Journal of Alloys and Compounds 505 (2010) 108–112

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Application of differential thermal analysis to investigation of magnetic field effect on solidification of Al–Cu hypereutectic alloy

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ARTICLE INFO

Article history:
Received 19 January 2010
Received in revised form 7 June 2010
Accepted 9 June 2010
Available online 18 June 2010

Keywords:
Metals and alloys
Diffusion
Anisotropy
Thermoelectric
Thermal analysis

ABSTRACT

Investigation of solidification in the Al–25 at.%Cu hypereutectic alloy in magnetic fields has been carried out by differential thermal analysis (DTA). The DTA results indicated that the nucleation temperatures of primary Al_2Cu phases and Al–Al_2Cu eutectics were lowered and the rates of crystal growth including primary phases and eutectics were reduced although the melting of the alloy was almost not affected in magnetic fields of 6 T and 12 T in comparison with those without a magnetic field. The suppression of nucleation and growth of primary phases and eutectics might be mainly attributed to reduction of diffusion rates of atoms in a magnetic field on the condition of suppression of convections. Primary Al_2Cu phases oriented along a magnetic field compared with disorder ones without a magnetic field, which was caused by the magnetic anisotropy.

1. Introduction

Electromagnetic processing of materials (EPM) has been a cutting-edge technique and many novel phenomena have attracted numerous scientists ever since the commercial superconducting magnet became more easily available. It is extremely important for materials processing to investigate phase transformations in a magnetic field, during which the structures and properties of materials can be generally modified. A lot of reports on the effect of a magnetic field on phase transformations of ferromagnetic substances, e.g., Fe-based alloys [1–3], Bi–Mn alloys [4], have been given in the past decades because Gibbs free energies of ferromagnetic phases could be significantly changed upon applying a magnetic field. Although the magnetic energies of non-magnetic substances induced by a magnetic field are negligible so that their transformations seem not to be influenced by the magnetic field of the order of 10 T in thermodynamics, an amount of researches showed that solidification of non-magnetic substances which is one of the most common phase transformations was significantly affected in a magnetic field. Among those reports, Tewari et al. [5] found that the magnetic field caused the severe distortion of the cellular arrays in directionally solidified hypoeutectic Pb–Sn alloys. Rango et al. [6] proposed that texture materials could be prepared by solidification in a magnetic field based on magnetic anisotropy. Li et al. [7] found that a magnetic field induced the solidification of pure bismuth with increase of the magnetic field and a 12 T magnetic field raised solidification point by about 6 K. These studies fully demonstrated that solidification of non-magnetic substances might be affected by a magnetic field in other aspects, e.g. kinetics.

Thus, it is necessary to investigate phase transformations of non-magnetic substances in order to provide some useful information for materials processing in magnetic fields. Moreover, controlling structures and properties of materials by applying magnetic fields has been one of the objectives of many scientists in the field of EPM. In the present work, we performed DTA experiments for the Al–25 at.%Cu hypereutectic alloy in magnetic fields on the base of previous studies [8] and found that the applied magnetic field delayed the nucleation and growth of the primary phases and eutectics. Furthermore, possible mechanisms of nucleation and growth in the Al–Cu alloy in magnetic fields have been discussed.

2. Experimental details

The Al–25 at.%Cu hypereutectic alloy was prepared with pure Al (99.99 wt%) and pure Cu (99.99 wt%) in Ar atmosphere in an induction melting furnace. The melt alloy was cast to ingots, from which samples suitable for Al_2O_3 crucibles in DTA were obtained by spark machining. The samples in DTA runs were placed in the position of the maximum magnetic field and treated in high pure Ar atmosphere at constant heating and cooling rates between 2.5 °C/min and 7.5 °C/min in different magnetic fields. DTA tests were performed in a temperature range from room temperature up to 750 °C.

The experimental apparatus is schematically shown in Fig. 1, which consists of the superconducting magnet (Oxford Instruments), the DTA apparatus, a program controller, a computer and a model 2700 (Keithley Inc.). The magnet could produce a static magnetic field with the maximum strength up to 14 T. The DTA apparatus was described in detail in Ref. [8]. The program controller could make sure that the temperature linearly rises or lowers in the furnace. The Model 2700 and a computer could collect signals from the DTA apparatus.

