Microstructure, Phase Constitution and Tensile Properties of Co–Ni–Ti–Al Base Multi-Phase Intermetallic Alloys

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Three multi-phase alloys were selected in the Co–Ni–Ti–Al system with microstructures consisting of combinations of such intermetallic phases as the B2, L1_2, and L2_1 (Heusler), and the primary solid solution denoted as (Co, Ni). They were hot fabricated after drop casting and were heat treated to obtain the multi-phase structures. Optical metallography and electron microprobe analyses revealed that the alloys contained B2/L1_2, L1_2/L2_1, and B2/L1_2/(Co, Ni) phases after annealing at 1273 K. It was found that limited tensile ductility can be achieved in the B2/L1_2 and B2/L1_2/(Co, Ni) alloys but not in the L1_2/L2_1 alloy. Fracture analyses on the former two alloys showed that the causes for the brittle fracture include: (1) cleavage fracture in the B2 phase, (2) intergranular fracture of the polycrystalline L1_2 phase, (3) separation of B2/L1_2 interfaces, and (4) environmental effect. Based on such analyses, a new alloy was designed to minimize the above factors for ductility improvement. The alloy consisting of L1_2/B2/(Co, Ni) three phases was found to exhibit over 20% room temperature ductility, with a yield strength of over 600 MPa.

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Keywords: cobalt-nickel-titanium-aluminum system, intermetallics, multi-phase alloy, ductility, alloy design, microstructure, fracture mode

I. Introduction

Recent efforts to develop structural intermetallic alloys have focused on improving room temperature ductility and toughness to raise their potential for practical applications. Although there has been considerable work on the effect of such factors as alloy composition, deviation from stoichiometry, and ternary alloying additions on the ductility and fracture behavior of a single phase alloy(43–45), the recent trend has been towards the study of multiphase intermetallic alloys with controlled microstructures and phases based on binary or multicomponent phase diagrams. A typical example of achieving some room temperature ductility by this approach is the well-known case of γ-TiAl and α2-Ti₃Al two-phase γ titanium aluminate alloys(46–48).

Along this line, there have been several studies of mechanical properties of the B2 type intermetallics such as NiAl and CoAl. Considerable efforts have been devoted to the ternary Ni–Co–Al system because multiple choices in the combination of the phases and their compositions become possible. In the ternary system, as shown on an isothermal section(49) at 1173 K in Fig. 1, NiAl and CoAl form a continuous solid solution, the primary solid solutions of both Co and Ni are also basically continuous throughout, and the L1_2 phase of NiₓAl at the Ni–Al edge of the ternary system extends into the ternary compositions along (Ni, Co)_3Al. Then the combination of phases of interest in the ternary system includes B2/(Co, Ni), B2/L1_2, and B2/L1_2/(Co, Ni), where the continuous primary solid solution is denoted as (Co, Ni). Several studies have been reported on design of B2/(Co, Ni) alloys by Ishida et al.(50) and B2/L1_2 alloys by Pank et al.(9–10), all of which were intended to ductilize the B2 NiAl. In the former effort it was shown that good room temperature compressive ductility can be obtained in B2/(Co, Ni) but not in B2/L1_2, whereas the latter work claimed that the ductility of the B2 alloys can be improved by having the L1_2 phase decorating B2 grain boundaries.

More recently, a systematic investigation has been carried out by Tian et al.(11) and Kimura et al.(12–16) on the constitution of the Co–Ni–Al ternary phase diagram with a clear intention of developing multi-phase intermetallic alloys based on B2 CoAl. Mechanical properties of B2/(Co, Ni), B2/L1_2 and B2/L1_2/(Co, Ni) have been reported in the ternary alloy system and even in the quaternary Co–Al–Ni–Ti systems(17–18). It has been shown that some measurable ductility, 2 to 10%, was obtained at room temperature by compression tests of these alloys in cast and annealed conditions. It is necessary, however, to evaluate the room temperature ductility and strength by tensile tests in order to realize the significance of such microstructural control in multi-phase intermetallic alloys for practical applications as a new class of structural material.

In the present study, two alloys were chosen based on the previous work by Kimura et al.(15) in the Co–Ni–Ti–Al system which contain B2 and L1_2 two phases and B2, L1_2 and (Co, Ni) three phases, respectively. A third alloy having the L2_1 (Heusler type) phase in the L1_2 matrix, was

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II. Experimental Procedures

The alloys weighing about 500 g were prepared by arc-melting under an argon atmosphere and drop casting into a copper mold. Compositions of the alloys and expected phase constitutions at 1073 to 1273 K are shown in Table 1. They were hot forged at 1373 K to a reduction in thickness of about 44%. The annealing was to produce the desired phases and microstructure were conducted in a vacuum (10^{-6} torr) for different durations at 1273 K.

