

## Effects of Zr Addition on the Microstructure and Mechanical Properties of NiAl/Cr(Mo)-Based Eutectic Alloys (Postprint)

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### Abstract

The effects of Zr addition on the microstructure and compressive properties of Ti- and Hf-containing NiAl/Cr(Mo)-based eutectic alloys were investigated. The results show that minor Zr addition significantly refines the NiAl/Cr(Mo) lamellae within the eutectic cells and optimizes the sizes of NiAl and Cr(Mo) phases in the eutectic cell boundary regions; with increasing Zr content, the NiAl and Cr(Mo) phases at the eutectic cell boundaries become noticeably coarsened, and the Heusler phase at the eutectic cell boundaries exhibits a semi-continuous distribution; when the Zr content increases to 1 at%, the Heusler phase at the eutectic cell boundaries forms a continuous network, and coarse Cr-rich phases are formed. Zr addition promotes the precipitation of coarse b-NiAl and a-Cr phases within the NiAl and Cr(Mo) phases in the alloy, and segregation of Heusler phase-forming elements at the precipitate interfaces leads to the formation of numerous interfacial dislocations. In addition, Zr addition results in the precipitation of fine Heusler particles in the Ni-Al phase. Appropriate Zr addition can significantly enhance the room-temperature and high-temperature compressive strength of the Ni-33Al-28Cr-5.5Mo-1.0Ti-0.3Hf eutectic alloy without significantly reducing its compressive ductility, while excessive Zr addition decreases the compressive ductility of the alloy.

### Full Text

## Effect of Zr Addition on Microstructure and Mechanical Properties of NiAl/Cr(Mo) Base Eutectic Alloy

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### Abstract

NiAl base eutectic alloy is an attractive material with promising potential for high-temperature applications. However, its inadequate high-temperature strength limits practical application. To improve its strength, Zr was added to Ti- and Hf-doped NiAl/Cr(Mo) base eutectic alloys, and the effect of Zr addition on the microstructure and mechanical properties was investigated. The results show that small additions of Zr can refine the NiAl/Cr(Mo) lamellae inside the eutectic cell and optimize the morphology of NiAl and Cr(Mo) phases in the intercellular zone. Moreover, Zr addition promotes precipitation of bulk Heusler phase along eutectic cell boundaries. With increasing Zr content, the eutectic cells become finer, but the NiAl and Cr(Mo) phases in the intercellular zone coarsen and the Heusler phase exhibits a semi-continuous distribution along the eutectic cell boundary. When the Zr content increases to 1% (atomic fraction), the NiAl and Cr(Mo) phases in both the eutectic cell and intercellular zone are significantly coarsened. Additionally, coarse Cr-rich phases precipitate in the intercellular zone and Heusler phase forms a continuous network along the eutectic cell boundary. The addition of Zr promotes precipitation of coarse  $\beta$ -NiAl and  $\alpha$ -Cr phases in the Cr(Mo) and NiAl phases, respectively. Furthermore, segregation of Heusler phase-forming elements along precipitate interfaces leads to formation of numerous interfacial dislocations. In addition, Zr addition results in precipitation of fine Heusler particles in the NiAl phase. Appropriate Zr addition can significantly improve the compression strength of Ni-33Al-28Cr-5.5Mo-1.0Ti-0.3Hf eutectic alloys at both room temperature and high temperature without reducing compression plasticity, but excessive Zr addition inevitably reduces compressive plasticity.

**KEY WORDS:** NiAl/Cr(Mo) base eutectic alloy, Zr, Heusler phase, microstructure, compressive property

## Introduction

The B2-structured NiAl intermetallic compound has attracted widespread attention as a candidate for next-generation high-temperature structural materials due to its excellent properties, including high melting point, low density, high Young's modulus, high thermal conductivity, and outstanding oxidation resistance. However, the room-temperature brittleness and inadequate high-temperature strength of NiAl seriously restrict its industrial applications [1-4]. To overcome these two major problems, numerous strengthening approaches have been employed, among which alloy strengthening through addition of refractory metals to form reinforcing particles or fibers has achieved significant progress [5-8]. The NiAl-28Cr-6Mo (abbreviated as NiAl/Cr(Mo)) eutectic alloy formed by adding Cr and Mo exhibits both improved room-temperature fracture toughness and reasonable high-temperature strength, making it the most promising NiAl-based alloy for practical applications [9-11]. Nevertheless, the high-temperature strength of this alloy still lags behind that of first-generation single-crystal superalloys [12,13], necessitating further improvement of its high-temperature performance for practical application.

