Effect of Denucleating Techniques on Undercooling of Co₂NiGa Alloys

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By using the method of glass fluxing combined with superheating-cooling cycling, the undercooling behaviour of Co₂NiGa alloy melts was investigated. The obtained degree of undercooling is very different with differently used glass due to different denucleating mechanisms. The denucleating agent composed by 70% Na₂B₄O₇ + 30% NaSiCa showing a moderate viscosity and good physicochemical purification ability was optimized to be an ideal denucleating agent. By using this kind of denucleating agent, a large (> 200 K) and stable undercooling can be obtained in Co₂NiGa melts after superheating over 200 K for 1.5 min. The effects of the superheating and holding time on undercooling have been discussed. [doi:10.2320/matertrans.M2010100]

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1. Introduction

Recently, as a new ferromagnetic shape memory system, Co-Ni-Ga has received considerable attention. As a promising smart material for the actuator and sensor applications, Co-Ni-Ga alloys exhibit several merits such as good ductility,¹⁾ high martensitic transformation temperature²⁾ and magnetic-controlled two-way shape memory effect.³⁾ The textured Co-Ni-Ga ribbons with a large magnetic-field-induced strain and good shape recovery ability can be achieved by rapid solidification, e.g. melt-spinning.⁴⁾

Rapid solidification of undercooled alloy melts is an attractive subject in both structural and functional materials.⁵⁾ The so-called undercooling refers to the phenomenon of pure liquid metal or alloy in a balance below a certain temperature range without crystallization or solidification. In order to achieve a reasonable undercooling, the most important way is to maximize the purification of metal melts, i.e. to be effectively inhibit the occurrence of heterogeneous nucleation in the melt.⁶⁾ Currently, the experimental methods of obtaining the large undercooling include emulsification,⁷⁾ electromagnetic levitation,⁸⁾ microgravity,⁹⁾ drop tube,¹⁰⁾ molten glass fluxing,¹¹⁾ superheating cycling¹²⁾ and combined above methods. Among them, the simple and effective one is glass fluxing combined with superheating cycling. Wei *et al.*¹³⁾ have carried out a systematic study on the glass fluxing undercooling method. However, the choice of glass for purifying the melts is still at the experimental stage. In our previous work,¹⁴⁾ we focused on the microstructure evolution of undercooled Co-Ni-Ga alloys, where the denucleating glass of Na₂B₄O₇ was used and a maximum undercooling beyond 200 K was achieved. However, it is difficult to achieve a theoretical degree of undercooling due to the instability of melt undercooling. In the present study, we expand the work on the undercooling of Co₂NiGa alloys to the effect of denucleating technique on undercooling and its stability during superheating-cooling cycles.

2. Experimental

Co₂NiGa master ingots were prepared from elemental Co,

Fig. 1 Sketch of the apparatus for undercooling experiments. 1. Vacuum chamber; 2. Up-down withdrawing system; 3. Double silica crucible; 4. SIT high frequency power supply; 5. Support frame; 6. Fluxing glass; 7. Induction coils; 8. Sample; 9. Infrared thermodetector; 10. Signal processing unit; 11. Grapher recording meter.

Ni and Ga of 99.99% purity by arc melting under pure argon atmosphere. The buttons were melted for four times in the water cooling copper crucible. After homogenization at 1273 K for 48 h, the master alloys were cut into small pieces and acoustically cleaned in acetone for 30 min. The Co₂NiGa pieces were embedded into the denucleating glass in a quartz crucible. B₂O₃, Na₂B₄O₇ and NaSiCa with different viscosity and crystal structure^{13,15,16)} were used as single-component denucleating agents. Na₂B₄O₇ were prepared from Na₂B₄O₇·10H₂O analytical reagents. NaSiCa glass is a commercial standard substance which consists of 74.0% SiO₂, 15% (Na₂O + K₂O), 7% CaO, 2% Al₂O₃, 1.8% MgO and 0.2% Fe₂O₃. We also prepared a two-component glass containing Na₂B₄O₇ and NaSiCa, which were mixed with various mass fraction and then sintered at 1273 K for 24 h.

The apparatus for undercooling experiment is shown in Fig. 1. The Co₂NiGa sample was firstly inductively superheated for a few minutes and then cooled till solidification. This heating-cooling cycle was performed by several times in order to obtain the large undercooling condition. The temperature change was monitored by an infrared pyrometer calibrated with a standard PtRh₃₀-PtRh₆ thermocouple, which possesses a relative accuracy of 5 K with a response time less than 1 ms.

