Journal of Thermal Analysis, Vol. 49 (1997) 1277-1281

SUPERCOOLING MEASUREMENT IN W, Ta, Nb AND Re LIQUID METALS BY STEREOPHOTOCALORIMETRIC METHOD

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Abstract

The technique of crystal growth coupled with a stereophotocalorimetric method has been used in a series of supercooling measurements on pure refractory metals. The cooling history of these metals is recorded on photographic films which are calibrated as a function of the temperature. High absolute amounts of supercooling has been observed in W, Ta, Nb and Re liquid droplets. It is noted that the brightness traces of the solidification process for highly supercooled Re droplets evidence of two successive phase transformations (Re cfc to Re hc) shows.

Keywords: dendritic crystal growth, nucleation, supercooling

Introduction

The supercooled behavior of the materials has been of interest for many years because the amount of supercooling the material sustain plays a major role in its solidification process. It determines not only growth velocity but also phase selection and formation of metastable phases. To study this state of the material, various techniques have been employed by metallurgists.

If nucleation can be supressed or at least drastically reduced a fluid can be cooled below its melting temperature T_m maintaining the liquid phase. This phenomenon is called supercooling and the degree of supercooling is given by $\Delta T = T_m - T^-$ where T^- is the nucleation temperature. The supercooled melt is a metastable state and the first step of the phase transition is known as nucleation. This phenomenon may occur at T^- by either a heterogeneous or a homogeneous process. In the first process the catalysts can be extraneous interfaces such as impurities, container walls, etc. The limit of liquid supercooling corresponds to homogeneous nucleation. The critical supercooling necessary for homogeneous nucleation was originally believed to be approximately equal to about 0.2 T_m of the metal in absolute scale [1]. However more recent experiments of dispersed droplets of low melting point alloys have shown that undercooling in excess of 0.3 T_m can be reached prior to nucleation [2].

Supercooling plays a major role in any solidification process. In fact, it is the driving force for solidification and determines not only the growth velocity but also

0368–4466/97/ $ 5.00

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phase selection and formation of metastable phases which offer a wide variety of useful properties that may differ markedly from realised those a material solidified close to equilibrium conditions. Several studies have been in this field [3, 4]. In order to put the term metastable state into the right perspective, it may be worthwhile to recall that diamond is such a state of carbon. The techniques to solidify liquid metals and alloys at large supercooling, such as small droplets processing and rapid quenching have been improved greatly in recent years. Consequently, the problem to clarify the necessary degree of supercooling for the formation of alternative phase is becoming increasingly important.

Experimental procedure

The apparatus used in this study of supercooling measurement in refractory liquid metals, is shown schematically in Fig. 1 and it is composed in two complementary parts.

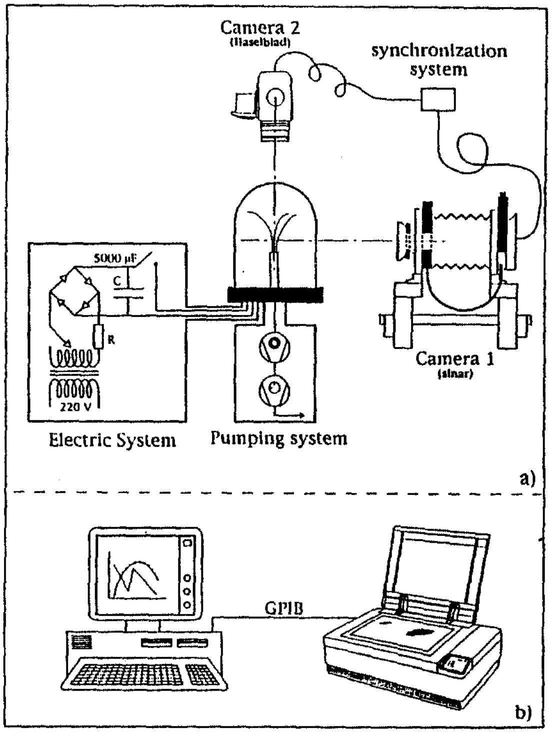

Fig. 1 Schematic arrangement of the apparatus a) System for production and record of the droplets; b) System for analysing images

i) The dendritic crystal growth system in which high purity wire from goodfellow (diameter in the range 0.2 to 0.4 mm) was transformed into dendritic crystal

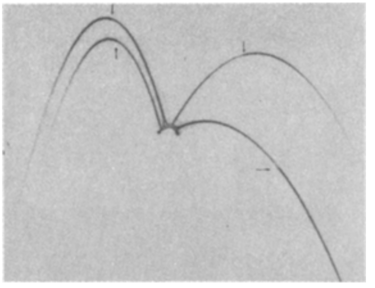

Fig. 2 Photographic record of the light emitted by free-falling tantalum droplets

spheres by the technique of capillary and pinch instability used previously by Meyer and Rinderer [5]. This technique involved a wire sample about 1 cm length, attached to electrodes inside a chamber filled with helium gas. The electric system was composed of a transformer which charges a condenser of large capacity. For certain values of the applied discharge, the wire is overloaded and liquified by the electric current produced. The wire is divided into liquid spheres which are then ejected into the space of the chamber. The variation of emitted light of the droplets recorded on negative films as is shown in Fig. 2, states that these droplets are cooled by radiation and convection in the helium gas. The observed recalescence phenomenon indicated by arrows in Fig. 2 is ascribed to the rapid freezing of the liquid droplet (6).

ii) Images analysis

The obtained films which contains brightness traces of droplet's solidification are transferred to computer by digitalisation process, where each droplet can be analysed by determination of the optical density attributed to these brightness traces is used here for analysing the rapid solidification of these supercooled liquids. From the calibration of the films agains temperature (Optical Density *vs.* temperature) the temperature of the droplet before, during and after rapid solidification can be obtained. We can also establish the cooling history of this droplets when the positions of their free-fall parabolic trajectory are converted into instants of time [12].

