Microstructure and mechanical properties of zirconium doped NiAl/Cr(Mo) hypoeutectic alloy prepared by injection casting

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Abstract. NiAl based materials has been considered as most potential candidate of turbine blade, due to its excellent high-temperature properties. However the bad room-temperature properties handicap its application. In the present paper, the zirconium doped NiAl/Cr(Mo) hypoeutectic alloy is fabricated by conventional casting and injection casting technology to improve its room-temperature properties. The microstructure and compressive properties at different temperatures of the conventionally-cast and injection-cast were investigated. The results exhibit that the conventionally-cast alloy comprises coarse primary NiAl phase and eutectic cell, which is dotted with irregular Ni2AlZr Heusler phase. Compared with the conventionally-cast alloy, the injection-cast alloy possesses refined the primary NiAl, eutectic cell and eutectic lamella. In addition, the Ni2AlZr Heusler phase become smaller and distribute uniformly. Moreover, the injection casting decrease the area fraction of primary NiAl phase at the cell interior or cell boundaries. The compressive ductility and yield strength of the injection-cast alloy at room temperature increase by about 100% and 35% over those of conventionally-cast alloy, which should be ascribed to the microstructure optimization.

1. Introduction
Compared with many NiAl-based alloys, NiAl-28Cr-6Mo (NiAl-Cr(Mo) for short) eutectic alloy is regarded as the most logical choice of the multielement system because of it good balance between elevated temperature creep resistance and room temperature fracture toughness [1-3]. But, the high temperature strength of the alloy still needs improve further [4-5]. The recent researches [6-8] reveal that the addition of Heusler phase forming elements (Ti, Zr, Hf) could increase the strength of the NiAl based eutectic alloy. However, the Heusler phase prefer to form along the eutectic cell boundary and is detrimental to the room-temperature mechanical properties [9,10]. Then improvement on the size and distribution of the strengthening precipitates is important for the alloy. It is well known that rapid solidification is a feasible way to refine the microstructure and decrease the segregation, which is helpful to adjust the morphology and distribution of precipitates [11-13]. Moreover, the refined eutectic structure is also beneficial to the strength and ductility of the eutectic alloy [14]. Additionally, the researchers [15-16] have found that appropriate amount of primary NiAl is helpful to the wear property. Then in the present paper, the zirconium (Zr) doped NiAl-24Cr-4.6Mo-0.4Zr alloy (at.%) hypoeutectic alloy is fabricated by conventional casting and injection casting. Its microstructural evolution and mechanical properties were investigated as well.
2. Experimental

Alloy ingots with a composition of NiAl-24Cr-4.6Mo-0.4Zr were prepared in a vacuum induction furnace with starting materials of 99.9% Ni, 99.9% Al, 99.8% Zr, 99.5% Cr and 99.9% Mo. The melted alloy was cast into the ceramic shell mould to obtain the conventionally-cast alloy with 40 mm in diameter. The slices cut from the conventionally-cast alloy ingot for the injection casting. The slices were re-melted in quartz tube and injected through a nozzle into Cu mold to obtain the injection-cast alloy with 10mm in diameter.

Specimens for microstructure characterization and mechanical properties test were cut from the conventionally-cast and injection-cast alloy. The S-3400 scanning electron microscopy (SEM) was employed to perform the microstructure characterization. Constitute phase composition in the composite was analyzed by the EPMA-1610 electronic probe microanalysis. The specimen for transmission electron microscope (TEM) characterization was cut from composite with thickness of 0.4 mm. Then the specimen was polished to 30 μm and shaped into φ3 mm in size followed by twin-jet electropolishing. JEOL-2100 was employed to perform the TEM observation and analyses. Compression sample (4×4×6 mm^3) was cut from the alloys and mechanical grounded by 800-grit SiC abrasive. Gleeble 3800 was employed to carry out the compression test at the initial strain rate of 1×10^-3/s.

3. Results and discussion

3.1. Microstructural characteristics

The SEM observations on conventionally-cast NiAl-Cr(Mo)-Zr alloy are shown in Figure 1. Clearly, the alloy mainly consists of black NiAl phase, gray Cr(Mo) phase and white Heusler phase, as shown in Figure 1 (a). The NiAl and Cr(Mo) phases form the eutectic cell with an average size of 50μm, as shown in Figure 1 (a). Analysis on the conventionally-cast alloy exhibits the eutectic lamella has an average thickness of 4μm and the size of primary NiAl phase is about 20μm. In the eutectic cell, black NiAl and gray Cr(Mo) plates emanate radially from the cell center to boundary, as shown in Figure 1 (b). Coarser Cr(Mo), primary NiAl phase and white Heusler phase mainly distribute at the intercellular zone. Furthermore, it also can find many Cr(Mo) precipitates in the NiAl phase and NiAl precipitates in the Cr(Mo) phase. TEM observation on the Heusler phase reveals that it contains cubic crystal structure (a=b=c=0.6123 nm) and Fm3m space group, as shown in Figure 1 (c).

