Boron Effect on Solidification in the Two Phase ($NiAl+Ni_3Al$) Alloy

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ABSTRACT

It was found that addition of boron improved room temperature fracture strength by formation of $Ni_3Al(\gamma')$ thin layer around the NiAl(β) phase after heat-treatment in the $NiAl+Ni_3Al$ two phase alloy. Directional solidification technique with quenching of the solidifying interface has been applied to understand the mechanism of formation of the γ' layer around the β phase. The quenched solid/liquid interface showed that solidification ended up with γ phase at the β interdendritic region in the boron added alloy, while the γ' phase formed at the interdendritic region in the binary alloy. It is thought that the γ' phase formed around the β dendritic phase grows between γ and β phases by a diffusion couple manner in the boron added alloy. It was also interesting to find that boron addition changed the phase field and solidification behavior.

1. INTRODUCTION

The grain boundary brittleness of Ni_3Al is a main obstacle in structural applications. However, a small amount of boron has been found to improve room temperature ductility in Ni_3Al alloy /1/. In order to improve its ductility two phase alloy of $NiAl+Ni_3Al$ was also considered as a high temperature material to use high temperature properties of the NiAl phase /2/. The recent study in the $NiAl+Ni_3Al$ two phase alloy reported that the addition of boron caused the thin layer of the $Ni_3Al(\gamma')$ phase around the NiAl(β) phase, which resulted in significant improvement in room temperature fracture strength /3/.

In this study, directional solidification technique has been applied to understand the mechanism for formation of the γ' layer around the β phase. The directional solidification technique with quenching of the solidifying interface has the advantage that the microstructures formed at the interface are preserved, thereby revealing the nature of the interface structure occurring during the solidification process. The quenched solid/liquid interface showed that solidification ended up with γ phase at the β interdendritic region in the boron added alloy, while the γ' phase formed at the interdendritic region. It was found that the γ' phase apparently formed around the β phase grew between γ and β phases and the γ phase was also transformed to the γ' phase by solid state phase transformation of the γ' precipitation in the γ phase in the boron added alloy. The formation of the γ' layer in the boron added two phase alloy was explained based on the phase diagram which was recently developed by a series of directional solidification studies in the Ni-Al system, where the eutectic occurred between γ' and β /4,5/. It was also interesting to find that boron addition changed the phase field and solidification behavior.

2. EXPERIMENTAL

Directional solidification studies have been carried out at 0.5-50μm/s solidification rates in two phase alloys of 1at.% boron added and binary Ni- 31at.%Al alloy in the 5 mmIDx8mmOD alumina tube. Bar type alloys were prepared by VAR melting and 4 mm dia.

rods were machined to fit the alumina tube. Briefly about the equipment and experimental procedure, a Super-Khantal furnace fitted with a water cooled Cu toroid at its bottom end was moved upward at controlled rates around the alumina tube filled with the alloy. The furnace melted the alloy down to a point near the bottom of the furnace under an Ar atmosphere. The carriage, cold finger, and furnace were raised upward at rates of 0.5-50 μm/s controlled by the computer connected to a stepper motor. After the desired volume fraction of original liquid had been solidified the alumina tube was dropped into a quenched bath of stagnant water, thereby preserving the solid microstructure formed at the solid-liquid interface. The samples were sectioned and polished to reveal the solid/liquid interface microstructures, and examined using an optical microscope and an analytical EPMA scanning microscope.

3. RESULTS AND DISCUSSION

A previous study /3/ showed that boron added 32.6at.%Al alloy exhibited a thin layer which was composed of two phases, γ′ at outside and γ + boron rich phase at the center region, along the grain boundary, where as the boron-free alloy did not show this feature, after homogenizing heat-treatment at 1300°C. A question arose as to how the layer could form in the boron added alloy in the previous study. The quenched solid/liquid interface studies present the growing microstructure and give important information about solid/liquid and solid state phase transformation ; i.e. from liquid to solid and from the solid near freezing temperature to room temperature. Fig. 1 shows (a) the quenched solid liquid interface at the interdendritic region, and the microstructures (b) 5 mm below and (c) 15 mm below this interface at the solidification rate of 5 μm/s. It was found that the microstructure of Fig. 1(b) was very similar to that of the heat-treated sample in the previous study of the boron added alloy. The phase identification was carried out by EPMA(electron probe micro-analysis) at the microstructure of Fig. 1(b), as shown in Fig. 2, and those results are summarized in Table 1. The boron could not be analyzed by EPMA and the boron rich phase was confirmed by boron mapping

Fig. 1: Transverse microstructures (a) at quenched solid/liquid interface in the interdendritic region, (b) at the 5 mm below position of (a), and (c) at the 15 mm / below position of (a)

analysis, as shown in Fig.3, where Al distribution was also mapped. This result indicated that boron was mainly distributed at the γ interdendritic phase.

