heat and coarser grain structure results.

3. Experimental investigation

An experiment was conducted in order to investigate the heat flow from ceramic* to the liquid. 6kg of commercial pure aluminium was melted in a clay graphite crucible and was superheated to 800°C. Three k-type thermocouples were used for recording the temperature, continuously. (*pottery clay

sphere coated with boron-nitride, baked at 200°C for 2weeks and pre-heated to 500°C before immersing in to the molten aluminium) The thermocouples were place in such a way that:

- tip of the first thermocouple was covered by a ceramic sphere (pottery clay) of 10mm dia., in such a way that the tip of the thermocouple is at the center of the sphere. This was coated with boron nitride, ensure poor wetting of the sphere with the melt.

- second thermocouple was placed at the surface of the sphere, to record the temperature in the liquid-ceramic interface region.

- third thermocouple was placed 10mm away from the surface of the sphere, in order to record the temperature away from the ceramic sphere.

All the thermocouples were fixed together to a rigid fixture in order to avoid disturbance and were immersed at a depth of 80mm from the melt-surface, at the centre of the crucible, and the melt was allowed to cool slowly. The temperatures recorded from the thermocouples described above are shown in the Fig.4. From the figure, it is evident that the thermocouple away (T_{liquid}) from the ceramic sphere reaches the nucleation temperature T_n first, owing to higher thermal conductivity of the molten metal (2.0 watt cm^{-1} K^{-1}) (Powell et al. (1966)). In contrast, the thermocouples at the liquid-ceramic interface ($T_{surface}$) and that inside the ceramic sphere (T_{center}) indicate higher temperatures. This observation is in agreement with the present theory, revealing that the ceramic particle present in the melt cools at a slower rate, owing to its poor wetting (smaller area of contact) and poor thermal conductivity (~ 0.08 watt cm^{-1} K^{-1}) (Powell et al. (1966)).
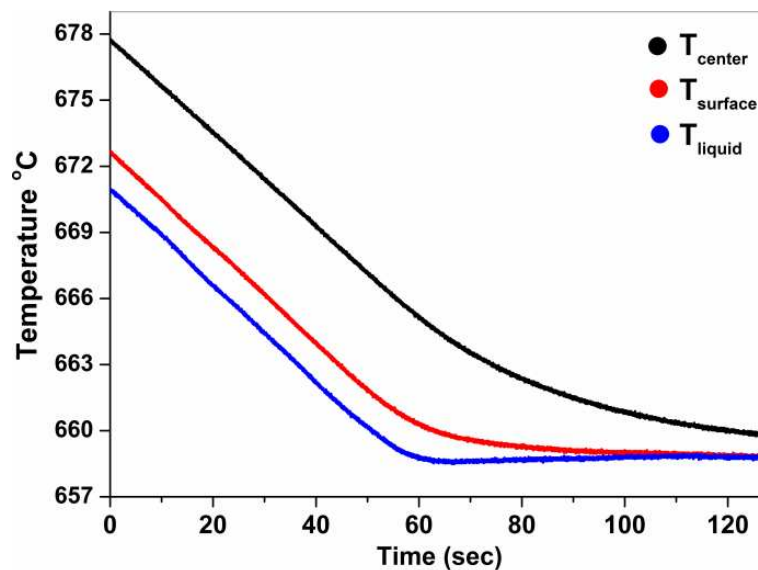

Fig. 4 Temperature profiles obtained during solidification of aluminium (T_{center} - temperature of ceramic sphere; $T_{surface}$ - temperature at the liquid-ceramic sphere interface and T_{liquid} - temperature at the liquid away from the ceramic sphere)

4   Nucleation Rate

It is well known that the homogeneous nucleation rate given by [2],

$$J = J_o \exp\left(\frac{-\Delta G^*}{kT}\right) \qquad (3)$$

Where ΔG^* is the energy barrier for nucleation, given by:

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G^2} \quad \text{and} \quad \Delta G = \frac{L\,(T_n - T)}{T_n} \qquad (4)$$