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3. Results and Discussion

The degree of undercooling during the superheating-cooling cycle by using different denucleating agents is presented in Fig. 2. For B_2O_3 glass (a), the maximum undercooling is only about 100 K. The obtained value of undercooling (ΔT) changes randomly during thermal cycles. For $Na_2B_4O_7$ (b) and NaSiCa glasses (c), the maximum undercooling beyond 200 K can be easily achieved in the first several cycles. The high undercooling insures homogeneous distribution of refined grains for Co_2NiGa undercooled alloys as shown in Fig. 3(a). However, ΔT gradually decreases during the following cycles. In the undercooling experiments, the selection of glass fluxing is one of the most important aspects. According to the studies of Powell¹¹⁾ and Drehman *et al.*,¹²⁾ sticky molten glass can eliminate heterogeneous nucleation particles through physical absorption, and certain special glass can melt some impurities through chemical reaction to achieve physicochemical purification. In addition, the molten glass protects the alloy melt from atmosphere to avoid the formation of oxide films and, as a high-damping isolation layer, eliminates nucleation by the interference of external vibration.

Fig. 2 Undercoolings obtained during superheating-cooling cycles by different denucleating agents: (a) B_2O_3 , (b) $Na_2B_4O_7$, (c) NaSiCa.

In accordance with the Random Network Model of glass,¹⁶⁾ pure B_2O_3 glass can be regarded as layer or chain network structure composed of disordering linked $[BO_3]$ triangles. While oxides of Co, Ni and Ga as the main impurities in Co_2NiGa melts cannot change the triangle structure of $[BO_3]$, they can be eliminated through viscous absorption and mechanical wrapping effect when absorbed into the molten glass. The arrangement of the oxides in the glass melt can be described by the Poisson distribution:¹⁷⁾ $X = \exp(-mv)$ where X is the nucleation free volume fraction, m the average number of nucleation per volume and v the volume. However, any randomly distributed metal oxides appearing in the interface of Co_2NiGa melts and B_2O_3 molten glass plays a main role in heterogeneity and in stimulating the solidification of the melt, as shown in Fig. 3(b). Consequently, it is difficult to obtain bulk undercooling and to keep the undercooling stable during the superheating-cooling cycles using B_2O_3 glass by physical absorption.

For $Na_2B_4O_7$ glass with a structure of $[BO_4]$ tetrahedron at high temperature, the presence of Na_2O leads to a transition from the layer structure of original two-dimension B_2O_3 glass into three-dimension network structure and a higher glass viscosity.¹⁶⁾ So, it is more effective in taking more particles of heterogeneous nucleation and reducing the oxidation of alloy melts in atmosphere. Moreover, once the metal oxides are absorbed into the three-dimension network structure, they will be difficult to be released. Therefore, the use of $Na_2B_4O_7$ glass can get a higher undercooling. Unfortunately, because the $Na_2B_4O_7$ glass shows a relatively lower viscosity at high temperature,¹⁶⁾ the solidified sample would drop down to the bottom of the crucible and thus the stability of undercooling was largely reduced during the following cycles.

The NaSiCa glass, a denucleating agent with a quite large high-temperature viscosity, can absorb metal oxides and integrate them into the glass network structure to form a kind of colored glass,¹⁶⁾ which tends to realize the chemical purification with the oxides by changing the glass composition and structure. The chemical purification greatly increases the ability of dissolving the oxides to avoid them to

Fig. 3 Microstructures of Co_2NiGa alloys: (a) $\Delta T = 200$ K denucleated by $Na_2B_4O_7$, (b) one heterogeneity.

Fig. 4 Undercoolings during superheating-cooling cycles by (100 - x)% Na₂B₄O₇ + x % NaSiCa denucleating agent.

be resolved in the subsequent electromagnetic stirring solution. However, due to its very high viscosity, probably an interfacial debonding crack tends to happen between the Co₂NiGa melt and the NaSiCa molten glass in the following cycles, thus leads to the reduction of ΔT during the remelting process.

From above, one can conclude that a suitable denucleating agent with a strong chemical purification capability as well as a moderate viscosity is of importance to stabilize the large ΔT . By comparing the experimental results and denucleating mechanism for Na₂N₄O₇ and NaSiCa agents, it is found that Na₂N₄O₇ shows comprehensively physical purification with lower viscosity, while NaSiCa owns strong chemical purification ability and higher viscosity, thus it can be expected that a combination of these two denucleating agents might give rise to a large and stable ΔT . Figure 4 shows the variation of undercoolings during superheating-cooling cycles by using Na₂B₄O₇ + NaSiCa denucleating agent with different mixing fraction. It is found when the volume ratio of NaSiCa is about 30%, the maximum undercooling of 230 K can be achieved and kept stable with cycles. Most likely, the moderate viscosity and strong physicochemical purification ability is available in this ratio between Na₂B₄O₇ and NaSiCa.