Optical metallography was carried out after normal mounting and polishing procedures followed by etching with aqua regia. Electron microprobe analysis (EPMA) was done on these samples for identification of phases present. A JEOL superprobe 733 with a Tracer X-ray detector was used for the measurement, and the ZAF calibration was conducted for quantitative analyses.

Tensile tests were carried out at room temperature using flat specimens with a gage length of 12.5 mm at an approximate strain rate of 3.3 \times 10^{-3} \text{s}^{-1}. Some tests were done in a vacuum system where pure oxygen was leaked in at a 0.66 atmosphere pressure (500 torr). The purpose of dry-oxygen tests is to see whether there was an environmental effect on the mechanical properties. Fractography followed on the fracture surface using a Hitachi S-4100 operated at 5 kV. Macroscopic fracture paths were also examined by optical microscopy on the longitudinal cross-sections of tensile specimens fractured at room temperature.

III. Results

1. Metallography

Figure 2 shows optical micrographs for the alloys as cast, (a) through (c), and after hot forging at 1373 K, (d) through (f); as cast microstructures are commonly dendritic in nature. It was found in alloy 1Q that there were some pores in groups mostly along or between the dendritic arms. Pores were also visible in alloy 2Q but were much less, and alloy 3Q appeared to have the least amount of pores. The presence of the pores is indicated by arrows in Figs. 2(a) and (b). Microstructures of the alloys after hot forging were much less dendritic in the as-cast alloys. It should be noted that pores were seldom seen in both alloys 1Q and 2Q after hot forging.

Figure 3 shows examples of optical micrographs of the alloys annealed after hot forging, in this case, at 1273 K for 14.4 ks (4h). Note that the micrographs were taken at a higher magnification than those in Fig. 2. In alloy 2Q, Fig. 2(b), there were two phases, one with a darker contrast having precipitates inside and one with a lighter contrast. Alloy 1Q exhibited similar microstructure as alloy 2Q; however, there was more of the darker phase with precipitates in a higher volume than in alloy 2Q. Note that there is another phase with an even lighter contrast within the interconnecting phase as shown in Fig. 3(a), though this feature is better visible in Fig. 4(a) which will be shown later. These observations are consistent with the previous results showing that alloy 2Q is two-phase whereas 1Q is three-phase after prolonged annealing at.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition (at.%)</th>
<th>Expected Phase Constitution at 1173 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Q</td>
<td>40.0 30.0 25.0 5.0</td>
<td>B2/L1_2/(Co, Ni)</td>
</tr>
<tr>
<td>2Q</td>
<td>40.0 30.0 20.0 10.0</td>
<td>B2/L1_2</td>
</tr>
<tr>
<td>3Q</td>
<td>33.3 33.3 16.7 16.7</td>
<td>L1_2/L2</td>
</tr>
</tbody>
</table>
Fig. 2 Optical micrographs of as-cast, (a) through (c), and hot-forged alloys, (d) through (f). (a) and (d) are for alloy 1Q, (b) and (e) for alloy 2Q, and (c) and (f) for alloy 3Q. Arrows indicate pores present in alloy 1Q and 2Q in their as-cast conditions.

1173 K\(^\circ\). The microstructure of alloy 3Q in Fig. 3(c) is found to be very similar to alloy 2Q, although the constituent phases are different.

2. Identification of phases by EPMA

Results of the chemical analyses by EPMA on the constituent phases in all the alloys annealed at 1273 K for three days are summarized in Table 2. In the table, a sum of Al and Ti concentrations are also included for a later discussion. The microstructural features of the phases are shown imaged by back scattered electrons in Fig. 4(a) to (c). Compositions given in the table are an average of 3 to 5 measurements on each phase with data scattered within \( \pm 1\) to 1.5 percentage points (except a little larger scattering for the case of fine precipitates), and the data are basically reproducible. The identification of the phases in alloys 1Q and 2Q given in the table can be rationalized by comparison with the information available from the quaternary system later in the discussion section. The compositional analyses of 3Q are based on the formation of the L1\(_2\) and L2\(_1\) phases, which were identified previously by X-ray diffractometry of the same alloy composition\(^\text{17}\).

Based on these results, it is confirmed that alloy 1Q is B2/L1\(_2\)/\((\text{Co, Ni})\) three-phase, 2Q is B2/L1\(_2\) two-phase, and 3Q is L1\(_2\)/L2\(_1\) two-phase. It should be noted that in all the alloys the L1\(_2\) phase with a lighter contrast is polycrystalline in structure. This is not readily seen in optical micrographs in Fig. 3 but is clearly visible in back scattered electron images in Fig. 4.