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doi:10.1016/j.jallcom.2010.06.056

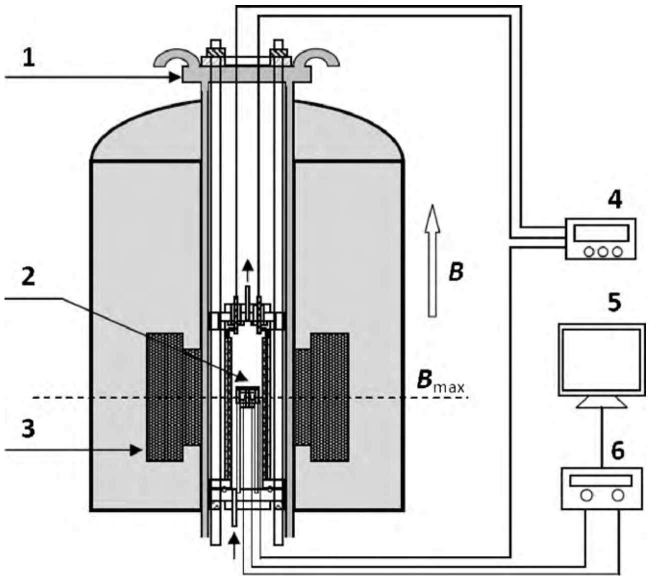

Fig. 1. Schematic illustration of the DTA apparatus in the superconducting magnet. 1: Water cooling jacket, 2: DTA apparatus, 3: Superconducting magnet, 4: Program controller, 5: Computer, 6: Model 2700.

The post-treated samples were sectioned along the longitudinal and transversal direction (parallel and perpendicular to a magnetic field, respectively.). Microstructures of the samples were examined in the etched conditions by an optical microscope.

3. Results and discussion

3.1. Analysis of nucleation and growth of primary Al_2Cu phases and eutectics

Fig. 2 shows DTA curves for the Al–25 at.%Cu hypereutectic alloy during the heating and cooling process in various magnetic fields. DTA curves for melting of the alloy at the heating rate of 5 °C/min in 0 T, 6 T, 12 T magnetic fields are indicated in Fig. 2(a). Two endothermic peaks can be clearly seen on each curve regardless of a magnetic field. The major peaks derive from melting of Al–Al_2Cu eutectics and minor ones are born of melting of primary Al_2Cu phases. Furthermore, all of the extrapolated onset temperatures T_{em} for melting of eutectics are equal to 551 °C within the experimental error of ±1 °C (The equilibrium melting temperature of Al–Al_2Cu eutectics is 448 °C). Hence, it is believed that the melting of Al–25 at.%Cu hypereutectic alloy is not affected by a magnetic field. As we know, the magnetic energy is expressed as $1/2\mu_0\chi H^2$, in which μ_0, χ and H is the vacuum permeability, magnetic susceptibility and magnetic field, respectively. For Al–Al_2Cu eutectics, the magnetic energy can be estimated to be of the order of 10^{-1} J/kg in a magnetic field with the order of 10 T provided that we take the following approximate value $\chi \approx 10^{-8}$ m^3/kg, which is negligible compared with specific heat of the alloy. Considering that the melting of crystals is generally determined by thermodynamic conditions, it is reasonable that the magnetic field with the magnitude of 10 T has almost no effect on melting of the alloy.

Nevertheless, DTA curves in Fig. 2(b) demonstrate that the solidification of the Al–25 at.%Cu alloy at the cooling rate of −2.5 °C/min has been markedly influenced in magnetic fields. From the curves, the extrapolated onset temperatures T_{ic1} and T_{ic2}, which stand for the nucleation temperatures of primary Al_2Cu phases and Al–Al_2Cu eutectics respectively, in a 12 T magnet field are significantly lower than those without a magnetic field. Additionally, two peak temperatures T_{pc1} and T_{pc2} shift to a lower temperature in 12 T magnetic field. Two extra sets of DTA experiments at other rates have been performed in order to confirm the above phenomena, showed in Fig. 3(c) and Fig. 3(d). Table 1 summarizes several parameters of crystallization for the Al–25 at.%Cu alloy in the DTA runs. It is explicitly learned that, on one hand, the nucleation temperatures T_{ic1} and T_{ic2} shift to a lower temperature in 6 T and 12 T magnetic fields, which thereby means that the nucleation of primary Al_2Cu phases and eutectics is suppressed by magnetic fields. Furthermore, the higher the magnetic field, the more noticeable the suppression. On

