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Characterization of rapidly solidified Ni–Si and Co–Al eutectic alloys in drop tube

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ABSTRACT

Containerless solidifications of Ni–Si and Co–Al eutectic alloys were carried out using an 8 m drop tube. Molten alloy ejected into a drop tube was rapidly cooled and solidified during free fall. The microstructures of the rapid solidified alloys were evaluated. It was seen that the microstructures of Ni–Si and Co–Al eutectics change from the lamellar and plate-like eutectic to the anomalous eutectic and needle-like forms with decreasing the sample size, respectively. The values of the enthalpy of fusion and specific heat were determined by means of differential scanning calorimetry (DSC) during the transformation from liquid to the solid state. The microhardness of rapid solidified alloys was measured by using a microhardness test device. According to the present measurements, the values of microhardness (HV) for rapid solidified Ni–Si and Co–Al eutectics alloys increase with decreasing the eutectic spacing.

1. Introduction

Non-equilibrium solidification provides possibilities to produce metastable phases with novel properties, and to broaden the study of solidification fundamentals such as nucleation and growth mechanisms, phase morphologies and interfacial stability [1]. Rapid solidification of metallic materials under high undercooling or cooling rate conditions can be accomplished by several ways, such as the glass-fluxing method [2–5], rapid quenching [6], spray atomization [7], electromagnetic levitation processing [8,9], drop-tube technique [10], melt-spinning [11], surface treatment [12], etc. The drop-tube technique combines the condition of reduced gravity during free fall with high undercooling and rapid cooling compared with the other methods.

Consequently, the drop tube is often used for investigating the kinetics of containerless rapid solidification processes [10,13] and can provide a containerless and reduced gravity environment for a short period of time of about one second, when a liquid alloy drops freely. In such a way, heterogeneous nucleation on container walls usually present in solidification of liquid material is completely eliminated. The liquid undercools below the equilibrium melting temperature prior to solidification. During such conditions, the undercooled melt solidifies far from equilibrium. The as-solidified material is, therefore, in metastable state leading to microstructure refinement, metastable phase formation, solid solubility extension, metallic glass formation and segregation-free solidification.

Eutectic alloys are the basis of most casting alloys. Research initially focused on materials for high-temperature structural applications, but it was soon broadened to non-structural materials for electric, magnetic, and optical applications [14]. Ni based alloys canters on their potential as new high-temperature structural materials with high melting point, good oxidation resistance and excellent high-temperature mechanical properties. Although cobalt-base alloys are not as widely used as nickel and nickel-base alloys in high-temperature applications, cobalt-base high-temperature alloys nevertheless play an important role, by virtue of their excellent resistance to sulfidation and their strength at high temperatures.

Until now, a small number of researches have been carried out on the characterization of Ni–Si and Co–Al eutectic alloys obtained by rapid solidification techniques. In the present study, Ni–Si and Co–Al eutectic alloys were containerlessly solidified in an 8 m drop tube. It was expected that the molten alloy would be undercooled and then solidified containerlessly during the free fall. The microstructures and constituent phases of the processed samples were examined. The values of the enthalpy of fusion (ΔH) and the specific heat (C_p) for determination of cooling rates were also calculated and the relationships between the microstructure and the microhardness were found.

2. Experimental procedure

Ni-21.4 at.% Si and Co-20 at.% Al eutectic alloys were prepared by arc-melting method using high purity elements (>99, 99%) under argon atmosphere. In order to compensate for mass loss during melting, an extra mass of 0.1% was added for Al, Ni, Si and Co. Fig. 1

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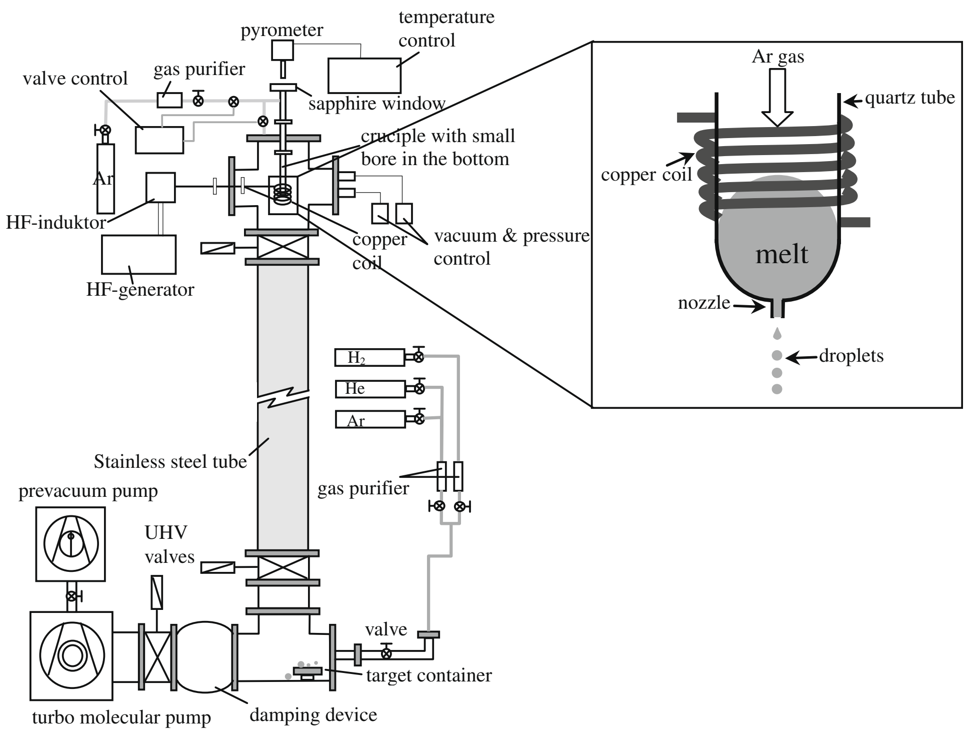

