# Rapid Solidification Characteristics of Highly Undercooled Liquid Ni-Cu-Mo-Ge Quaternary Alloy under Electromagnetic Levitation Condition

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***Abstract*—The dendritic growth characteristics of undercooled liquid Ni-5%Cu-5%Mo-5%Ge quaternary alloy were investigated by electromagnetic levitation method. The measured dendritic growth velocity of α-Ni phase increases with undercooling according to a power law relation, which attains a value of 28 m/s at the maximum undercooling of 321 K (0.19$T_L$). The microstructure morphology appears as coarse dendrites at small undercoolings, while it is refined into equiaxed grains at substantial undercoolings. Furthermore, all the solute elements Cu, Mo and Ge exhibit a significant solute trapping effect during rapid dendritic growth.**

***Keywords-dendritic growth; high undercooling; solute trapping.***

## I. INTRODUCTION

Rapid dendritic growth within highly undercooled liquid alloy has aroused great research interest, which significantly influences the microstructures, solute distribution and application performances of alloys[1-5]. The dendritic growth velocity is an important and fundamental parameter for revealing nonequilibrium solidification process and controlling the alloy properties[6-10]. High dendritic growth velocity results in the remarkable solute trapping and almost segregationless solidification according to rapid solidification studies of binary alloys[11, 12]. However, the investigations about dendritic growth of alloys mainly focused on pure metals and binary alloys[13-17]. Experimental studies of rapid solidification for multicomponent alloys are scarce and the mechanism of interactions between different solutes is still unclear. It is desirable to perform the systematic study about the rapid solidification of multicomponent alloys.

Based on the previous study of ternary Ni-5%Cu-5%Mo alloy[18], semiconductor element Ge is chosen to form a Ni-5%Cu-5%Mo-5%Ge quaternary alloy in order to explore the dendrites growth mechanism and different segregation profiles of three solute elements.

## II. EXPERIMENTAL PROCEDURE

Ni-5%Cu-5%Mo-5%Ge quaternary alloy samples were prepared from 99.99% Ni, 99.999% Cu, 99.97% Mo and 99.9999% Ge by arc melting under an Ar atmosphere and the mass of each melted sample is about 0.8 g. All rapid solidification experiments were performed in a vacuum chamber evacuated to a pressure of $10^{-5}$ Pa, then backfilled with a mixture of He and Ar gases in the volume rate of 1:1. The alloy sample was containerlessly melted in the center of the electromagnetic levitation coil, as shown in Figure 1. Its temperature was monitored by a Raytek Marathon MR1S infrared pyrometer. By cooling with He gas which was refrigerated by liquid nitrogen, the liquid alloy sample achieved substantial undercooling. The dendritic growth velocity was determined by a photodiode device.

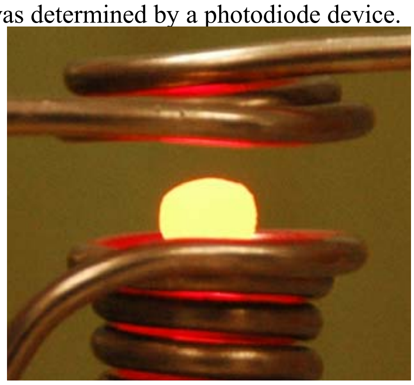


Figure 1. Electromagnetic levitation of an alloy sample

After rapid solidification experiments, the samples were sectioned, polished and etched with chromotropic acid. The phase constitution, microstructure and solute distribution were analyzed by a Rigaku D/max2500 x-ray diffractometer, a Zeiss Axiovert 200 Mat optical microscope and an Oxford INCA Energy 300 energy-dispersive spectrometer. The equilibrium phase transformation characteristics were determined by a Netzsch 404C differential scanning calorimeter.

