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Numerical simulation on rapid melting and nonequilibrium solidification of pure metals and binary alloys①

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[Abstract] A heat and mass transfer modelling containing phase transformation dynamics is made for pure metals and binary alloys under pulsed laser processing. The nonequilibrium effects of processing parameters and physical properties are evaluated on the melting and solidification of pure metals (Al, Cu, Fe and Ni) and Al-Cu alloys. It is shown that the energy intensity of laser beam and physical properties of metals and the solute concentration of alloys have important effect on the interface temperature, melting and solidification velocity, melting depth and non-equilibrium partition coefficient. This situation is resulted from the interaction of heat transfer, redistribution of solute, solute trapping and growth kinetics.

[Key words] rapid melting; nonequilibrium solidification; pulsed laser processing; heat and mass transfer; growth kinetics

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1 INTRODUCTION

High intensity laser surface processing has become one of the important technologies for the fabrication of new materials and the improvement of their microstructure and properties. Most of the benefits of the laser processing are due to the rapid melting of the surface and then the non-equilibrium solidification. The classical assumption of local thermodynamic equilibrium becomes invalid because of the large interface growth velocity introduced by the large kinetics driving force (the interface undercooling)[1]. In that case, the interface attachment kinetics, which is assumed to be very fast in traditional (equilibrium) solidification analysis, would become a limiting factor in rapid solidification process. So far as present, large experimental investigations have been conducted on the microstructure and properties of the materials processed by laser technique[2~4]. Some theoretical modellings have also been done on the mass and heat transfer during the rapid solidification process on the basis of the equilibrium or nonequilibrium phase transformation[5~8]. Takeshita et al[9] and Simon B et al investigated the formation of molten pool and its correlation with the solidification process during laser surface and electron beams melting. However, relatively few works have been focused on the interaction among the heat transfer mass, the nonequilibrium melting and solidification kinetics. In this paper, the authors present a complete theoretical model of rapid melting and non-equilibrium solidification under pulsed laser processing. The influences of various parameters, such as substrate materials, energy intensity of laser beams, and concentration of solute on the solidification interface temperature, growth velocity and partition coefficient are also discussed.

2 THEORETICAL FORMULATION

Now one considers a metallic plate under the pulsed laser processing. The physical properties do not change during the heating and solidification. When the plate is radiated by laser beam, the surface temperature of plate begins to increase. Melting process occurs when the temperature reaches the melting point. The longer the radiating time, the larger the melting depth. When the radiation finishes, the melting process of metal will keep for a certain time due to the superheat in the melt. The melting process terminates when the equilibrium of the heat flux occurs at the interface. Then the re-solidification process begins. It can be seen that the melting and solidification process caused by pulsed laser radiation is a complicated problem that involves moving interface and rapid heat and mass transfer. In order to simplify the analysis, the following hypotheses are made.

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1) The metal is an infinite big plate. 2) The distribution of laser energy is uniform on the surface of metal. The laser beam is static. The heating surface is infinitely large as compared with the melting thickness. 3) The melting pool is very shallow, in which there is only diffusion of atoms and no convection effect is considered. 4) The liquid/ solid interface during the melting and solidification process is planar. There is no homogenous nucleation in the melt. With the above assumptions, this melting and solidification can be simplified to be a one-dimensional problem.

For binary alloys, the controlling equations of heat and mass transfer are expressed as

$$\frac{\partial T_j}{\partial t}=\frac{\partial}{\partial y}\left(\alpha_j\frac{\partial T_j}{\partial y}\right) \tag{1}$$

$$\frac{\partial C_j}{\partial t}=\frac{\partial}{\partial y}\left(D_j\frac{\partial C_j}{\partial y}\right) \tag{2}$$

where T is temperature; C is the concentration of solute; D is diffusion coefficient; the subscripts refers to liquid or solid.

The controlling equations are subjected to the following initial and boundary conditions:

$$q=q_0 \qquad t\leq\Delta t \qquad y=0 \tag{3}$$

$$q=0 \qquad \Delta t\leq t \qquad y=0 \tag{4}$$

$$T=T_0 \qquad y=S \tag{5}$$

where Δt is the radiation time; S is the thickness of the substrate.