Quenched solid/liquid interfaces showed the β dendrites with γ′ interdendritic structures in the 31 at.% Al alloy while the β dendrite with apparent γ (+γ′

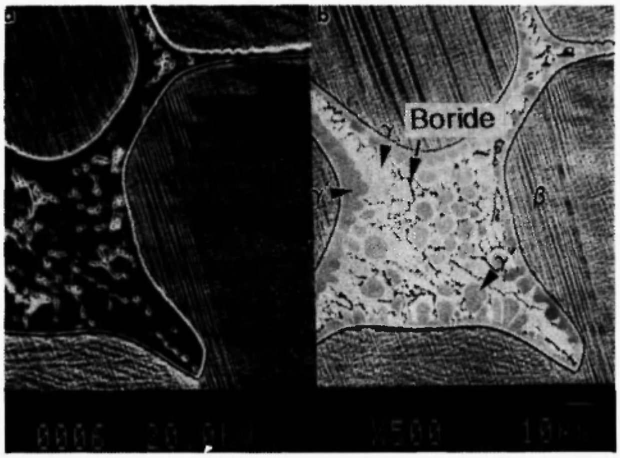

Fig.2: SEM micrographs of (a) secondary electron image and (b) back scattered image of Fig.2(b)

shows phase transformation sequence from the forming temperatures of primary dendrite and interdendritic phases to the temperatures far below the interface temperature.

Based on these results, the mechanism of the γ' layer formation found in the previous study of heat-treatment could be explained in the schematic diagram of Fig. 5. The quenched solid liquid interface structure must be the original microstructure before the phase transformation, and it is easy to understand what is the phase formed from the liquid at the interdendritic region and how this phase is transformed in the solid state. However, the interface microstructure appeared to be already transformed, as shown in Fig. 1(a). The γ' layer was formed between β dendrite and γ interdendritic

Table 1. Phase determination of Fig.2(b).

Phase	Expected Phase	This study EPMA(Al at.%)	Previous study[3]	
			EPMA (Al%)	Other analyses
White(a)	γ'	24	24	TEM/Micro XRD
Gray(b)	γ	15	16	TEM
Black (c)	$Ni_{41}Al_5B_{15}$	-	-	TEM/AES

precipitates) interdendritic structures in the boron added alloy. The quenched liquids, which were directly quenched from liquid above growing dendrite tips, were clearly different between 31 at.% Al and 31at% Al-1at.% B alloys, as shown in Fig 4. In the quenched liquid of the binary alloy, the β dendrite was formed with γ' interdendritic phase, and it appeared that the phase transformation occurred between β and γ' during the quenching process. However, in the quenched liquid of the boron added alloy, the γ' layers surrounded the β dendrites, which are a similar structure to Fig.1(a). In the quenched sample during directional solidification, the microstructure 5 mm below the interface(Fig.1(b)) has the same effect of heat-treatment for 17min between 1380°C (approximate melting temperature) and 1359°C (5 mm below the solid/liquid interface, where the temperature gradient at the solid near the melting temperature was measured as 42°C/cm). The microstructure 15 mm below the interface (Fig.1(c)) has the same effect of heat-treatment for 51 min between 1380°C and 1317 °C . This indicates that Fig. 1 (a,b,c) region and the γ' phase was precipitated in the γ phase. The phase transformation was unexpected because it was thought that the quench should have been able to freeze the microstructure at the growth front. If one think a time to cool down from the interface temperature, after dropping the sample in side of the 1.5 mm wall Al_2O_3 tube into stagnant water, it is reasonable that phase transformation occurs during quenching process. This kind of phase transformation appeared in the other studies /4,5/. It is thought that the γ phase was formed as the β interdendritic phase and γ' precipitated in the γ phase upon quenching, as shown in Fig.1(a). The γ' layer between β and γ at the interface (Fig.1(a)) might be formed upon quenching, however, the γ' layer 5 mm below interface must be formed by diffusion couple manner between β and γ phases. Lee and Verhoeven /4/ evaluated the γ' growth between γ and β eutectic phases by the model of Wagner and Jost /6/. The γ' thickness, Z_{tot}, which is sum of Z_β and Z_γ in Fig.5(a), is