Recent studies on this alloy [14-16] have found that addition of Heusler phase-forming elements such as Ti, Zr, and Hf can further improve the high-temperature strength of NiAl/Cr(Mo) eutectic alloys, though the strengthening mechanisms differ among these elements. Specifically, Ti addition forms Ni<sub>2</sub>AlTi precipitates at phase boundaries and within the NiAl phase [17], while Zr and Hf additions primarily form Ni<sub>2</sub>AlZr or Ni<sub>2</sub>AlHf phases at alloy phase boundaries, with small amounts of Hf solid solution also present [18,19]. Our previous investigations on the role of Hf [20-22] revealed that appropriate Hf addition can significantly improve the high-temperature properties of NiAl/Cr(Mo) eutectic alloys, but the segregation of Hf-rich phases at phase boundaries and eutectic cell boundaries reduces room-temperature compressive plasticity. Therefore, combining the strengthening characteristics of Ti, Zr, and Hf elements and adjusting the distribution and size of Heusler phases in NiAl/Cr(Mo) eutectic alloys is crucial for optimizing both room- and high-temperature performance. However, few studies have reported on the combined effects of adding all three Heusler phase-forming elements on the microstructure and properties of NiAl/Cr(Mo) eutectic alloys. Consequently, this work investigates the effects of adding various amounts of Zr to Ti- and Hf-containing NiAl/Cr(Mo) eutectic alloys on the microstructure and compressive properties.

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## 1. Experimental Methods

High-purity Ni, Al, Cr, Mo, Ti, Hf, and Zr (mass fraction >99.9%) were used as raw materials. Alloy ingots with different total contents of Ti, Hf, and Zr were melted in a water-cooled Cu crucible using a non-consumable W electrode under

Ar atmosphere. The nominal alloy composition was Ni-33Al-28Cr-5.5Mo-1.0Ti-0.3Hf-xZr (atomic fraction, %), where  $x = 0, 0.3, 0.5, 1$ , hereafter referred to as alloys A1, A2, A3, and A4, respectively. Each ingot was remelted at least five times to ensure compositional homogeneity. Since the mass loss during melting was less than 0.5%, the actual composition was considered consistent with the nominal composition.

The microstructure of the alloys was examined using an S-3400 scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). The chemical compositions of various phases were analyzed using a 1610 electron probe microanalyzer (EPMA). The microstructure and precipitates in different alloys were investigated using a JEM-2010 transmission electron microscope (TEM). Compression test specimens with dimensions of  $4 \text{ mm} \times 4 \text{ mm} \times 6 \text{ mm}$  were cut from the alloy ingots by wire electrical discharge machining. All specimen surfaces were mechanically ground with 800-grit sandpaper prior to testing. Compression tests were conducted on a Gleeble testing machine at room temperature and 1273 K with an initial strain rate of  $1.0 \times 10^{-3} \text{ s}^{-1}$ . For high-temperature tests, a thermocouple was welded at the specimen center to measure and control temperature with an accuracy of  $\pm 2 \text{ K}$ . After reaching the test temperature, the specimen was held for 20 s before compression. Room-temperature specimens were compressed to fracture, while 1273 K specimens were compressed to 35% engineering strain. The automatically recorded load-displacement curves were converted to true stress-true strain curves assuming uniform deformation and volume conservation.