3. Tensile tests and fractography

(1) Room temperature tensile tests

Room temperature tensile tests revealed that plastic elongation is detected in alloy 2Q in annealed conditions and in alloy 1Q under only limited conditions. However, alloy 3Q fractured prematurely in all conditions used in the present work. Selected stress strain curves are shown in Fig. 5, while Table 3 summarizes the room temperature tensile properties of the alloys.

Based on the more complete set of data for alloy 2Q, it may be concluded that the room temperature ductility of the alloy is controlled by three important factors. First, a simple decrease in the strength level by a prolonged annealing does not provide a significant increase in plastic elongation prior to fracture. This means that the brittleness is most probably related to the intrinsic nature of the constituent phases, not to the dispersion characteristics of the L1\(_2\) precipitates in the B2 phase, which coarsen during annealing. Second, testing under a dry oxygen atmosphere does appreciably improve the room temperature ductility of alloy 2Q, as compared to the result obtained in air. The importance of the environmental effect on the ductility of ordered intermetallics has often been observed mainly in single phase alloys. Here it is observed in the multi-phase alloy 2Q whose ductility and fracture behavior are also influenced by the intrinsic features of its constituent phases as well. Finally, it is noted
that a double annealing, 1273 K for 4h plus 1173 K for 3d, provided better ductility not only in alloy 2Q but also in alloy 1Q. This would suggest that microstructural control is a key factor in controlling the ductility of these two alloys. This point will be further discussed in a later section.

(2) Fractography
SEM fractographs of the alloys tensile tested at room temperature are shown in Fig. 6 for alloy 1Q and in Fig. 7 for alloy 2Q in both as-forged and annealed conditions. It is first found that fracture facets are obviously larger for the as-forged conditions in both alloys than those after annealing at 1273 K for 3d. This is because the precipitation of L12 particles in the B2 phase region after annealing branches fracture paths and refines fracture facets, as compared with fracture paths in precipitate-free B2 phase. Figure 8 shows a back scattered electron image, (a), and an optical micrograph, (b), in the vicinity of the fracture surface of alloy 2Q sectioned longitudinally. It can clearly be seen in both (a) and (b) that crack propagation is often interrupted by L12 precipitates, resulting in non-flat fracture surfaces. Note that in Fig. 8(b) the cracks are also found at phase boundaries between the B2 and the L12 phases. Also, curved smooth surfaces are seen in Figs. 6(a) and 7(a) for as-forged alloys. These are probably associated with solidification defects, such as interdendritic shrinkage pores. Such defects are clearly seen in Figs. 2(a) and (b) for as-cast materials. It is possible that these defects persisted even after hot forging with a total reduction of 44%.

Characteristic fracture appearance of the annealed 1Q and 2Q alloys includes cleavage fracture in the B2 phase and intergranular fracture in the L12 phase, as clearly seen in Fig. 7(b) for alloy 2Q. The occurrence of intergranular fracture of the L12 phase is consistent with the polycrystalline structure observed for the phase shown in Fig. 4.

IV. Discussion

1. Phase constitutions
The chemical compositions of the constituent phases in alloys 1Q and 2Q are shown in Figs. 9 and 10, where the composition of each phase (open circles) is expressed on a hypothetical ternary isothermal section of the Co–Ni–(Al+Ti) system. Phase boundaries shown as broken lines in the 1173 K section for the 5Ti alloy in Fig. 9 and the 10Ti alloy in Fig. 10 are estimated based on the previous work by Kimura et al.15. Two-dimensional depiction of the phase equilibria for a quaternary system is impossible, so Ti at levels of 5 at.% and 10 at.% is treated as Al for the "ternary" sections. One reason for this construction is based on the consideration that the (Al+Ti) concentration would be an important factor controlling the room temperature ductility of one of the constituent phases, the L12 phase, which will be discussed in the next section. The phase compositions of the Co–Ni–Ti–Al alloys are reasonably represented in these figures based on the Co–Ni–Al ternary system, although a direct comparison between the composition of the present result and the previous results is not easy at all.