$$Z_{tot} = 2a\sqrt{Dt} + 2b\sqrt{Dt}$$

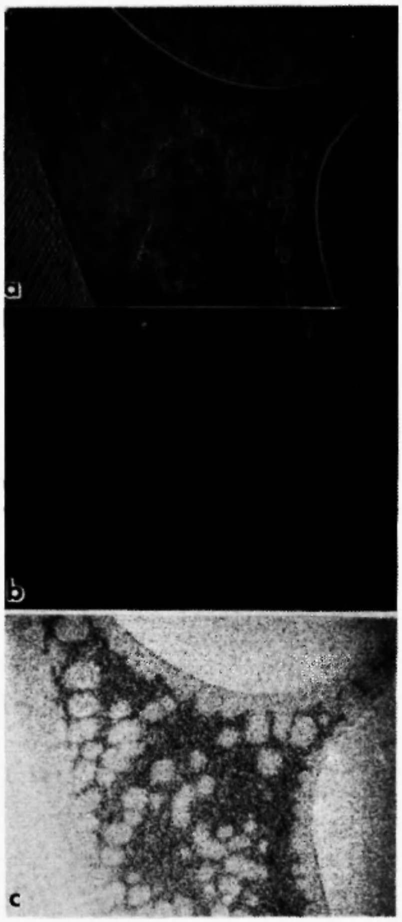

Fig.3: SEM micrographs of (a) secondary electron image, and (b) boron and (c)Al mappings by SEM-EDS at Fig 2(b).

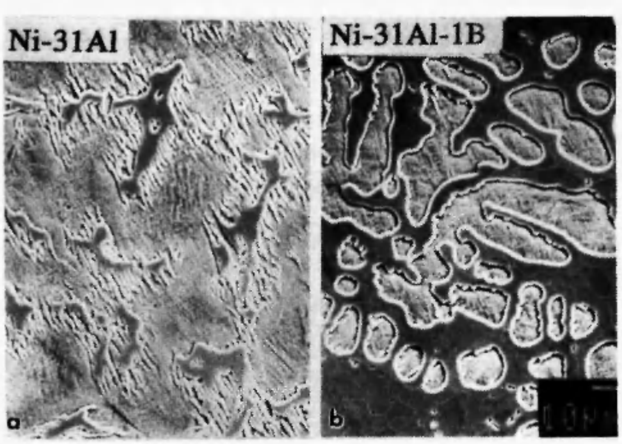

Fig.4: Quenched liquid microstructures above the dendrite tips in a) 31at.%Al and b) 31at.%Al-1at.%B alloys