![Figure 1](image)

Figure 1. (a) SEM image of conventionally-cast alloy, (b) Morphology of precipitates and eutectic structure, (c) TEM image of Ni2AlZr Heusler phase

The typical microstructure of injection-cast NiAl-Cr(Mo)-Zr alloy is shown in Figure 2. Apparently, the microstructure of injection-cast alloy is quite different from that of conventionally-cast alloy as a result of high cooling rate during injection casting. The morphology of primary NiAl phase exhibits dendritic crystal characteristic and its amount decreases a little, as shown in Figure 2 (a). The eutectic cell size in injection-cast alloy is about 25-35μm, which is smaller than that of conventionally-cast alloy, as shown in Figure 2 (a). The primary NiAl dendrites in injection-cast alloy with an average size of 15μm mainly distribute at the eutectic cell boundary. Moreover, the thickness of the NiAl/Cr(Mo)
eutectic lamella in eutectic cell is less than 1 μm, but that near the eutectic boundary is about 2 μm, as shown in Figure 2 (c). In addition, TEM observation also reveals plentiful nano-scale NiAl and Cr(Mo) precipitates. By comparing Figure 1 (a) with Figure 2 (a), it can be specific that the Heusler phase has been distinctly fined and evenly distributes at cell boundaries.

![Figure 2. (a) SEM image of the injection-cast alloy, (b) Morphology of the precipitates and eutectic structure, (c) TEM image of the ultrafine NiAl/Cr(Mo) eutectic structure](image)

According to the former research [9], the eutectic cell size and lamellar thickness of NiAl-Cr(Mo) eutectic alloy would decrease with the growth rate increasing. In the present research, the cooling rate of the injection casting is higher than that of the conventional casting, so the NiAl/Cr(Mo) eutectic structure and eutectic cell become finer. Compared with the conventionally-cast alloy, the precipitation in the injection-cast alloy is smaller and less. The EPMA analyses of different phase in conventionally-cast and injection-cast alloys are enumerated in Table 1. For injection-cast alloy, the solubility of Cr, Mo and Zr in primary NiAl phase, Ni, Al in Cr(Mo) phase and Cr in Heusler phase are higher than that of conventionally-cast alloy. Although 7.67% Cr was detected in primary NiAl phase of injection-cast alloy by EPMA, the solid solution of Cr in NiAl phase should be less than the measured result, because the precipitation in NiAl and Cr(Mo) phase could result in some deviation. However, the results still exhibit that the rapid solidification could restrict the element diffusion and increase the solid solution of the matrix. Moreover, it can be understood that why the NiAl and Cr(Mo) phase near the eutectic cell boundary are coarser than those in the center. Because the alloy element concentrating along liquid/solid interface could increase the constitutional supercooling, that would result in the rapid growing of the NiAl and Cr(Mo) phase.

| Table 1. Composition of different phases in conventionally-cast and injection-cast alloys (at.%) |
|-----------------|---|---|---|---|---|---|
| Alloys          | Phase | Ni  | Al  | Cr  | Mo  | Zr  |
| Conventionally- | Primary NiAl | 47.32 | 50.08 | 2.50 | 0.20 | 0.20 |
| cast            | Cr(Mo) | 3.30 | 4.90 | 80.18 | 11.62 | -  |
| Heusler         | 50.78 | 23.37 | 3.20 | -  | 22.25 |
| Primary NiAl    | 44.66 | 45.82 | 7.67 | 0.85 | 0.36 |
| Injection-cast  | Cr(Mo) | 9.20 | 10.08 | 69.88 | 10.84 | -  |
| Heusler         | 47.07 | 26.38 | 6.27 | -  | 20.28 |

### 3.2. Mechanical properties

The true stress-strain curves and mechanical test data at RT of conventionally-cast and injection-cast alloys were shown in Figure 3 and Table 2, respectively. It can be seen that the alloys fabricated by different technologies have the similar stress-strain curves, which exhibit continuous work hardening. The injection-cast alloy attains yield strength of 1360 MPa and compressive strength of 1920 MPa, both of which are about 25% higher than those of conventionally-cast alloy. Compressive strain values at RT are calculated based on practical plastic deformation in order to eliminate the contribution from the compliance of the testing system. The injection-cast alloy has a better RT compressive ductility with about 18% than about 8% for conventionally-cast alloy. It means that the RT ductility and
strength of injection-cast alloy have been improved at the same time. The compression tests at 1273 K and 1373 K reveal that the yield strength and compressive strength of the injection-cast alloy are almost similar as that of the conventionally-cast alloy, which indicates that the rapid solidification could improve the room temperature mechanical properties obviously but no influence on the high temperature mechanical properties.

