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# MICROSTRUCTURE AND HARDNESS OF NiAl/$Ni_2AlX$ TWO-PHASE ORDERED INTERMETALLIC ALLOYS

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Microstructures of several NiAl/$Ni_2AlX$ two-phase alloys with a composition of Ni-35 at.% Al-13 at.% X (X=Ti, Zr, Hf, V, Nb, Ta) have been studied by X-ray diffraction and scanning electron microscopic analyses. The alloy with vanadium exhibits a single phase of B2 structure, and others have two phases of B2 and $L2_1$ structures. The lattice parameter of the B2 phase in these alloys remains almost unchanged of about 2.888Å, whereas the lattice parameter of the $L2_1$ phase in the two-phase alloys varies in the range of 5.876 to 6.110 Å, depending on the atomic radii of the elements X. The lattice misfit between the two phases is the smallest (1.5 %) in the alloy with titanium and is the largest (6.1 %) in the alloy with zirconium. The smaller the misfit, the more stable is the microstructure at elevated temperatures.

## 1. Introduction

Alloys with bcc ordered crystal structures such as NiAl and $Ni_2AlTi$, have received considerable attention because of their potential use as high-temperature structural materials [1-7]. The excess addition of groups IV and V elements to NiAl (β) with a B2 crystal structure is known to form the Heusler phase with the composition of $Ni_2AlX$ (β'). The Huesler phase has a cubic $L2_1$ structure, in which the unit cell comprises eight bcc unit cells with Al and X atoms occupying two sets of octahedral sites located at body-center sublattice positions. Because of the similar lattice structure between B2 and L21, it is possible to improve the high-temperature properties of NiAl by precipitation hardening of the $Ni_2AlX$ phases, just like $\gamma/\gamma'$ nickel base superalloys [8,9]. In order to develop a new type of alloys based on β/β', the microstructural factors such as solubility of X elements in NiAl as well as lattice misfit between the two phases have to be unveiled. Considerable studies have been done on the microstructure and mechanical properties of Ni-Al-Ti [8-13] and other Ni-Al-X systems [14-18]. In addition, there are number of studies on the phase diagram of Ni-Al-X systems [19-24]. However, there is a lack of a systematic study of the crystallographic relationship in the pseudobinary NiAl/$Ni_2AlX$ alloys. In this study, a series of NiAl/$Ni_2AlX$ two-phase alloys (X=Ti, Zr, Hf, V, Nb, Ta) were prepared, and their microstructures as well as crystal structures were examined by X-ray diffraction and scanning electron microscopic analyses. The hardness of these alloys is also measured and correlated with microstructural features.

## 2. Experimental

Alloys used in this study have a composition of Ni-35 at.% Al-13 at.% X. The alloys containing 13 % of Ti, Zr, Hf, V, Nb or Ta are denoted as HT, HZ, HH, HV, HN and HTA**, respectively, and the alloy containing 6.5 % Ti and 6.5 % Zr is referred as HTZ (all compositions are given in at. %). The alloys were prepared by arc-melting six times, followed by drop casting into chilled copper molds in an argon atmosphere. All the alloys were given a heat treatment of 1423 K/1d plus 1173 K/5 ds in vacuum. An electron microprobe equipped with a wavelength dispersive spectrometer was used for analyzing the chemical compositions of the phases present in the heat-treated samples. For X-ray study, powder samples were prepared by crashing the heat-treated alloys, followed by sieving with a 325 mesh. The analyses were made on diffractometer

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** The alloy HTA was used only for lattice parameter measurement and hardness test.

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·using Cu Kα radiation. A graphite monochrometer was used, in order to reduce the background radiation. The volume fraction of β and β' phases was determined by direct comparison of the integrated intensity of the fundamental reflections of (110) and (220), [26]. In calculating the volume fraction, the structural factor was compensated by the analyzed composition of each phase.

## 3. Results and Discussions

### 3.1 Lattice parameter and lattice misfit

Variation of lattice parameters of the β and β' phases in the alloys examined is shown in Fig. 1, where the lattice parameters of the β' phase is given in a half of the value. The lattice parameter of the β phase in these alloys remains almost unchanged of about 2.888Å. There are no indication of the β' phase formed in the alloy HV. The lattice parameter of the β' phase in the two-phase alloys varies in the range of 5.876 Å, the smallest for HT, to 6.110 Å, the largest for HZ. Note that the lattice parameter of the β' phase in HTZ falls the middle of those of HT and HZ, indicating that it is possible to control the β' lattice parameter by a partial substitution of the X elements. Table 1 summarizes our results which suggest (1) the substitution of X for Al in the B2 structure is low except that their atomic size is not much different, (2) the X elements are interchangeable in the L$2_1$ phase and consequently its lattice parameter can be easily adjusted by the substitution.