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## 2. Results and Discussion

### 2.1 Effect of Zr Addition on Microstructure

Figure 1 [Figure 1: see original paper] shows SEM images of Ni-33Al-28Cr-5.5Mo-1.0Ti-0.3Hf-xZr (A1-A4) alloys with different Zr contents. All alloys consist of NiAl/Cr(Mo) eutectic cells and precipitates at the cell boundaries. Within the eutectic cells, the black NiAl matrix and gray Cr(Mo) phase exhibit a chrysanthemum-like morphology, growing from the cell center toward the boundary. Compared with the fine NiAl and Cr(Mo) lamellae inside the cells, the NiAl and Cr(Mo) phases at the cell boundaries are much coarser, with irregularly shaped white precipitates distributed discontinuously at the boundaries, as shown in Fig. 1a. For the alloy with 0.3% Zr, the average eutectic cell size is approximately 30  $\mu\text{m}$ , significantly refined compared with the 80  $\mu\text{m}$  average cell size of the Zr-free alloy, and the NiAl/Cr(Mo) lamellae within the cells are also slightly refined.

When the Zr content increases to 0.5%, the eutectic cells begin to coarsen, with an average size of approximately 40  $\mu\text{m}$ . However, the NiAl and Cr(Mo) phases at the cell boundaries show a spheroidization tendency, and the white precipitates at the cell boundaries become more numerous and form a near-

continuous network, as shown in Figs. 1b and 1c. Composition analysis results (Table 1) indicate that these white phases are primarily Heusler phases. When the Zr addition increases to 1%, the eutectic cells further coarsen to an average size of approximately 50 nm, and numerous spherical and dendritic gray-white phases appear, distributed semi-continuously at the cell boundaries, as shown in Fig. 1d. Additionally, 1% Zr addition significantly coarsens the NiAl/Cr(Mo) lamellae within the eutectic cells.

These microstructural changes are directly related to the total amount of Heusler phase-forming elements in the alloy. As Zr increases, the total Heusler phase-forming elements increase from 1.3% to 2.3%. Zr has a larger atomic radius and extremely low solubility in both NiAl and Cr(Mo) phases, meaning that the additional Heusler phase-forming elements will primarily segregate to grain boundaries and phase boundaries. Table 1 shows that Hf and Zr contents are extremely low in the Cr(Mo) phase and only modestly soluble in the NiAl phase, indicating that during solidification, Hf and Zr will be rejected to the solid-liquid interface front, increasing undercooling and accelerating the growth of NiAl and Cr(Mo) phases, thereby refining the NiAl/Cr(Mo) eutectic lamellae. Due to the solubility differences of Hf and Zr in NiAl and Cr(Mo) phases, NiAl grows slightly faster during solidification, causing significant coarsening of the microstructure at the eutectic cell boundaries compared with the cell interior. This phenomenon becomes more severe as the total Heusler phase-forming elements increase. When the total amount reaches 2.3%, Heusler phase formation consumes considerable Ni and Al, shifting the alloy composition away from the eutectic point and resulting in the formation of coarse Cr-rich phases. Since the composition deviation is small and Cr-rich phase precipitation consumes excess Cr, the NiAl/Cr(Mo) eutectic remains the dominant feature, though the lamellae are slightly coarser than in other alloys. Further compositional analysis reveals that as Zr content increases, Zr in the Heusler phase increases continuously, while Ni and Al in the Cr(Mo) phase and Mo in the NiAl phase decrease.

## 2.2 Effect of Zr Addition on Precipitates

Figure 2 [Figure 2: see original paper] shows XRD spectra of Zr-free and 1% Zr alloys. The peaks of Heusler phase  $\text{Ni}_2\text{AlX}$  (where X represents a mixture of Ti, Hf, and Zr) increase in number and intensity, indicating that the added Zr exists primarily as Heusler phase in the alloy. Additionally, some peaks of the Cr(Mo) phase are significantly enhanced, which according to SEM observations is closely related to the formation of substantial  $\alpha$ -Cr phase.