![Figure 3. True stress-strain compression curves c of conventionally-cast and injection-cast alloys at room temperature](image)

![Table 2. Results of compressive tests under the nominal strain rate of 2x10-3 s-1](image)

| Alloy            | Test temperature(K) | Yield strength (MPa) | Compressive strength (MPa) | Compressive strain (%) |
|------------------|---------------------|----------------------|---------------------------|------------------------|
| Conventionally-cast | RT                  | 1010                 | 1510                      | 8                      |
|                  | 1273K               | 324                  | 395                       | >30                    |
|                  | 1373K               | 205                  | 225                       | >30                    |
| Injection-cast   | RT                  | 1360                 | 1920                      | 18                     |
|                  | 1273K               | 340                  | 420                       | >30                    |
|                  | 1373K               | 205                  | 265                       | >30                    |

Figure 4 shows the typical RT compressive fractographies of conventionally-cast alloy and injection-cast alloy, both of which exhibit similar fracture morphologies, i.e. typical stripping of NiAl/Cr(Mo) interface and cleaving of primary NiAl. However, many dimple-like cavities can be observed on the fracture surface of SC alloy. These cavities were formed by thin Cr(Mo) phase and NiAl phase in eutectic cell pulling out from each other, which are propitious to attain good compressive ductility and strength.

![Figure 4. Typical RT fracture surface of (a) conventionally-cast alloy and (b) injection-cast alloy](image)
The refinement of eutectic cells, the decrease of lamellar spacing, the extended solubility and the increased area fraction of cell eutectic as well as the refinement of Heusler phase particles may be the main factors that are relevant to the improved strength and ductility of injection-cast alloy at RT. The decrease of lamellar spacing and increase of cell eutectic zone produce more interfaces between NiAl and Cr(Mo) phases. Investigations [17-19] demonstrated that the dislocation network between NiAl and Cr(Mo) phase interface plays an important role on the strength of NiAl based alloys. The more NiAl/Cr(Mo) interfaces result in more dislocation network at the interface, so the strength of alloys can be enhanced accordingly. The increcent solubility of alloying elements in NiAl and Cr(Mo) is beneficial to the room temperature strength by solution strengthening. Besides, the remarkable increase in the total area of cell boundaries or phase boundaries by injection casting also induces a significant decrease in the segregated concentration of Heusler phase per unit area of cell boundaries that is beneficial to the strength improvement by particle strengthening. The improvement of ductility can be attributed to the increased area fraction of eutectic cell as well as the fine NiAl and Cr(Mo) plates.

The mechanical test data by compressive test at 1273K and 1373K of conventionally-cast and injection-cast alloys (Table 2) show that both alloys have the similar high temperature strength. For injection-cast NiAl-Cr(Mo)-Zr alloy, the high solid solution of alloying element in NiAl and Cr(Mo) phase, the great area fraction of eutectic cell and fine lamellar spacing should be propitious to the improvement of the strength at 1273K and 1373K. However, it exhibits similar high temperature strength to the conventionally-cast alloy. The causation can be ascribed to the weak intercellular zone. For NiAl-Cr(Mo)-Zr lamellar eutectic alloy, crack is easy to pass along the cell boundary when stress is applied to the eutectic alloy due to the coarser NiAl/Cr(Mo) plate and primary NiAl at intercellular zone, as shown in Figure 5. During injection casting process, the eutectic cell fined due to high cooling rate and the total area of cell boundary increases distinctly. The failure of the boundaries may become the dominant factor in determining the high temperature strength. Then it can be deduced that the strengthening effect of dislocation networks and solid solution was counteracted by the weaken effect from the weak cell boundary.

4. Conclusions

- The Zr doped NiAl-Cr(Mo) hypoeutectic alloy is mainly composed of coarse NiAl/Cr(Mo) eutectic cell and primary NiAl phase. The Zr addition results in the Ni2AlZr Heusler phase, which prefers to segregate along eutectic cell boundary.
- The microstructure of injection-cast alloy presents a fine microstructure including the refinement of eutectic cell size, interlamellar spacing and intercellular zone as well as primary NiAl phase and Ni2AlZr Heusler phase. In addition, the extension of solid solubility occurred in the alloy.
- The injection-cast alloy attains room temperature yield strength of 1445 MPa and compressive ductility of about 14%, which are higher than 1168 MPa and 7% for conventionally-cast alloy respectively. Both alloys possess the similar high temperature strength.

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