Results

A-Maximum supercooling

When analyzing the brightness traces of solidification of the droplets and using calibration curve, it was found that the temperature of the droplet can be determined at each position of its trajectory before, during and after the rapid recalesence. From the graph presented in Fig. 4, it is easy to determine the nucleation temperature and the supercooling realized by the droplet. (W, $\Delta T=1022$ K; Ta, $\Delta T=1114$ K; Nb, $\Delta T=548$ K and Re, $\Delta T=1000$ K) which are the maximum supercoolings for this refractory metals.

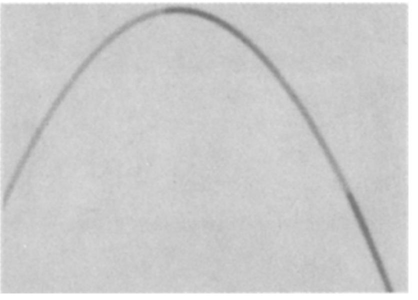

Fig. 3 Brightness trace during solidification of rhenium droplet. Two recalescence are observed. The moments of the liquid-solid and solid–solid transformation are indicated respectively by the arrows 1 and 2

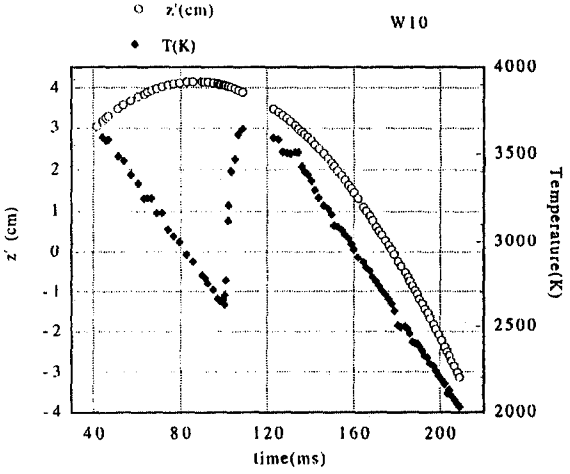

Fig. 4 Simultaneous representation of the temperature and the vertical positions of tungsten droplet *vs*. the instants of time during the flight. This graph permit observation of the cooling history and determination of the supercooling realised by the droplet

B-Double recalescence

In Fig. 3 we observe (arrows 1 and 2) on the brightness trace of solidification of Re droplet a double recalescence phenomenon. By using the calibration curve the evidence of two successive phase transformations Re cfc structure to Re hc structure can be noted. The identification of these structures are predicted by the Full Potential Linear Muffin-Tin orbitals method (FPLMTO) [7].

Conclusion

Application of the stereophotocalorimetric method to the study of supercooling of refractory metals leads to:

Determination of the cooling history of the droplets during their flight and then supercooling can be easily determined. A large supercooling was obtained in these metals.

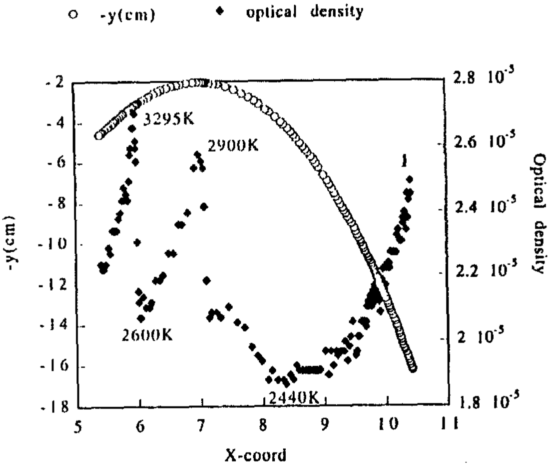

Fig. 5 Brightness trace the Re droplet during solidification process. Two recalescence are observed in this case which are associated with two successive phase transformation (Re cfc to Re hc)

A highly supercooled rhenium droplet shows evidence of two successive transformation phase (Re cfc to Re hc). The high supercooling of a liquid is favorable to the formation of metastable phases. In the case of Re the observed metastable phase during the solidification process is a transitory one.

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We thank the Fonds National de Recherche Scientifiques of Switzerland.

References

1 D. Turnbull and R. E. Cech, J. Appl. Phys., 21 (1950) 804.
2 J. H. Perepezko, D. H. Rasmussen, I. E. Anderson and C. R. Lopes, Jr., 'Solidification and casting of metals' Proceeding of an International Conference on Solidification, The Metals Society, 1979, p. 169.
3 C. M. Adams and R. E. Lewis, in Rapidly solidified crystalline alloys, Eds. S. K. Das, B. H. Kear and C. M. Adams, 1985, p. 157–83.
4 H. Jones, J. Mater. Sic., 19 (1984) 2043.
5 E. Meyer and L. Rinderer, J. Crystal Growth, 28 (1975) 199.
6 D. Houch, V. Soares and L. Rinderer, Mater. Sci. Forum, 179–1181 (1995) 747–752.
7 M. Methfessel, Phys. Rev., 38 (1988) 1537.