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ScienceDirect

Scripta Materialia 106 (2015) 21–25

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

In situ small angle X-ray scattering investigation of ultrasound induced nucleation in a metallic alloy melt

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Received 6 February 2015; revised 13 April 2015; accepted 14 April 2015
Available online 4 May 2015

An in situ synchrotron small angle X-ray scattering (SAXS) method was employed to probe the change of scattering structures in an Al–Cu alloy melt after ultrasonic melt treatment. The size distribution and fractal geometry of the scatterers were evaluated by quantitative SAXS analysis. Results show that cavitation induced nuclei on the clusters or impurities, and the remnants, showing bigger sizes and lower surface fractal dimensions in a melt of lower superheating, could preserve grain refining potential for at least 20 min.

Keywords: Nucleation; SAXS; Ultrasonic; Cavitation

Introduction of acoustic waves with a frequency above 17 kHz into liquid metal in either the liquid state or semisolid state, *i.e.* ultrasonic melt treatment (UST), is known to induce grain refining in many metallic alloy systems, such as aluminum alloys [1,2], magnesium alloys [3], steel [4] and super alloys [5]. The mechanism of ultrasound induced grain refinement is still under discussion and many theories have been proposed, which can fall in two categories [3,6]: (1) grain multiplication due to dendrite fragmentation [7] and (2) cavitation induced nucleation. The latter is further explained by three different hypothesis: (1) the activation of nonwettable impurities (oxides, carbides, and borides, etc.) as heterogeneous nucleation sites [8], (2) the change in melting point arising from the pressure spike accompanying the collapse of a cavity or gas filled bubble [3], which can undercool the liquid and cause homogeneous nucleation [9], and (3) the undercooling of the melt at the bubble surface due to isentropic expansion and evaporation [10]. In the presence of intermetallics or dispersed inoculants, such as primary Al_3Zr or TiB_2 particles in aluminum melt, ultrasonic grain refining effect is not only related to the size of particles which are refined and/or dispersed by UST, but also related to an undercooling available for activation of these particles as nucleation sites in the solidification process [11].

In order to upscale this technology to industrial processes, *e.g.* DC and investment casting, grain refinement should be achieved after the UST in the liquid state. Experiment work of T.V. Atamanenko et al. [2] shows that the effect of UST on the grain size of Al-2.5 mass pct Cu-0.22 mass pct Zr-0.06 mass pct Ti alloy is stable for at least 2 min isothermal holding prior to solidification. In this case, cavitation induced heterogeneous nucleation based on fragmenting and activating Al_3Zr particles is the leading mechanism of grain refinement. Nevertheless, although tiny crystals were observed being nucleated in the cavitation bubble pre-settled region in super-cooled liquids of transparent materials, such as water and sucrose solution [12–14], with the help of high-speed photography, cavitation induced nucleation in metals has been far from accessible, and almost all of the previous efforts were postmortem.

Our previous work presented the synchrotron radiation X-ray imaging of cavitation bubbles in Al–Cu melt [15], but it is difficult to observe cavitation induced nucleation events due to the spatial and temporal resolution limit. Recently, in situ and time-resolved synchrotron radiation small angle X-ray scattering (SAXS) has been widely applied to study the structural information about the process of nucleation and crystallization of organic molecules and noble metal nanoparticles from solution [16,17]. This technology has also been used to study the effect of addition of TiB_2 particles on the melt structures of Al-15 wt.% Cu [18]. In this article, we report a preliminary SAXS study of Al-18 wt.% Cu melt under different UST conditions and

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http://dx.doi.org/10.1016/j.scriptamat.2015.04.011
1359-6462/

analyzed data on the characteristic structural parameters of the non-uniformities which can cause scattering, known as scatterers in the melt.

The material used in experiments was Al-18 wt.% Cu alloy of a liquidus temperature of 611.3 °C determined by differential scanning calorimetry. The as-cast alloy ingot was cut into a thin slice of 15 × 10 × 1.8 mm (height × width × thickness) with surfaces cleaned and embedded in an open-top cell sealed with two alumina plates of a thickness of 0.15 mm. The obtained sample was then sandwiched between two small heating plates with a hole of 10 × 4 mm (height × width) to allow the light to penetrate and installed in a specially designed miniature hot-stage (105 × 105 × 48 mm) mounted on a bracket with an upright column. The transducer and the ultrasonic horn with a radiation face of 3 × 1 mm (width × thickness) can be descended into the sample from the open top along an guide rail via an step drive numerical control instrument. The horn was made of titanium alloy (Ti-6 wt.% Al-4 wt.% V). The schematic view of the experimental setup is shown in Figure 1.