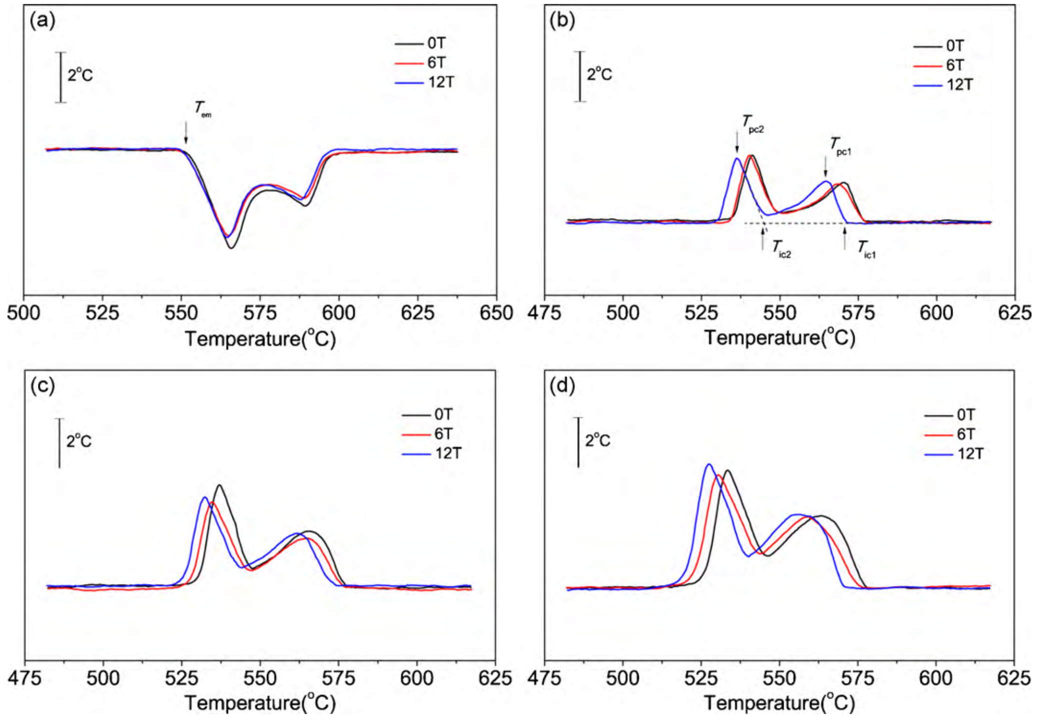

Fig. 2. DTA curves of Al–25 at.%Cu alloys in various magnetic fields at the heating rate of 5 °C/min (a) and at different cooling rates of (b) −2.5 °C/min, (c) −5 °C/min, (d) −7.5 °C/min.

Table 1
Some parameters of crystallization in the Al–25 at.%Cu alloy obtained from the DTA runs.

Rates (°C/min)	B(T)	T_{ic1} (°C)	T_{pc1} (°C)	T_{ic2} (°C)	T_{pc2} (°C)	$(T_{ic1}-T_{pc1})$ (°C)	$(T_{ic2}-T_{pc2})$ (°C)
2.5	0	576.6	570.3	548.8	541.1	6.3	7.7
	6	576.2	568.5	548.6	540.2	7.7	8.4
	12	571.5	564.5	544.8	536.1	7.0	8.7
5	0	576.7	565.8	548.0	537.1	10.9	10.9
	6	576.3	565.1	547.2	534.8	11.2	12.4
	12	573.2	561.7	544.3	532.3	11.5	12.0
7.5	0	576.9	563.8	547.7	533.3	13.1	14.4
	6	574.7	558.8	546.1	530.2	15.9	15.9
	12	570.2	554.4	542.4	527.4	15.8	15.0