The present result clearly demonstrates that the lattice mismatch between the β and β' phases exists in the alloy HTA. According to Pak et al.[14], the lattice parameter of the β' phase was exactly twice as large as that of the β phase in NiAl/Ni$_2$AlTa two-phase alloys, suggesting no lattice mismatch between the two phases (see Fig. 1). We are not in a position to discuss the reason for the difference; however, the present data are fairly consistent with those reported by Nash et al. [22]. The change in lattice parameter of the β' phase seems to be well correlated with the atomic radius of the X elements.

Figure 2 plots the lattice misfit between the β and β' phases in the two-phase alloys as a function of covalent radius of the X[*] elements. The lattice misfit between the two phases increases linearly with increasing the covalent radius of the X element: the smallest (1.5 %) for the alloy with titanium and the largest (6.1 %) for the alloy with zirconium. Since the covalent radius of vanadium is small enough for no formation of the β' phase, the lattice misfit between the β and β' phases is expected to be reduced by a partial substitution of vanadium for other X elements in the alloys.

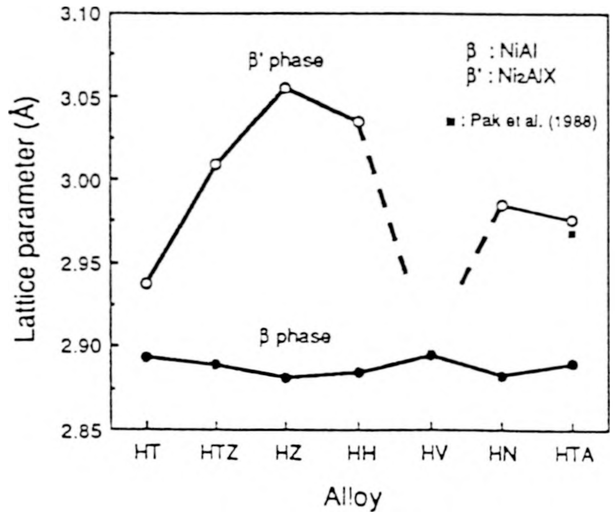

Fig. 1 Lattice parameters of the β and β' phases in NiAl/Ni$_2$AlX alloys.

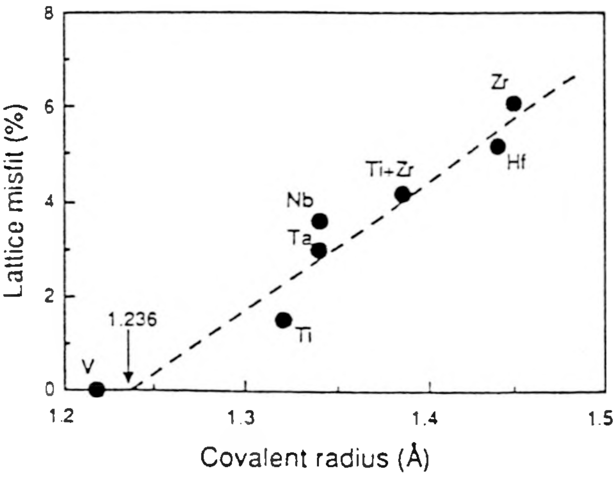

Fig. 2 Relationship between the lattice misfit for β/β' phases and covalent radii of the X elements in NiAl/Ni$_2$AlX Alloys.

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[*] The change in lattice parameter of the β' phase shown in Fig. 1 can be better correlation with the covalent radius rather than the Goldschmidt radius of the X elements, indicating that the atomic bonding in the Huesler phase is of the covalent nature rather than the metallic nature.

Table 1. Phase present, lattice parameter, a, chemical compositions of the phases and volume fraction of the Heusler phase, $V_f$ (H), in the NiAl/$Ni_2AlX$ alloys, together with reported lattice parameters.