The energy and mass balance conditions must be satisfied at the solid/ liquid interface:

$$\rho L v_i=\lambda_S\frac{\partial T_S}{\partial y}\bigg|_i-\lambda_L\frac{\partial T_S}{\partial y}\bigg|_i \tag{6}$$

$$(C_L^i-C_S^i)\frac{dY_i}{dt}=D_S\frac{\partial C_S}{\partial y}\bigg|_i-D_L\frac{\partial C_L}{\partial y}\bigg|_i \tag{7}$$

where L is fusion heat; v_i is interface velocity; C_L^i, C_S^i are concentrations in liquid and solid at the interface; ρ is density; λ is conduction coefficient; i refers to the interface.

Besides the energy conservation equations at the interface shown above, additional interface conditions are needed to complete the description of nonequilibrium melting and solidification. A well-known kinetics relationship was proposed by Turnbull and Jackson[10] based on collision-limited growth theory:

$$v_i=\beta(D_0/\delta)\exp\left(-\frac{\Delta G_{am}}{\kappa T_i}\right)\cdot\left[-\frac{\Delta H_M\Delta T_i}{\kappa T_i T_M}\right] \tag{8}$$

where D_0 is self-diffusion coefficient of melt; δ is the thickness of interface and is equal to the diameter of molecular; ΔG_{am} is the activation energy for the molecular migration; ΔH_m is the fusion heat; T_i and ΔT_i are the temperature and undercooling at the interface; β is a factor introduced by Cahn[11] to account for molecular diffusion across the interface and reorientation of asymmetrical molecule. This factor is often taken to be 1. κ is the Boltzmann constant, and T_M is the equilibrium melting point.

For small and medium undercooling, equation can be approximated by

$$v_i=K_M\Delta T_i \tag{9}$$

where the linear kinetics coefficient K_M is defined by

$$K_M=\exp\left(-\frac{\Delta G_{am}}{\kappa T_m}\right)\frac{\beta D_{LM}\Delta H_M}{\delta\kappa T_M^2} \tag{10}$$

For binary alloy, the interfacial kinetics relationship is expressed as

$$v_i=K_M(T_m+m_L C_L^i-T_i) \tag{11}$$

the liquidus slope m_L for the nonequilibrium solidification is given by[12]

$$m_L=m_L^e\left[1+\frac{k_e-k\left[1-\ln\frac{k}{k_e}\right]}{1-k}\right] \tag{12}$$

In equation (12), nonequilibrium partition coefficient k is introduced. According to Aziz's continuous growth theory, k is expressed as[13]

$$k(v_i)=\frac{k_e+v_i/v_D}{1+v_i/v_D} \tag{13}$$

where v_D is characteristic diffusion velocity at interface.

3 RESULTS AND DISCUSSION

3.1 Melting and solidification of pure metal

Fig. 1 shows the dependence of interface velocity and temperature on the non-dimensional interface location during the process of melting and solidification under the condition of energy intensity $Q=2\times10^{11}$ W/m^2 and radiation interval $\Delta t=35$ ns. It is shown that the interface velocity and temperature increase rapidly at the initial stage of radiation. After they attain the maximum value, these parameters decrease obviously with the increase of melting depth for Al and Fe and keep for relatively long time for Cu and Ni. It can be seen that the interaction between the heat transfer and interface dynamics plays an important rule in the melting. At the initial stage, the flux of energy from surface to the interface is so high that the melting is limited by the interface dynamics. Heat resistance increases with increasing melting depth. The molecular migration becomes more easily, i. e the limiting effect of interface dynamics decreases, whereas the effect of heat resistance increases. This coupled effect of heat transfer and dynamics results in the occurrence of maximum melting velocity and interface temperature at the same time. After the melting velocity reaches the maximum value, the melting process is limited by heat transfer.