the other hand, it is readily seen that the quantities $(T_{ic1}-T_{pc1})$ and $(T_{ic2}-T_{pc2})$, which may characterize the total crystallization rates [9] of primary Al_2Cu phases and eutectics respectively, are larger in magnetic fields than those without a magnetic field, that is to say, the growth rates of primary Al_2Cu phases and eutectics are reduced by magnetic fields. Hence, the DTA experiments at three cooling rates obviously indicate consistent reduction of nucleation temperature and growth rates of primary phases and eutectics in magnetic fields.

For the Al–25 at.%Cu alloy, we cannot expect that magnetic fields influence its solidification in thermodynamics from aforementioned analysis. Therefore, solidification kinetics of the alloys might be affected in magnetic fields. According to Al–Cu phase diagram [10], primary Al_2Cu phases firstly precipitate from the melt with the decrease of temperature and then Al–Al_2Cu eutectics grow. As we know, the convection of liquid metals can be effectively suppressed in magnetic fields [11]. Some investigation showed a 4 T magnetic field was considered to be sufficient for damping convection [12]. Thus, in the presence of magnetic fields of 6 T and 12 T, it is believed that diffusion of atoms dominates redistribution of solute atoms in the liquid alloys instead of convection. Nucleation process generally requires long-range diffusion in alloy systems and Al–Cu alloys are no exception as well. Consequently, it becomes more difficult for nucleation in case the diffusion of Al and Cu atoms in the melt is suppressed in magnetic fields. Actually, Youdelis et al. [13] investigated diffusion in the Al–Cu system and found that diffusivity was decreased by about 25% in a 3 T magnetic field. Moreover, it was theoretically claimed that the coefficient of diffusion in a magnetic field could be decreased by the factor $1/(1+\omega_e{}^2/\upsilon_e{}^2)$, where ω_e and υ_e are cyclotron and collision frequencies of diffusion transported electrons, respectively. The decreased diffusion coefficient D occurred through a change in the frequency factor D_0, which was closely related to the atom-vacancy jump frequency or interchange. Since the solute distribution was completely dominated by diffusion in solid state and a magnetic field decreased the diffusivity in the solid Al–Cu alloy, a magnetic field also inhibited the atom diffusion in liquid Al–Cu alloys in the absence of convection. In order to clearly exhibit motion behaviors of atoms in a magnetic field, Fig. 3 schematically illustrates diffusion of atoms in the melt in the process of nucleation. Provided that some atom with a velocity of V moves to the germ nucleus, the atom with a velocity component perpendicular to a magnetic field will be subject to Lorentz force. It will migrate to the nucleus in spiral trajectory (atoms will move in straight line before collision without a magnetic field). In the case, the probability of Cu or Al atoms which collides with other atoms increases. Correspondingly, the mean time for migration will be prolonged in the process of diffusion. Thus, the nucleation of primary Al_2Cu phases would be delayed in magnetic fields, which is characterized as the reduction of nucleation temperature T_{ic1}. Moreover, the higher the magnetic field, the higher the cyclotron frequency of atoms. The collision frequency of atoms with peripheral atoms in the range of mean free path further increases. The diffusion rates of atoms are decreased with increase of a magnetic field. The nucleation temperatures, therefore, are reduced in a magnetic field of 12 T compared with those in 6 T.

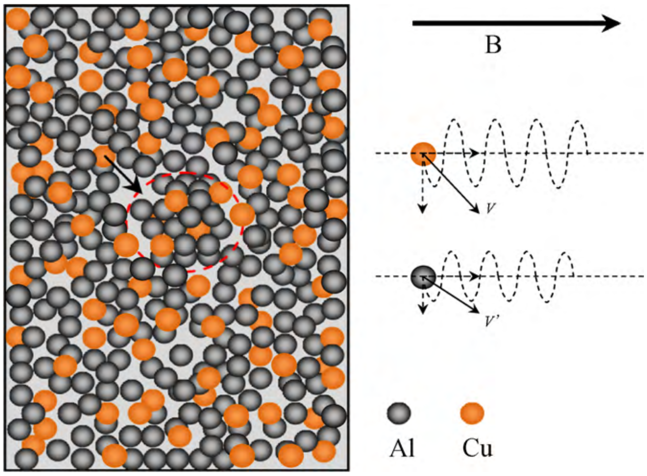

Fig. 3. The schematic illustration of migration of atoms in the process of nucleation indicates that the atom with some velocity which is not parallel to a magnetic field will move in spiral trajectory. The increase of probability of collision with other atoms due to spiral motion results in increase of mean time for migration.