## III. RESULTS AND DISCUSSION

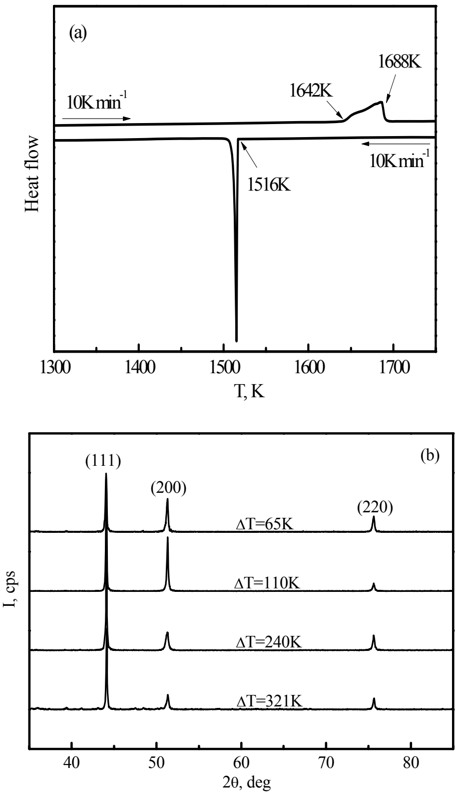



Figure 2. DSC curve (a) and X-ray diffraction patterns (b) of Ni-5%Cu-5%Mo-5%Ge alloy with different undercoolings

Thermal analysis and X-ray diffraction analysis were carried out to determine the phase constitution of Ni-5%Cu-5%Mo-5%Ge alloy. The DSC curve of this alloy is presented in Figure 2(a). It illustrates that there is only one peak during melting or solidification process, which indicates that one phase transformation occurs. Furthermore, the liquidus temperature is determined to be 1688 K. The undercooling obtained under 10 K/min cooling velocity condition is 172 K, it is slightly smaller than 202 K which is obtained in the thermal analysis of Ni-5%Cu-5%Mo alloy under the same condition[18]. Figure 2(b) shows the diffraction patterns of four samples prepared at 65, 110, 240 and 321 K undercooling. All four diffraction patterns are quite similar to that of pure Ni even when the undercooling reaches 0.19$T_L$. A tiny offset of the diffraction peaks compared with pure Ni is detected because of the extended solubility of Cu, Mo and Ge elements. Therefore, it can be confirmed that no new metastable phase exists and the samples are composed of a single α-Ni solid solution phase.

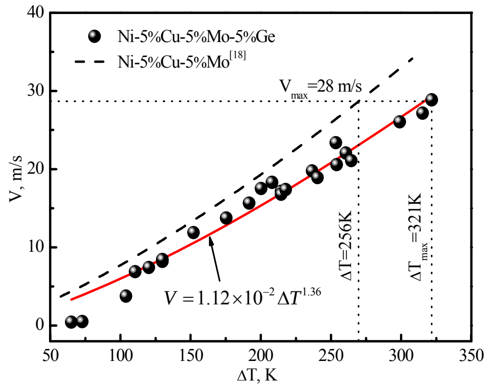
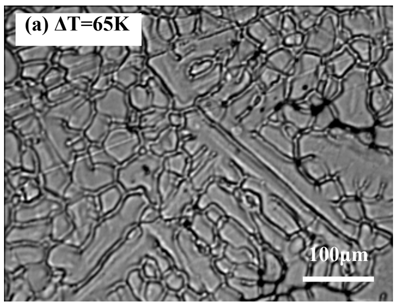



Figure 3. Dendrite growth velocity of α-Ni phase as a function of undercooling

Figure 3 presents the dendritic growth velocity of α-Ni phase measured at different undercoolings. It shows a power relation to undercooling $\Delta T_L$, which can be described as:

$$V = 1.12\times10^{-2}\Delta T^{1.36} \text{ m/s.} \quad (1)$$

At the maximum undercooling of 321K (0.19$T_L$), the growth velocity attains 28 m/s. Whereas the growth velocity of α-Ni phase in Ni-5%Cu-5%Mo alloy attain the value of 28 m/s at the undercooling 256 K. Therefore, the introduction of Ge remarkably decreases the dendritic growth velocity.