When solidification process begins, the interface

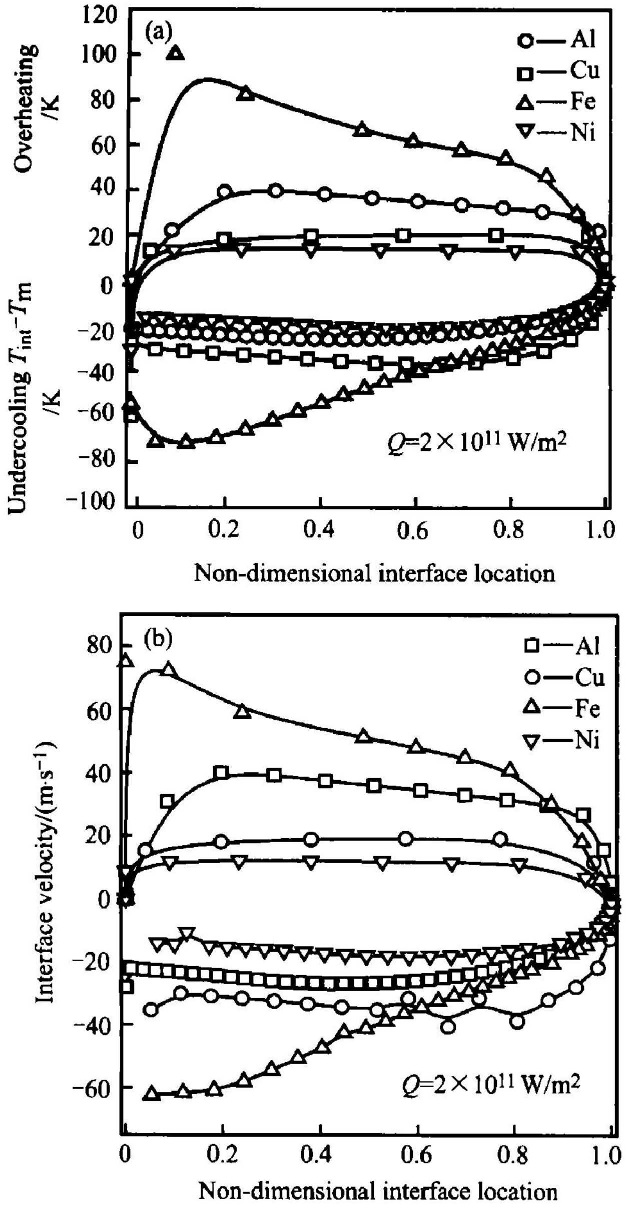

Fig. 1 Dependence of temperature(a) and interface velocity(b) on non-dimensional interface location for pure metals

velocity first increases to a maximum value due to the decrease of superheat. Because the temperature of substrate increases with the evolution of interface toward the surface, the interface velocity then decreases. The interface velocity increases again until the interface is near the surface. The interface temperature varies with the same situation as the interface velocity. It is easily understood that high undercooling is needed in order to maintain high solidification velocity because the linear kinetics relationship is used in the calculation.

It is seen that the physical properties have an obvious effect on the melting and solidification process. The superheating and solidification velocity of Al and Fe is higher than that of Cu and Ni during the melting. The undercooling and solidification velocity of Cu and Fe is higher than that of Al and Ni. The fusion heat of Fe is very low (only 1/26 of Al). These changes are caused by the interaction among heat transfer coefficient, fusion heat, melting point and growth kinetics. The absorbed heat is almost used to increase the temperature of melt. High interface undercooling is maintained because relatively small amount of heat is exhausted into the melt despite high solidification velocity. The effect of conduction coefficient is illustrated in the melting and solidification process of Cu. Because the conduction coefficient of Cu is very high, the fusion latent is easily conducted so that the interface velocity may be always high. For Al, although the conduction coefficient is high, the undercooling is low when compared with those of Fe and Ni because great amount of fusion heat is exhausted. Due to the low melting point, larger superheat of Al can be obtained than those of Cu and Ni.