| Alloy | Phase present | a (Å) | Analyzed compositions (at %) | | | | $V_f$(H) (%) | a (Å)** from literature |
|---|---|---|---|---|---|---|---|---|
| | | | Al | X | X* | Ni | | |
| HT | B2 | 2.894 | 39.0 | 8.7 | - | Bal. | | |
| | $L2_1$ | 5.876 | 30.8 | 17.9 | - | Bal. | 48.5 | 5.843 [7]<br>5.89-5.92 [20] $^{a)}$ |
| HTZ | B2 | 2.889 | 43.0 | 3.7 | 0.17 | Bal. | | |
| | $L2_1$ | 6.018 | 24.8 | 10.6 | 13.9 | Bal. | 44.0 | |
| HZ | B2 | 2.881 | 44.8 | 0.2 | - | Bal. | | |
| | $L2_1$ | 6.110 | 22.7 | 25.1 | - | Bal. | 51.1 | 6.123 [18] $^{b)}$, 6.09 [19] $^{b)}$ |
| HH | B2 | 2.885 | 49.1 | 1.2 | - | Bal. | | 2.882-2.897 [21] |
| | $L2_1$ | 6.069 | 23.8 | 23.1 | - | Bal. | 48.2 | 6.073-6.082 [21]<br>6.081 [18] $^{b)}$ |
| HV | B2 | 2.894 | 35.1 | 13.1 | - | Bal. | 0 | 6.330 [17], no $L2_1$ [19] |
| HN | B2 | 2.882 | 46.2 | 0.68 | - | Bal. | | |
| | $L2_1$ | 5.972 | 24.9 | 23.4 | - | Bal. | 52.2 | 5.974 [18] $^{b)}$, 5.962 [19] $^{a)}$<br>5.970 [23] $^{b)}$ |
| HTA | B2 | 2.890 | not analyzed | | | | | 2.968 [14], 2.894 [22] |
| | $L2_1$ | 5.953 | | | | | - | 5.936 [14], 5.940 [22]<br>5.949 [18] $^{b)}$, 5.904 [19] $^{a)}$ |

* : For HTA, X = Ti and X* = Zr. ** : Lattice parameters of the B2 phase listed here are obtained from either two-phase alloys with the $L2_1$ phase or multiphase alloys with the $L2_1$ and C14 phases. a) : data from $L2_1$/C14 two-phase alloys. b) : data from a $L2_1$ single-phase alloy.

## 3.2 Microstructures

Backscattered electron images of the alloys HT and HZ with the smallest and largest misfit at the β/β' interface, respectively, among the alloys are shown in Fig. 3. The alloy HT exhibits a lamellar structure, together with brightly imaged small particles dispersing in the darker matrix, as shown in Fig. 3 (a). The EPMA analyses revealed the darker regions having an average composition of Ni-39.0 % Al-8.7 % Ti and the brighter regions having that of Ni-30.8 % Al-17.9 % Ti, indicating β and β' phase, respectively. On the other hand, the alloy HZ exhibits a coarser microstructure, which contains large dark areas together with gray regions having relatively small, dark particles, as shown in Fig. 3 (b). The dark areas correspond to β phase with a composition of Ni-44.8 % Al-0.2 % Zr on average, whereas the gray regions was found to be β' phase with a composition of Ni-22.7 % Al-25.0 % Zr. Some brightest spots seen in HZ contain a large amount of zirconium, indicating a possibility of a $Ni_2Zr_7$-type phase [25]; however the amount of this phase is negligibly small. The fact that the alloy HT has the microstructure finer than that of the alloy HZ indicates that the smaller the misfit, the finer the microstructure even after prolonged annealing at high temperatures.

Microstructure analyses revealed no β' phase in the alloy HV, i.e. there is at least 13 % or

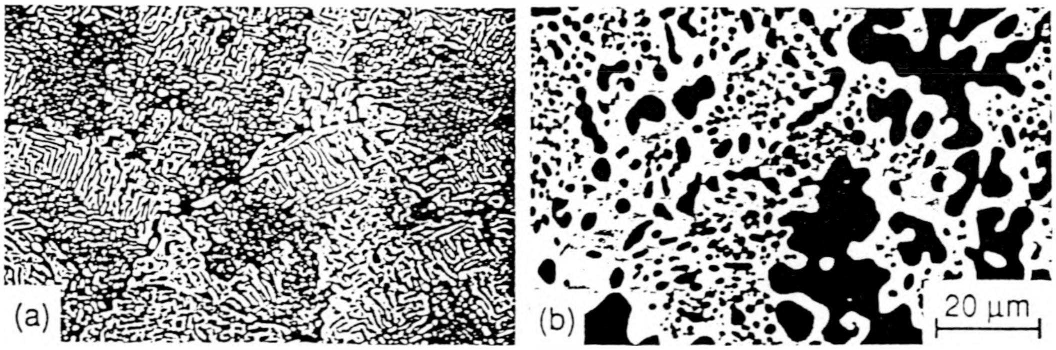

Fig. 3 Backscattered electron images of the alloys HT (a) and HZ (b) after annealing.

more solubility of vanadium in NiAl. In contrast, only a level of 1 % or less zirconium, hafnium and niobium can be dissolved in the NiAl-β phase (see Table 1). The solubility of zirconium or hafnium in NiAl-β phase obtained here is in good agreement with the results reported by Nash et al. [21, 25]

By assuming that the element X and excess nickel substitute for aluminum in the ideal composition of NiAl-β phase and that the excess nickel occupies both aluminum and X sublattice sites in $Ni_2AlX$-β' phase, the volume fraction of the β' phase in these alloys were calculated based on the analyzed compositions of each phases and the integrated intensities of their fundamental peaks. The results are also summarized in Table 1. All the alloys except HV have a volume fraction of β' phase of nearly 50 %, indicating that the same amount of single phase region exists on either side of the pseudobinary NiAl-$Ni_2AlX$ diagram. Although the $Ni_2AlV$ phase was reported to exist [17], our results clearly indicate no formation of this phase in the Ni-Al-V system. This is in agreement with the early work by Raman and Schubert [19].