Fig. 1. Schematic illustration of the drop tube.

shows the schematic drawing of the drop tube used in the present experiment, the free-fall length of which is 8 m. An alloy of 1 g was placed in a quartz tube with an orifice of 0.5 mm in diameter at its bottom. The quartz tube was placed in a copper coil fixed at the top of drop tube [15–17]. After evacuation to a pressure in the order of 10^{-4} Pa, the drop tube was backfilled with pure helium (99.999% purity) up to a pressure of about 50 kPa. The temperature of the sample in the crucible before dispersion was measured by an infrared pyrometer. The alloy was inductively melted, and heated to a temperature of 100–200 K above its melting point. The melt was ejected through the nozzle by an argon gas pressure into the quartz tube, and diameter of droplets was atomized into ranging from 100 to 1000 μm. The ejected liquid alloy stream dispersed into droplets, which rapidly solidified during free fall into the drop tube. The spherical as solidified samples were collected at the bottom of the drop tube and classified into several size groups according to their diameter from 100 to 1000 μm. More details on the drop-tube technique and the evaluation of such experiments are given elsewhere [17].

The particles of each group size were mounted in an epoxy resin. The samples were ground flat with 320, 500, 1000, 2400, 4000 grit SiC paper, and polished with 6, 3, 1, 0.25, 0.05 μm diamond paste. Finally the Ni–Si and Co–Al eutectic samples were etched with suitable acid solutions (97 ml HCl, 2 ml H_2SO_4, 1 ml HNO_3 for Ni–Si eutectic; 96 ml H_2O, 2.5 ml HNO_3, 1.5 ml HF for Co–Al eutectic) for 10 s. After metallographic process, the microstructures of samples were characterized using an Olympus BX-51 optical microscopy and LEO scanning electron microscopy (SEM).

3. Results and discussion

In drop tube, a liquid jet of material is produced that disperses into many small droplets [1]. Droplets of size ranging from 100 to 1000 μm are formed. In particular, the cooling rate and the undercooling are higher in samples with a smaller diameter compared to larger droplets. Therefore, it is crucial to investigate the influence of the sample size on the microstructure formation.

The cooling rate of the falling droplets can be calculated on the basis of the heat transfer to the environment by heat radiation and thermal conductivity in the environmental gas. The heat balance of a falling drop is given by

$$\Delta H + \Delta Q = 0, \tag{1}$$

where ΔH is the heat content of the sample and ΔQ is the heat transferred from the sample to the environment. The heat content of the liquid drop can be written as

$$\Delta H = V\rho C_p \delta T, \tag{2}$$

where V is the volume of the droplet with diameter D, ρ is the mass density of the melt, C_p is the specific heat of the liquid and δT is a temperature difference. The heat flow (dQ/dt) through the surface of the droplet ($A = \pi D^2$) is determined by radiation of heat and heat transfer to the environmental He-gas of pressure of 1000 mbar:

$$\dot{Q} = \frac{dQ}{dt} = A[h(T - T_0) + \varepsilon\sigma(T^4 - T_0^4)], \tag{3}$$

where A is the surface area of the droplet, h is the heat-transfer coefficient for heat conductivity in the gas, T is the droplet temperature during free fall, T_0 is the ambient temperature (room temperature), ε is the surface emissivity and σ is the Stefan–Boltzmann constant. The heat transferred to the environment during the time from the formation of the drop ($t = 0$ s) until nucleation sets in ($t = tn$) is given by

$$\Delta Q = \int_0^{tn} \dot{Q} dt. \tag{4}$$

For an average cooling rate, $\dot{T} = -dT/dt$, which is supposed to be constant, the integral of Eq. (4) can be replaced by

$$\Delta Q = \frac{1}{\dot{T}} \int_0^{tn} \dot{Q} dt. \tag{5}$$