3.2 Melting and solidification of binary alloy

Fig. 2 illustrates the dependence of interface

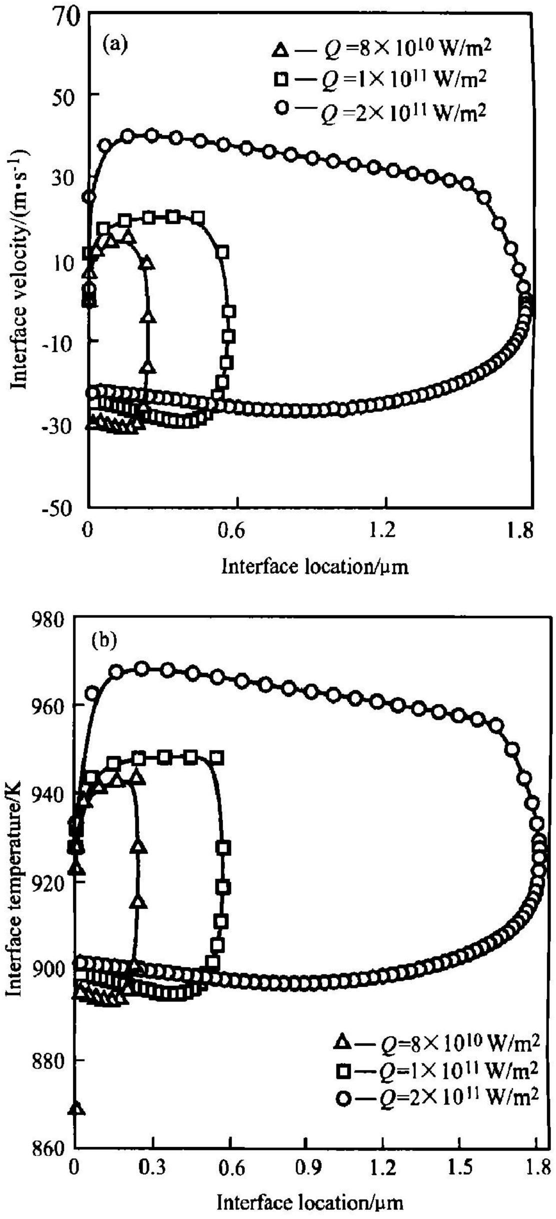

Fig. 2 Dependence of interface velocity(a) and temperature(b) on non-dimensional interface location for Al-2%Cu

velocity and temperature of Al-2% Cu on the non-dimensional interface location at the condition of energy intensity $Q = 2 \times 10^{11}$ W/m^2 and radiation interval $\Delta t = 35$ ns. It is known that the interface velocity and temperature of Al-Cu alloy changes in similar mode with that of pure metals. The lower the energy intensity of laser beam, the smaller the melting depth and maximum melting velocity and the larger the maximum solidification velocity. The correlation between the partition coefficient of Al-2% Cu alloy during the solidification process and non-dimensional location is shown in Fig. 3. The partition coefficient increases sharply at the initial stage of solidification. After the partition coefficient reaches the maximum value, it decreases slightly with evolution of solidification. The higher the energy intensity of laser beam, the lower the partition coefficient. The variation of solute concentration at the interface of Al-2% Cu alloy is shown in Fig. 4. It is seen that the solute concentration increases sharply with the rapid increase of interface velocity at the beginning of solidification. Then the solute concentration decreases with the interface moving towards the surface. When the interface is near the surface, the solute concentration increases again. From the above results, it can be seen that there is interaction among the heat and mass transfer, growth kinetics and solute trapping. The increase of solute concentration decreases the liquidus temperature, and the undercooling decreases correspondingly. The solute concentration is also affected by the non-equilibrium partition coefficient. The higher the non-equilibrium partition coefficient, the larger the solute trapping. Because the partition coefficient increases with decreasing energy intensity as shown in Fig. 3, the solute concentration increases with increasing energy intensity.

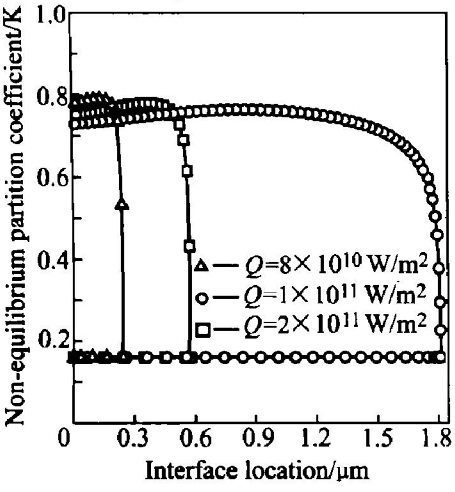

Fig. 3 Variation of non-equilibrium partition coefficient of Al-2% Cu alloy with interface location

The effect of composition on the interface velocity and non-equilibrium partition coefficient of Al-Cu alloys is shown in Fig. 5. The melting point decreases with increasing solute concentration. The effect of melting point on the melting process is not obvious during the radiation. When the radiation terminates, the melting process continues until the balance of the heat fluxes between the liquid and solid at the interface is attained. The higher the solute concentration, the higher the interface temperature and the melting depth. At initial stage of solidification, the higher the solute concentration, the larger the nonequilibrium partition coefficient and interface velocity. When the evolution of solidification is 1/5 of the whole melting depth, the nonequilibrium partition coefficient and the interface velocity decreases with increasing solute concentration. This situation is caused by the variation of temperature field and concentration field. At the beginning of solidification, the temperature gradient in melt of Al-5% Cu is higher than that of Al-2% Cu. Therefore the interface temperature of Al-5% Cu decreases more rapidly than that of Al-2% Cu. With the evolution of solidification, the effect of concentration field on the solidification process become more and more important. There is an accumulation of solute because the diffusion coefficient is not large enough to transfer all the solute from the interface. The maximum solute concentrations are 3.2% and 8.3% for Al-2% Cu and Al-5% Cu respectively. The diffusion velocity increases sharply because the concentration gradient increases. At the same time, the increase of solute concentration results in a decrease of undercooling and growth velocity at the interface.