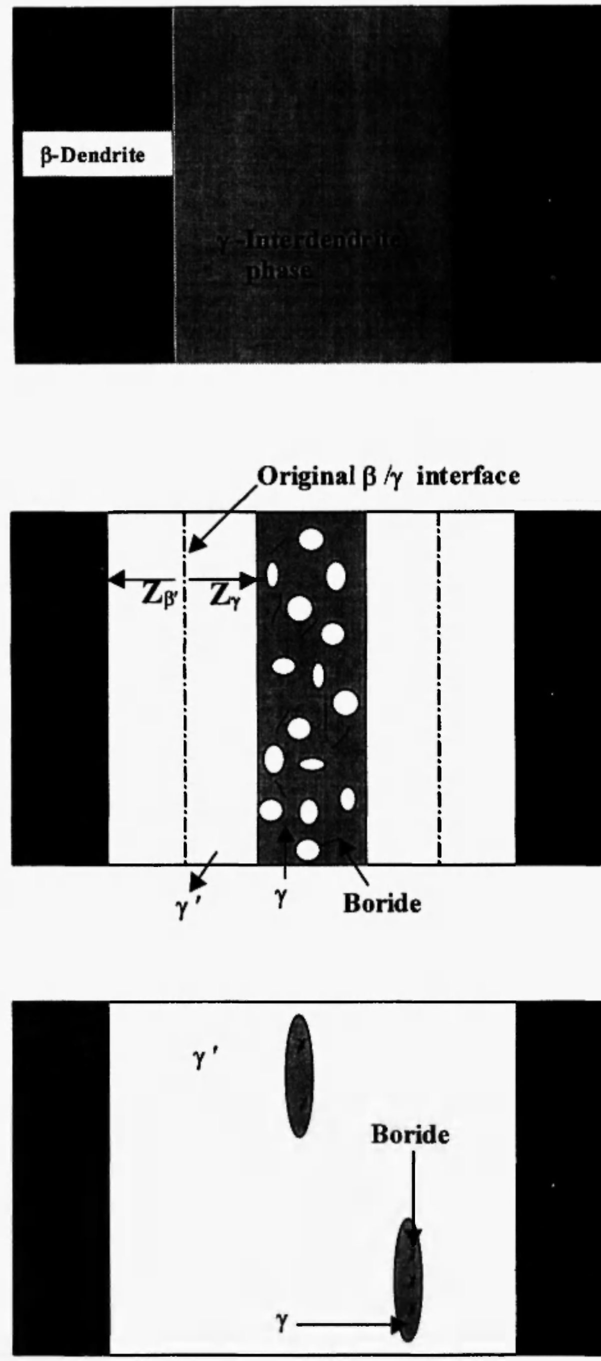

Fig.5: Schematic of the γ' layer formation in the boron added NiAl /Ni_3Al two phase alloy.

where a and b are constants, t is time. The constants a and b are functions of phase boundary compositions. The γ' layer growth could be calculated by this prediction, but mutual diffusion coefficient and the phase boundary composition data are not available in the boron added Ni-Al system. However, the γ' layer growth between β dendrite and γ interdendritic phase is quite predictable through the diffusion model. At the position 5 mm below solid liquid interface, the γ' precipitated phase was also grown in the γ phase and the boride was precipitated in the γ phase region, where the boron was proved to be segregated at the γ interdendritic phase, as shown in Fig. 3.

The γ' phase grew further with increasing the distance from the solid/liquid interface, and only small amount of γ phase including some boride remained at the interdendritic region 15 mm below the interface, as shown in Fig. 1 (c) . It was also interesting to find the γ phase as the interdendritic phase in the boron added alloy. The γ' interdendritic phase in the binary alloy is predictable from the Ni-Al binary phase diagram. A small amount of eutectic phase is expected to be formed at the interdendritic region, and then this eutectic phase transforms to γ' phase. This phase transformation was observed in other studies near Ni_3Al alloy /4,5/. Lee and Verhoeven /4/ reported that a small amount of impurities, such as Fe, Cr, might induce a metastable phase in the Ni-Al system. However, in the boron added alloy, a large amount of boron, 1 at.%, was added, and also boron was proved to be segregated in the interdendritic region. The amount of boron at the interdendrites is expected to be quite large to change the phase field in the phase diagram. It is thought that an interface reactive element, boron, may cause the phase field to change, and also suppress the formation of the γ' phase which results on forming the γ phase. A further directional solidification study is ongoing to evaluate the phase diagram by addition of boron.

4. CONCLUSIONS

1. A thin layer of the $Ni_3Al(\gamma')$ phase around the NiAl(β) phase after heat-treatment, which resulted in significant improvement in room temperature fracture strength, was found in the boron added NiAl+Ni_3Al two phase alloy /3/. Directional solidification technique has been applied to understand the mechanism of formation of the γ' layer around the β phase. The quenched solid/liquid interface showed that solidification ended up with γ phase in the β interdendritic region in the boron added alloy, while the γ' phase formed in the interdendritic region in the binary alloy. It is thought that the γ' phase formed around the β dendritic phase grows between γ and β phases by a diffusion couple manner in the boron added alloy.
2. It was also interesting to find the γ phase as the interdendritic phase in the boron added alloy. Boron was proved to be segregated in the interdendritic region. Segregated boron at the interdendrites is expected to be quite large to change the phase field in the phase diagram. An interface reactive element, boron, may cause the phase field to change, and also suppress the formation of the γ' phase which results in forming the γ phase as an interdendritic phase.

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