### 3.3 Hardness changes

The room-temperature hardness of the alloys is shown in Fig. 4. The hardness of the alloy HV without the β' phase is the lowest (4.7 GPa), whereas the alloy HH shows the highest value of 6.7 GPa. The hardness of the alloy HT (5.5 GPa) is in between. Note that no cracks were observed around the indents only for the alloys HV and HT. The hardness follows the same general trend of the β' lattice parameter shown in Fig.1, indicating an important role of the β' phase in the overall hardness of the alloys. Since the volume fraction of the phase remains almost unchanged of about 50 %, the alloy hardness is apparently associated with the β' hardness, which is controlled by the intrinsic *lattice strain** in the Huesler phase. Details of this lattice strain in the β' phase are explained elsewhere [15].

Figure 5 shows the hardness as a function of total lattice strain of the β' phase** in each alloy, where the hardness is normalized with respect to the alloy HV. The hardness increases with increasing the lattice strain. Thus, the lattice strain is a key factor contributing to the high hardness of the alloys.

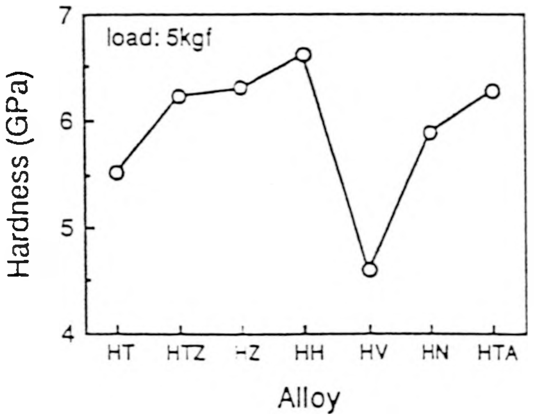

Fig.4 Room-temperature hardness of the NiAl/Ni2AlX alloys studied.

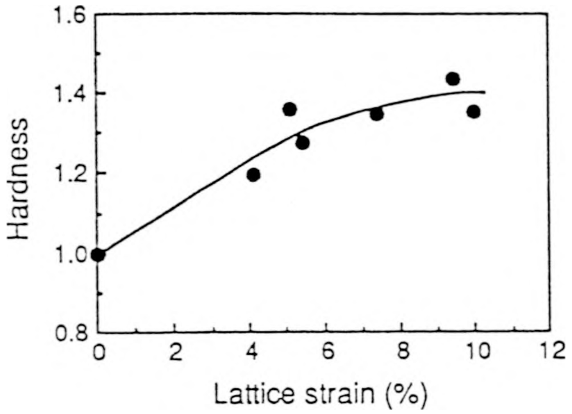

Fig. 5 Change in hardness with the total lattice strain in the β' phases.

## 4. Summary

The systematic study of microstructures and hardness of β/β' two-phase alloys (Ni-35 % Al-13 % X, where the X is Ti, Zr, Hf, V, Nb or Ta) by X-ray diffraction and scanning electron

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*The two B2 structures, AB and AC, with different lattice parameters should be either expanded or contracted in forming the Huesler phase, $A_2BC$, with a cubic crystal symmetry, thereby producing the lattice strain.

** The total lattice strain is taken as a sum of the strains due to the expansion and contraction of the B2 lattices. Since there is no NiX compound with a B2 structure except NiTi, a lattice parameter of the NiX is estimated from their covalent radii with a correction factor of 1.057 obtained by the experimental data (3.015Å) divided by the calculated value from the covalent radii (2.852Å) of the NiTi compound.

microscope draws the following conclusions:

1. (1) The alloy with vanadium exhibits a single phase of B2 structure, and others have two phases of B2 and $L2_1$ structures.
2. (2) The lattice parameter of the B2 phase in these alloys remains almost unchanged of about 2.888Å, whereas the lattice parameter of the $L2_1$ phase in the two-phase alloys varies in the range of 5.876 to 6.110 Å, depending on the covalent radius of the X element .
3. (3) The difference in lattice misfit between the two phases is the smallest (1.5 %) for the alloy with titanium and is the largest (6.1 %) for the alloy with zirconium. The smaller the misfit , the more stable is the microstructure after prolonged annealing at elevated temperatures.
4. (4) The lattice strain stored intrinsically in the $\beta'$ phase is primarily responsible for the high hardness of the $\beta/\beta'$ two-phase alloy at ambient temperatures.

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