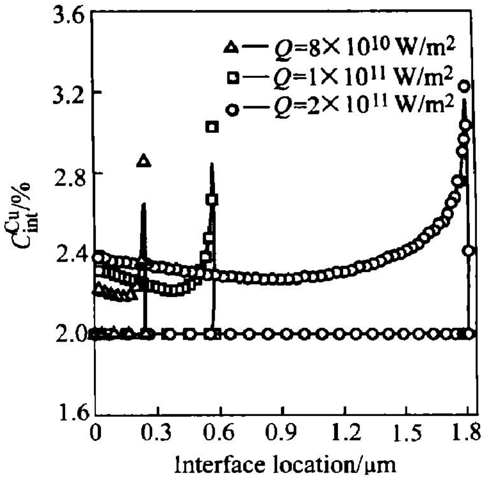

Fig. 4 Variation of solute distribution of Al-2% Cu alloy with interface location

4 CONCLUSIONS

1) The energy intensity of the laser beam and the properties of the base materials obviously affect

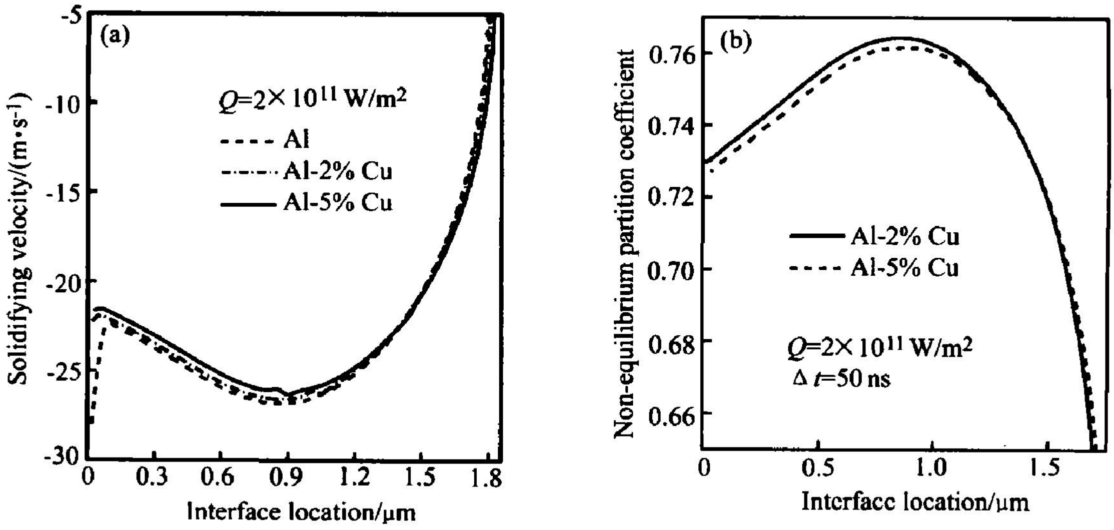

Fig. 5 Correlation of interface solidifying velocity (a) and non-equilibrium partition coefficient (b) with interface location for Al-Cu alloys

the remelting and solidifying velocity. The solidifying velocity is controlled by the energy intensity of the laser beam. The higher the energy intensity of laser beam, the lower the interfacial velocity and the higher the concentration accumulation of the solute at the interface.

2) During the initial stage of the solidification, the interfacial velocity and temperature vary drastically, which is caused by the interaction among the heat transfer, the redistribution or trapping of the solute and growth kinetics.

3) The initial concentration of the alloy can affect the interfacial temperature and velocity and redistribution of the solute. The higher the concentration of the solute, the higher the interfacial velocity at initial stage.

4) There is obvious solute trapping in the solidification process of Al-Cu alloys. The non-equilibrium partition coefficient in Al-2% Cu alloy is in the range of 0.7 to 0.8 under the condition of $Q = 8\times 10^{10}$ to 2×10^{11} W/m^2.

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