Further observation of precipitates at eutectic cell boundaries in alloy A2 reveals two distinct types: brighter polygonal phases and darker irregularly shaped phases, as shown in Fig. 3a [Figure 3: see original paper]. EDS analysis shows that the brighter phases contain over 50% Heusler phase-forming elements, while the darker phases contain over 60% Ni and Al. TEM observations confirm that the two types of precipitates at eutectic cell boundaries are Heusler phase and (Ti, Hf, Zr) solid solution phase (abbreviated as (Ti, Hf, Zr)ss), as shown in

Figs. 3b-3d. The Heusler phase is  $\text{Ni}_2\text{AlX}$  with a cubic crystal structure, lattice constant of 0.6810 nm, and Fm3m space group. The (Ti, Hf, Zr)ss has a cubic crystal structure with lattice constant of 0.4400 nm and Fm3m space group. Although both phases have cubic structures, no crystallographic orientation relationship was observed between them. SEM and TEM results show that large Heusler phases are distributed mainly at eutectic cell boundaries, while fine Heusler particles tend to precipitate along NiAl/Cr(Mo) phase boundaries within the cells. The (Ti, Hf, Zr)ss phases are relatively fine and preferentially precipitate at phase boundaries, as shown in Fig. 3e.

TEM observations of alloy A1 reveal that the NiAl/Cr(Mo) lamellae in the central region of eutectic cells remain very fine, with some interfacial dislocations present at phase boundaries but no precipitates observed, as shown in Fig. 4a [Figure 4: see original paper]. Examination of the NiAl phase in the eutectic cell region shows numerous fine lenticular  $\alpha$ -Cr particles approximately 20 nm in size, as shown in Fig. 4b. According to previous studies [23,24], these precipitates have a coherent relationship with the NiAl matrix, primarily due to the common cubic crystal structure and similar lattice constants of NiAl and Cr(Mo). In addition to the fine coherent  $\alpha$ -Cr particles, a few large Cr-rich precipitates with high dislocation density exist in the NiAl phase, having a semi-coherent relationship with the NiAl matrix. This phase formation may be attributed to enrichment of Ti, Hf, and Zr elements at the phase interface [25]. Observation of the Cr(Mo) phase within eutectic cells reveals numerous  $\beta$ -NiAl particles approximately 20 nm in size, which have a coherent relationship with the Cr(Mo) phase, as shown in Fig. 4c.

TEM observations of alloy A4 show that the increased total amount of Heusler phase-forming elements resulting from large Zr addition leads to precipitation of Heusler phase in various morphologies within the NiAl phase, as shown in Fig. 5a [Figure 5: see original paper]. At eutectic cell boundaries, relatively coarse NiAl phases contain rod-like and spherical Heusler precipitates ranging from 10 to 120 nm in size. According to Li et al. [26], the presence of large amounts of Ti and Hf promotes precipitation of fine Heusler particles within the NiAl phase. Although the maximum Zr addition in this study is only 1%, Zr has very low solubility in both NiAl and Cr(Mo) phases, and Sheng et al. [27,28] found that simultaneous addition of multiple large-atom elements promotes mutual enhancement of their precipitation at eutectic cell boundaries. Consequently, alloy A4 shows significantly more Heusler phase at cell boundaries than the 0.5% Zr alloy. Besides the Heusler phase from the additional Zr, the induced segregation of Ti and Hf elements to eutectic cell boundaries also contributes to this effect. Therefore, the later-solidified eutectic cell boundary region becomes enriched with Ti, Hf, and Zr elements, which on one hand increases undercooling at the solid-liquid interface and promotes crystal growth, allowing the 1% Zr alloy to maintain more complete NiAl/Cr(Mo) lamellar structure at cell boundaries compared with the more disorganized structure in the 0.5% Zr alloy. On the other hand, the enrichment of Ti, Hf, and Zr elements leads to supersaturation of Heusler phase-forming elements in the NiAl phase at cell boundaries,