Upon reaching radii of critical nuclei, primary phases begin to grow and latent heat will be gradually released as the furnace temperature homogeneously falls. In the conditions, the temperature gradient appears near the interfaces between primary phases and the melt. The thermoelectric currents are produced between the melt and primary phases, both of which have different thermoelectric powers. As a result, the electromagnetic force will be produced under the interplay between a magnetic field and thermoelectric currents, which causes thermoelectromagnetic convection (TEMC) [14]. The TEMC accelerates redistribution of solute atoms in the melt. However, the TEMC is rather feeble due to small temperature gradient near the interface and minor difference in thermoelectric powers between primary phases and melt and its effect on to mass transfer is accordingly negligible. In addition, Note that solute rejection in the front of interface inevitably induces the natural convection in normal conditions which accelerates the mass transport and increases the rates of crystal growth. Nevertheless, a magnetic field can effectively damp kinds of convections of electrically conducting liquids and make solute concentration in the crystal grown more uniform [15,16]. A magnetic field similarly damps the natural convection induced by solute accumulation. Finally, we should consider the effect of a magnetic field on heat transfer. There were reports [17] showing that a magnetic field increased the effective viscosity of the melt and further led to diminish thermal convection and therefore to decrease heat losses, which delays the growth rates of primary phases as well. Hence, it can be concluded that solute