From the above equations it can be understood that: Nucleation rate,

$$J \propto \exp\left(\frac{-\Delta G^*}{kT}\right) \qquad (5)$$

(or)

$$J \propto \exp\left(\frac{-1}{(\Delta T)^2 (T)}\right) \qquad (6)$$

Therefore the nucleation rate at particle-liquid interface (where liquid-particle interface temperature, T_p and $\Delta T_p = (T_p - T_n)$), can be expressed as:

$$J_p \propto \exp\left(\frac{-1}{(\Delta T_p)^2 (T_p)}\right) \qquad (7)$$

Similarly, the nucleation rate at the TGF interstitial (where the liquid temperature at the interstitial is, T_i) and $\Delta T_i = (T_i - T_n)$.

$$J_i \propto \exp\left(\frac{-1}{(\Delta T_i)^2 (T_i)}\right) \qquad \dots (8)$$

From Fig.4, it is evident that the temperature at the particle-liquid interface (T_p) is higher than that away from the particle (TGF interstitial temperature, T_i).

Therefore,

$$\left[\exp\left(\frac{-1}{(\Delta T_i)^2 (T_i)}\right)\right] > \left[\exp\left(\frac{-1}{(\Delta T_p)^2 (T_p)}\right)\right] \qquad (9)$$

In other words, the nucleation rate at the TGF interstitial, $J_i > J_p$ the nucleation rate at particle-liquid interface. This confirms that the nucleation occurs 'first' at the TGF-interstitial and not at the particle-liquid interface.

5. Conclusion

The proposed *"Temperature Gradient Field Theory"* explains the nucleation mechanism in liquid metal inoculated with ceramic particles. According to this theory, nucleation does not initiate at the particle-liquid interface; rather it occurs at the interstitial regions of the TGF network. Present theory also believes that simultaneous nucleation and growth takes place when these TGFs are uniformly distributed in the system; eventually resulting in fine equiaxed grain structure. However, if the particles possess good thermal conductivity, wettability and atomic-adsorption at the solid-liquid interface, it is possible that these particles trigger the nucleation heterogeneously.

References

[1]   Turnbull D and Fisher JC, The J. Chem. Phy., 17(71) (1949) 71.

[2]   Cantor B, Phil. Trans. Royal Soc. Lond. A, 361 (2003), 409.

[3]   Li HT, Wang Y and Fan Z, Mater. Sci. Engg., 27 (2011) (doi: 10.1088/1757-899x/27/1/012047)

[4]   Zuo Y, Li H, Xia M, Jiang B, Scamans GM and Fan Z, Scripta Mater., 64 (2011) 209.

[5]   Guzman-Castillo ML, Bokhimi X, Rodriguez-Hernandez A, Toledo-Antonio A, Hernandez-Beltran F and Fripiat JJ, J. Non-Cryst. solids, 329 (2003) 53.

[6]   Hunt JD and Fan Z, "A simple method for the nucleation and growth of equiaxed grains", Proceedings of the John Hunt International symposium, edited by Z. Fan and I.C. Stone, Brunel University Press, Brunel University, Uxbridge, Middlesex, UB8 3PH, United Kingdom, (2011) p.59.

[7]   Murty BS, Kori SA and Chakraborty M, Inter. Mater. Rev., 47 (1) (2002) 3.

[8]   Qian Ma, Acta Mater., 55 (2005) 943.

[9]   Rhee SK, J. Amer. Cera. Soc., 53(7) (1970) 386.

[10]   Powell RW, Ho CY and Liley PE,"Thermal conductivity of Selected Materials", (http://www.nist.gov/data/nsrds/NSRDS-NBS-8.pdf), National standard reference data series-National Bureau of standards-8 (Category 5- Thermodynamic and Transport Properties) 25th November, USA, 1966.

[11]   Jones GP and Pearson J, Metall. Trans., 7B (1976) 223.

[12]   Mohanty PS and Gruzleski GE, "Mechanism of grain refinement in Aluminium", Acta Metall. Mater. 43(5), (1995) 2001 2012