resulting in extensive Heusler phase precipitation from the coarse NiAl phase after solidification. Observation of NiAl and Cr(Mo) phases within eutectic cells reveals significant differences in precipitate characteristics compared with the 0.3% Zr alloy, as shown in Figs. 5b and 5c. Two types of  $\beta$ -NiAl particles appear in the Cr(Mo) phase: smaller particles approximately 50 nm in size and larger particles approximately 300 nm in size. Both types of precipitates contain numerous interfacial dislocations. Within the NiAl phase, besides the dispersed coherent  $\alpha$ -Cr particles, many coarse semi-coherent  $\alpha$ -Cr particles with high interfacial dislocation density are present. Based on the previous analysis, the existence of these semi-coherent precipitates can be partially attributed to the supersaturation of Ti, Hf, and Zr elements in this region, which creates numerous nucleation sites in the NiAl and Cr(Mo) phases, leading to precipitation and rapid growth of some  $\beta$ -NiAl and  $\alpha$ -Cr precipitates. This supersaturation also causes segregation of Ti, Hf, and Zr at precipitate-matrix interfaces, resulting in formation of extensive interfacial dislocations that may cover entire precipitates.

### 2.3 Effect of Zr Addition on Compressive Properties

Table 2 presents the compressive properties of alloys with different Zr contents at room temperature and 1273 K. The results demonstrate that different Heusler phase-forming elements exert significant influence on compressive properties. Compared with the Zr-free alloy, Zr addition increases both room-temperature and high-temperature yield strength and compressive strength but reduces compressive plasticity. With increasing Zr content, room-temperature strength, room-temperature compressive strain, and high-temperature strength all exhibit an initial increase followed by a decrease.

The observed property variations can be attributed to microstructural changes induced by Zr addition. According to recent studies on NiAl-based eutectic alloys [29,30], both the morphology of eutectic cell boundaries and the size of NiAl/Cr(Mo) lamellae within cells significantly influence properties. Fine NiAl/Cr(Mo) lamellae within eutectic cells benefit room-temperature strength and can fully utilize the ductile phase to improve compressive plasticity. Narrow eutectic cell boundary regions with fine, discontinuous strengthening phases are beneficial for both strength and plasticity, while relatively coarsened NiAl and Cr(Mo) phases at cell boundaries contribute to high-temperature strength. Based on this analysis, 1% Zr addition leads to formation of continuous Heusler phase at eutectic cell boundaries, which severely reduces compressive plasticity and causes rapid crack propagation in the cell boundary region during early stages of compressive deformation. Additionally, the coarse Cr-rich phases at cell boundaries further deteriorate room-temperature compressive plasticity. Therefore, despite having a continuous and regular NiAl/Cr(Mo) eutectic structure, the 1% Zr alloy does not exhibit optimal performance. In contrast, the 0.5% Zr alloy demonstrates the best combination of room- and high-temperature properties, which can be attributed to fine NiAl/Cr(Mo) lamellae within eutectic cells, appropriate microstructure in the cell boundary region, and discontinuous

Heusler phase distribution.

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## Conclusions

- (1) Small Zr additions significantly refine the NiAl/Cr(Mo) lamellae within eutectic cells and the eutectic cell size of Ni-33Al-28Cr-5.5Mo-1.0Ti-0.3Hf alloys. With increasing Zr content, the eutectic cell size increases, the NiAl and Cr(Mo) phases at cell boundaries further coarsen, and the Heusler phase at cell boundaries exhibits semi-continuous distribution. The 1% Zr addition coarsens both the NiAl/Cr(Mo) lamellae within cells and the cell size, leading to precipitation of spherical and dendritic Cr-rich phases in the intercellular region and formation of a continuous Heusler phase network along cell boundaries.
  - (2) Zr addition promotes precipitation of coarse  $\beta$ -NiAl and  $\alpha$ -Cr particles in the Cr(Mo) and NiAl phases, respectively. Segregation of Heusler phase-forming elements at precipitate interfaces leads to formation of numerous interfacial dislocations. The 1% Zr addition causes Heusler particle precipitation in the NiAl phase at cell boundaries.
  - (3) Appropriate Zr addition can significantly improve the room-temperature and high-temperature compressive strength of Ni-33Al-28Cr-5.5Mo-1.0Ti-0.3Hf eutectic alloys without reducing compressive plasticity, but excessive Zr addition reduces compressive plasticity. A Zr content of 0.3%-0.5% represents a relatively optimal addition level.
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