There has been limited information available in the literature for the phase relationships among the B2 phases (CoTi, CoAl and NiTi), Heusler phases (Co₂Al₇Ti and Ni₃Al₇Ti), and L12 phases (Ni₃Al and Co₃Ti) in the Co–Al–Ni–Ti quaternary system. Matano et al.15 have shown a portion of the isothermal section of the Co–Al–
Fig. 4  Back scattered electron image of (a) alloy 1Q, (b) alloy 2Q, and (3) alloy 3Q annealed at 1273 K for 4h. Identification of constituent phases is made in each micrograph.

| Table 2  Results of chemical analyses* of constituent phases by EPMA. |
|----------------|----------------|----------------|----------------|----------------|
| Phase Contrast and Morphology | Chemical Composition (at.%) | Phase Identification |
|----------------|----------------|----------------|----------------|----------------|
| Darker Phase | 36.97 | 29.69 | 28.60 | 4.74 | 33.34 | B2 |
| Lighter Interconnecting Phase and Precipitates | 44.28 | 33.20 | 14.81 | 7.70 | 22.51 | L12 |
| White Phase in the Lighter Phase | 56.27 | 26.83 | 12.44 | 4.47 | 16.91 | (Co, Ni) |
| Darker Phase | 38.22 | 25.34 | 27.75 | 8.70 | 36.45 | B2 |
| Lighter Interconnecting Phase | 42.88 | 32.46 | 11.90 | 12.77 | 24.67 | L12 |
| Precipitates in Darker Phase | 41.89 | 30.50 | 15.86 | 11.76 | 27.62 | L12 |
| Lighter Interconnecting Phase | 33.75 | 39.69 | 9.00 | 17.56 | 26.56 | L12 |
| Darker Phase | 32.61 | 25.23 | 22.62 | 19.54 | 42.16 | L2 |
| White Precipitates in the Darker Phase | 32.06 | 34.04 | 16.35 | 17.56 | 33.91 | ** |

*Data scatter was within ±2.5% in the analyses for the precipitates. Since the scatter in all other phases was within ±1 to 1.5%, the relatively large scatter here would arise from the fine precipitate size.

**The result of the analyses was about equal to the alloy composition of the alloy, possibly because of volume analysis including both phases.

Ti ternary system involving the B2 CoAl and CoTi, the Heusler Co2AlTi, and the L12Co5Ti. A similar but more detailed study has been made on the phase relationship in the Ni–Al–Ti system by Yang et al. (106(1)). With all these recent efforts, the phase equilibria among the L12, B2, and Heusler phases are becoming clearer. The Heusler phase has been reported to be brittle at room temperature by a number of investigators (106(10)). In the present study, alloy 3Q did not exhibit any plastic deformation at room temperature regardless of the annealing conditions. This is apparently due to the presence of the extremely brittle Heusler phase. In addition, the concentration of (Al+Ti) in the L12 phase, being over 25%, would be detrimental for the ductility of the phase. This point is going to be discussed in the following section.

Fig. 5  Selected tensile stress-strain curves at room temperature of alloys 1Q and 2Q after different heat treatments and under different test environments.


<table>
<thead>
<tr>
<th>Heat Treatment (Time/K)</th>
<th>Test Environment</th>
<th>( \sigma_y )</th>
<th>( \sigma_f )</th>
<th>Plastic Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot forged</td>
<td>Air</td>
<td>677</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d/1173</td>
<td>Air</td>
<td>988</td>
<td>988</td>
<td>0.3</td>
</tr>
<tr>
<td>4h/1273</td>
<td>Air</td>
<td>844</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d/1273</td>
<td>Air</td>
<td>634</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4h/1273 + 3d/1173</td>
<td>Air</td>
<td>823</td>
<td>893</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Alloy 2Q**

<table>
<thead>
<tr>
<th>Heat Treatment (Time/K)</th>
<th>Test Environment</th>
<th>( \sigma_y )</th>
<th>( \sigma_f )</th>
<th>Plastic Elongation (%)</th>
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<tbody>
<tr>
<td></td>
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<td></td>
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<tr>
<td>Hot forged</td>
<td>Air</td>
<td>487</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d/1173</td>
<td>Air</td>
<td>624</td>
<td>647</td>
<td>0.9</td>
</tr>
<tr>
<td>4h/1273</td>
<td>Air</td>
<td>613</td>
<td>662</td>
<td>0.8</td>
</tr>
<tr>
<td>4h/1273</td>
<td>Dry ( \text{O}_2 )</td>
<td>586</td>
<td>711</td>
<td>1.7</td>
</tr>
<tr>
<td>3d/1273</td>
<td>Air</td>
<td>557</td>
<td>596</td>
<td>0.9</td>
</tr>
<tr>
<td>4h/1273 + 3d/1173</td>
<td>Air</td>
<td>654</td>
<td>713</td>
<td>1.0</td>
</tr>
<tr>
<td>4h/1273 + 3d/1173</td>
<td>Dry ( \text{O}_2 )</td>
<td>621</td>
<td>770</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Alloy 3Q**