Small angle X-ray scattering measurements were carried out at the BL16B1 beamline of Shanghai synchrotron radiation facility (SSRF), China. The samples were first heated to 680 °C in the hot-stage and isothermally held for 30 min under an argon atmosphere to ensure complete melting, then slowly dropped to specified temperatures of different overheating degrees above the liquidus at a rate of 1 °C per minute. The ultrasonic horn, which had been preheated in the hot-stage, was moved downwards into the sample to an immersion depth of 5 mm and a continuous imposition of ultrasound treatment for 1 min was made. To avoid excessive titanium dissolved into the melt, the ultrasonic horn was withdrawn from the melt immediately after the UST. Simultaneously, two dimensional scattering data were collected by a 2D MarCCD165 detector (2048 × 2048 pixels with a pixel size of 80 μm) where X-rays of energy 17 keV (wave length $\lambda = 0.729$ Å) were transmitted through the sample. The beam was focused to a size of approximately 0.5 × 0.5 mm and the scattering position was targeted to a distance of about 8 mm below the radiation face to avoid scattering noise caused by possibly survived cavitation bubbles. The sample to detector distance was 2110 mm, accessing a q value ranging between 0.1 and 3 nm^{-1}. Here q is the magnitude of the scattering wave vector defined as $q = (\frac{4\pi}{\lambda})\sin(\frac{\theta}{2})$ and θ is the scattering angle. The accumulated time for each measurement was 20 min due to an intensive X-ray absorption by the near 2 mm thick sample. Background subtractions were conducted using the collected data of an empty cell.

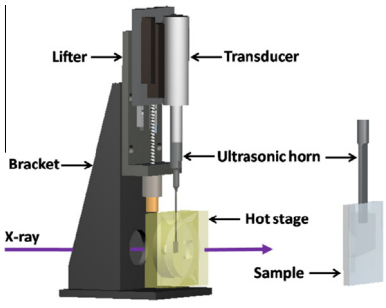

Fig. 1. Schematic graph of the ultrasonic treatment system (left) and experimental sample (right) used for SAXS. All the control systems for heating, movement and ultrasound collected to the setup via different cables are not shown here.

Scattering data analysis is based on an assumption that spherical scatterers are well dispersed in the melt. The scattering intensity I from a set of monodispersed particulates obeys [16,19]

$$I = \gamma n(\Delta\rho)^2 \int_0^\infty P(R)\left[\frac{4\pi R^3}{3}\text{Ø}(qR)\right]^2 dR, \quad (1)$$

$$\text{Ø}(qR) = \frac{3}{(qR)^3}[\sin(qR) - (qR)\cos(qR)], \quad (2)$$

where R and n are the radius and total number of spherical particles respectively; $P(R)$ is a normalized size distribution function describing a number density of particles with radius R; $\Delta\rho$ is an electron density difference of the scattering objects to the surround matrix, and γ is a constant independent of q and R. Here $P(R)$ is a presumed Gaussian distribution [20]

$$P(R) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(R-R_0)^2}{2\sigma^2}\right), \quad \int_0^\infty P(R)dR = 1, \quad (3)$$

where R_0 is the mean size and σ is the standard deviation. Eqs. 1–3 were best fitted by the scattering data to get the parameters R_0 and σ of certain Gaussian distributions and n of the total number.

To further reveal the geometrical features of the scattering structure in the melt, the fractal dimension α was determined from its scattering profile according to a power law form [21]

$$I(q) = q^{-\alpha}, \quad (4)$$

where exponent α is obtained by calculating the slope of the $\ln(I) - \ln(q)$ curve in the linear region. Depending on the value of the exponent α, it is possible to distinguish whether we have mass or surface fractals or just non-fractals. If $1 < \alpha < 3$, the scatterers show mass fractals which are weakly branched polymeric systems and the mass fractal dimension $D_m = \alpha$; while if $3 < \alpha < 4$, the scatterers show surface fractals which are uniformly dense but have a rough surface and the surface fractal dimension $D_s = 6 - \alpha$. Generally, surface roughness increases with D_s. Specially, if α equals 4 there are non-fractal structures with smooth interfaces.

Before SAXS experiments, the synchrotron radiation X-ray imaging of solidification processes of Al–Cu samples with and without UST had been conducted on the BL13W1 beamline of SSRF. The detailed parameters for X-ray imaging, such as the energy, beam flux, and acquisition rate, were same as adopted in a previously published article [15] for imaging cavitation bubbles. The amplitude of vibrations was about 70 μm based on measurement from X-ray imaging photos and the ultrasonic intensity was determined as 460 MW m^{-2}.

Figure 2 shows X-ray imaged video frames of Al–Cu melt at 625 °C without (Fig. 2a) and with UST (Fig. 2b) and the corresponding solidified structures after 20 min isothermal holding (Fig. 2c–d), respectively. Violent cavitation can be observed in the super-heated melt as ultrasound applied. As expected, a significantly refined solidified structure formed after UST, indicating that cavitation can induce nucleation sites in the melt and their potential for