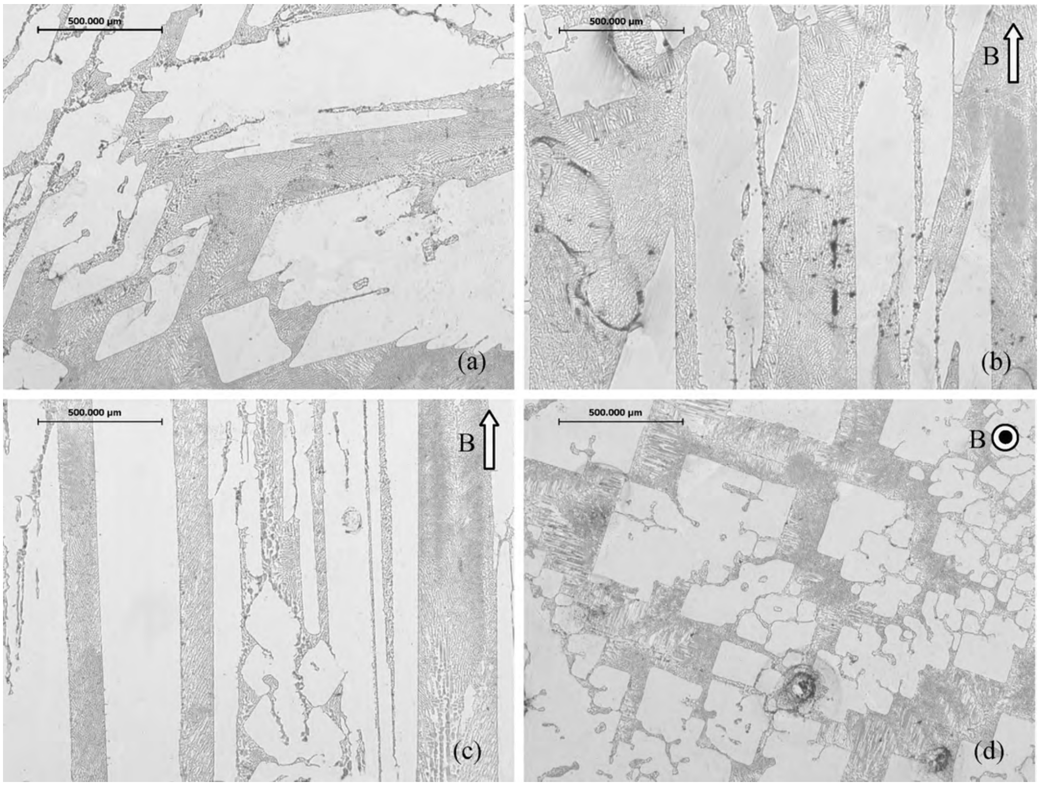

Fig. 4. Microstructures of the Al–25 at.%Cu hypereutectic alloy at the cooling rate of 2.5 °C/min. (a) longitudinal, 0 T; (b) longitudinal, 6 T; (c) longitudinal, 12 T; (d) transversal, 12 T.

redistribution in the process of growth of primary phases is mainly finished via atom diffusion in present experiments (6 T and 12 T). The growth rates of primary phases are reduced due to decrease in diffusivity in magnetic fields.

The Al–Al_2Cu eutectics begin to grow when primary phases completely precipitate. On the analogy of nucleation and growth of primary phases, larger undercoolings will be needed in the process of nucleation of eutectics in magnetic fields owing to reduction in diffusivity. From the Table 1, the nucleation temperature T_{ic2} of eutectics decreases with increase of a magnetic field. Furthermore, Al–Al_2Cu eutectics are typically lamellar and the formation of the structures must depend on diffusion of Al and Cu atoms [8]. On the base of the preceding analysis, the growth of eutectics is necessarily dominated by diffusion in a magnetic field. Their growth rates in magnetic fields were slowed down as well, which was characterized as the reduction of the quantity ($T_{ic2} - T_{pc2}$).

3.2. *Orientation of primary Al_2Cu phases in magnetic fields*

The resulting microstructures of samples are showed in Fig. 4. It is clearly seen that primary Al_2Cu phases (white) in the eutectics (gray) disorderly distribute without a magnetic field in Fig. 4(a). However, the phase orientation occurs along the direction parallel to magnetic fields of 6 T and 12 T, showed in Fig. 4(b) and (c), and just the orientation degree of primary phases in 12 T is higher than those in 6 T. Additionally, primary Al_2Cu phases on the transversal section distribute in the form of incomplete square or rhombus, shown in Fig. 4(d). As early as 1981, Mikelson and Karklin [18] studied the effect of a magnetic field on crystal growth in a series of alloys including the Al–Cu alloy and obtained oriented structures. Herein, for Al_2Cu crystals with magnetic anisotropy, the force moment causes the crystals in the melt to orient in a homogeneous magnetic field once the magnetization energy is larger than thermal energy, and the force moment can be expressed as $K = (\Delta\chi/2\mu_0)B^2V \sin 2\alpha$, where $\Delta\chi$ is the difference of magnetic susceptibilities between the two mutually perpendicular axes. μ_0 vacuum permeability, B magnetic field strength, V volume of the crystal, α is the angle between a magnetic field and the axis with the maximum susceptibility. From the expression, the higher the magnetic field, the larger the force moment. Accordingly, the orientation degree of primary phases in 12 T is higher than that in 6 T.

4. Conclusion

Investigation of solidification in the Al–25 at.%Cu hypereutectic alloy in magnetic fields has been performed by using the DTA apparatus. The DTA curves showed that the melting of the alloy was nearly not affected by magnetic fields. However, its solidification was markedly influenced, namely, the nucleation and growth of primary phases and eutectics were suppressed in magnetic fields which could be mainly attributed to the reduction of diffusion rates of atoms. The resulting microstructures indicated that primary Al_2Cu phases oriented along the direction parallel to a magnetic field, which could be caused by the magnetic anisotropy. The present results further demonstrate that phase transformations of non-magnetic substances can be influenced from kinetics.

Acknowledgements

The authors are grateful for the financial support of Natural Science Foundation of China (Grant Nos. 50911130365, 50701031), Science and Technology Committee of Shanghai (Grant Nos. 09510700100, 08dj1400404, 08DZ1130100) and Shanghai Postdoctoral Science foundation (Grant No. 09R21412600).

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