Meanwhile, the superheating temperature (ΔT_{sh}) and the holding time are analyzed for affecting ΔT . Figure 5 shows the effect of superheating and holding time on undercooling by using 70% Na₂B₄O₇ + 30% NaSiCa denucleating agent. It can be seen that the increase of superheating temperature from 80 to 200 K can reduce the number of cycles for achieving the maximum undercooling, but the further higher superheating of 300 K causes the maximum undercooling unstable and reduces the crucible life. As for the effect of holding time at superheating temperature on ΔT , a large undercooling above 180 K can be easily obtained when the holding time is about 1~2 min.

The effect of the appropriate superheating and holding time is remarkable on the undercooling of the denucleating agent. Previous reports confirm that the solidification of undercooled melts is still initiated by heterogeneous nucleation.^{14,18} The nucleation particles always appear in the interface of purified alloy and molten glass. The heteroge-

Fig. 5 Effect of superheating (a) and holding time (b) on undercooling by 70% Na₂B₄O₇ + 30% NaSiCa denucleating agent.

neous nucleation rate J_a of the melt surface can be expressed as:¹⁹⁾

$$J_a = 10^{21} \xi \varphi_0 \eta^{-1} \exp[-\Delta G^* f(\theta) / (kT)] \quad (1)$$

where ξ refers to the activating factor, φ_0 the area fraction of heterogeneous nucleation particle, η the viscosity of liquid metal or alloy, ΔG^* the nucleation activation energy, $f(\theta)$ the heterogeneous nucleation factor, and k the Boltzmann constant. The study on Ni-Si alloys²⁰⁾ pointed that ξ depends on the effect of passivation of heterogeneity, φ_0 lies with the balance of fusion and adsorption of oxide during undercooling, and $f(\theta)$ is mainly determined by the oxides in the undercooled melts. When the system is confirmed as to Co₂NiGa alloys, $f(\theta)$ is determined by the oxides of Co, Ni and Ga. Thus k , η and $f(\theta)$ are all constants, and J_a is only related with ξ , φ_0 and ΔG^* . During the cycling superheating purification process, an appropriate increase in the superheating and holding time will help improve the passivation effect of the heterogeneous nucleation particle (i.e. reduce ξ), advance the dissolution of oxide substrate in the molten glass (i.e. reduce φ_0), decompose and vaporize the impurity with low melting point in the melt, and increase the cluster size to promote the melt homogenization of structure and composition (i.e. increase ΔG^*). It is also beneficial in separating the melt from the melted glass, thus to decrease the heterogeneous nucleation rate J_a . According to the kinetic condition of achieving the maximum undercooling:²¹⁾

$$J_a \cdot S \cdot \tau = 1 \quad (2)$$

S means the interface area of melt and molten glass, exhibiting a constant for the confirmed melts; τ is the time of molten metal cooled to the nucleation temperature T_N . Based on the above discussion and eq. (2), the decrease of J_a will lead to the increase of τ , which implies the increase of maximum undercooling and the decrease of cycling time in achieving the maximum undercooling. The previous research on Ni-Si alloys²⁰⁾ found similar results and proved the parameters credible. However, if the sample was superheated by a very high level and dwelled for a long time, the molten metal is prone to volatilize and deposits on the crucible as the site of heterogeneous nucleation. In this case, a reasonably large undercooling is not possible during subsequent cooling. Moreover, a severe oxidation might occur in the molten sample with an over-high superheating and too long holding time. The oxides absorbed by glass are saturated in the glass and tend to be released back into the melt assisted by electromagnetic stirring, thus the purifying effect is reduced and undercooling is interrupted. Therefore, the selection of a proper denucleating glass, a moderate superheating and holding time is essential to achieve a stable bulk undercooling.

4. Conclusion

A large undercooling can be obtained in Co₂NiGa melts by glass fluxing combined with superheating cycling method for the different kinds of denucleating glass: B₂O₃, Na₂B₄O₇ and NaSiCa. For B₂O₃ glass, the maximum undercooling is about 100 K with the purification mechanism of physical absorption; for Na₂B₄O₇ and NaSiCa glass, the high undercooling beyond 200 K can be achieved respectively with the effect of comprehensively physical and physicochemical purification. The denucleating agent 70% Na₂B₄O₇ + 30% NaSiCa, which has moderate viscosity and physicochemical purification ability, was selected as a better denucleating agent; and it is possible to obtain a stable

undercooling exceeding 200 K in Co₂NiGa melts when they are superheated at about 200 K for 1.5 min.

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