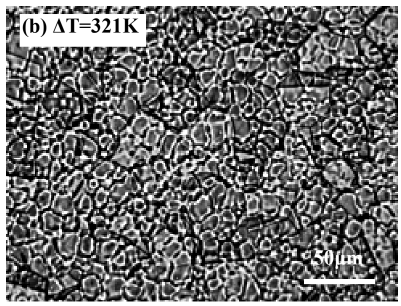



Figure 4. Microstructure characteristics of undercooled Ni-5%Cu-5%Mo-5%Ge alloy at (a) 65K and (b) 321K undercoolings.

The typical microstructures of Ni-5%Cu-5%Mo-5%Ge alloy are illustrated in Fig. 4. Figure 4(a) displays that the microstructure is characterized by coarse dendrites when the samples are solidified at a low undercooling of 65 K. At high undercoolings, the microstructural morphology transforms from dendrites to equiaxed grains with a grain refinement effect, as shown in Figure 4(b).

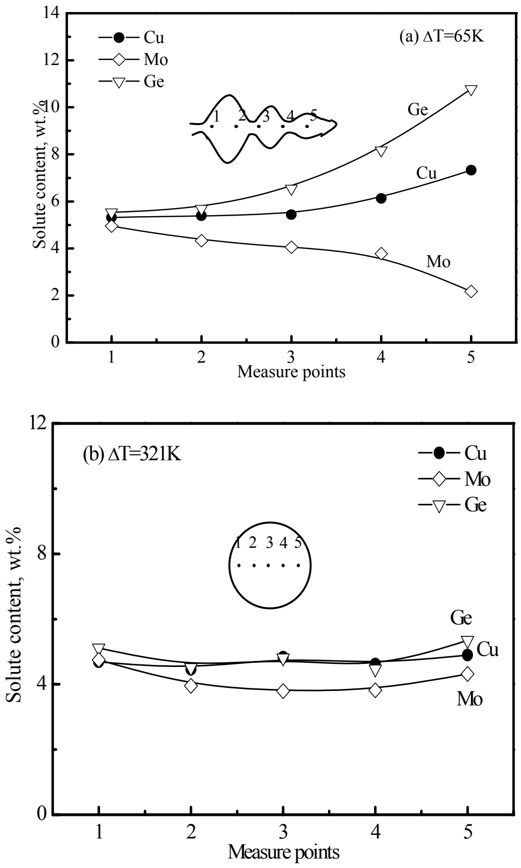



Figure 5. Solute distribution in the samples undercooled by (a) 65 K and (b) 321 K

The solute distributions of Cu, Mo and Ge inside the α-Ni solid solution phase were investigated by EDS analysis, as shown in Figure 5. In the center of primary dendrite trunk obtained at low undercooling of 65 K, the solute concentration of Ge is larger than that of Cu. Both of them are larger than the original composition and increase along the growth direction of the primary dendrite trunk. Meanwhile, the solute concentration of Mo is smaller than the original composition and decrease along the primary dendrite trunk. The solute distributions of Cu and Mo in this quaternary alloy are opposite with those in Ni-5%Cu-5%Mo alloy in which the solute concentration of Cu is smaller than that of Mo. This is mainly due to the addition of Ge which has different interactions with Cu and Mo.

With the rise of undercooling, the solute trapping effect becomes more remarkable. Figure 5(b) reveals that the concentrations of Cu, Mo and Ge are close to the original composition at the maximum undercooling of 321 K. All solute distributions are quite uniform and microsegregation can be hardly detected in the equiaxed grains.

## IV. CONCLUSIONS

The high undercooling state of liquid Ni-5%Cu-5%Mo-5%Ge alloy was achieved by electromagnetic levitation method. The maximum undercooling in the experiments was 321 K ($0.19T_L$). At such a substantial undercooling, no new metastable phase exists and the samples are composed of a single α-Ni solid solution phase. Its dendritic growth velocity increases with undercooling by following a power law relation. The measured maximum growth velocity is 28 m/s. As compared with Ni-5%Cu-5%Mo alloy, the introduction of solute Ge remarkably decreases the dendritic growth velocity of α-Ni phase. The solidified microstructure is mainly characterized by a morphological transition from coarse dendrites to equiaxed grains with the rise of undercooling. The rapid dendritic growth results in remarkable solute trapping effect for all the three solute elements and segregationless solidification was almost achieved.

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