<table>
<thead>
<tr>
<th>Heat Treatment (Time/K)</th>
<th>Test Environment</th>
<th>( \sigma_y )</th>
<th>( \sigma_f )</th>
<th>Plastic Elongation (%)</th>
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<tr>
<td></td>
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</tr>
<tr>
<td>Hot forged</td>
<td>Air</td>
<td>699</td>
<td></td>
<td></td>
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<tr>
<td>1d/1173</td>
<td>Air</td>
<td>366</td>
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<tr>
<td>4h/1273</td>
<td>Air</td>
<td>456</td>
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<td></td>
</tr>
<tr>
<td>4h/1273 + 3d/1173</td>
<td>Air</td>
<td>386</td>
<td></td>
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</table>

* \( \sigma_y \) is the 0.2% offset yield strength, and \( \sigma_f \) is the fracture stress.

**Plastic elongation here is defined as the elongation to fracture estimated from the stripchart.

Fig. 6 SEM fractographs on tensile test pieces for alloy 1Q, (a) as hot-forged, and (b) after annealing for 4 h at 1273 K.

Fig. 7 SEM fractographs on tensile test pieces for alloy 2Q, (a) as hot-forged, and (b) after annealing for 4 h at 1273 K.

2. Importance of (Al+Ti) concentration in the L1₂ phase

It is well-known that in L1₂ Ni₃Al the effect of deviation from the stoichiometry drastically alters various mechanical properties⁹. The polycrystalline Ni₃Al alloys are brittle, with intergranular fracture at all binary compositions. However, the importance of alloy composition on the brittle behavior of the alloys is realized since it has been shown that an improvement of room temperature ductility of the L1₂ Ni₃Al polycrystals can readily be achieved by addition of small amount of boron if the alloy composition is at the Ni-rich side of stoichiometry⁹(258-259). On the other hand, boron is ineffective in ductilizing Ni₃Al with over 25 at.% Al.

In the ternary Ni₃Al alloys, a ternary element substitutes for the Al-site, Ni-site or both sites, depending on the chemical nature of the element. Such substitution behavior, as well as the solubility limit, in the ternary L1₂ Ni₃Al alloys has been extensively investigated⁹(258-259). It is well-known from these works that Ti substitutes for the Al-sites, while Co substitutes for the Ni-sites. Therefore, in the present quaternary system the L1₂ phase should be denoted as (Ni, Co)(Al, Ti). Then, by drawing an analogy from the Ni₃Al alloys, the ductility of the L1₂ phase with (Al+Ti) concentration less than 25 at.% can be im-
Fig. 8  A back scattered electron image (a) and an optical micrograph (b) taken near the fracture surface of alloy 2Q specimen sectioned longitudinally.

Fig. 9  Results of electron microprobe analyses on the composition of constituent phases in alloy 1Q, being three-phase after annealing for 4h at 1273 K, as plotted on a hypothetical Co–Ni–(Al+Ti) ternary system. Open circles are the composition of the phases, a filled circle is the composition of alloy 4Q, and dotted lines are the phase boundaries at constant 5Ti at 1173 K evaluated in the previous work\(^{(13)}\).

Fig. 10  Results of electron microprobe analyses on the composition of constituent phases in alloy 2Q, being two-phase after annealing for 4h at 1273 K, as plotted on a hypothetical Co–Ni–(Al+Ti) ternary system. Open circles are the compositions of the phases, a filled circle is the alloy composition, and dotted lines are the phase boundaries at constant 10Ti at 1173 K evaluated in the previous work\(^{(13)}\).
proved by boron doping.

Table 3 shows that tensile ductilities are detected in 1Q and 2Q alloys by annealing the alloys at 1173 K, and that both of the alloys annealed at 1173 K for prolonged time after 1273 K exhibited the best room temperature ductility. These results can be rationalized by considering the (Al+Ti) concentration, which is expected to be lower at 1173 K than at 1273 K. As pointed out in the preceding section, the (Al+Ti) concentration of the L12 phase in alloy 3Q is higher than 25% (see Table 2), indicating that this may contribute to the brittleness of the alloy, in addition to the brittleness caused by the brittle Heusler phase that is present.

In the above discussion, it should be stressed that such compositional consideration or modification of a constituent phase as a part of the alloy design effort becomes possible only in ternary or higher-order multi-component systems. It is an important advantage in developing multi-phase intermetallic alloys, as compared to the case in the binary alloy system where the composition of co-existing phases is fixed at a temperature regardless of the alloy composition.

3. Fracture paths and causes for brittleness

Figures 6 through 8 show that three major brittle fracture paths, and therefore three reasons for brittleness, exist in alloy 1Q and 2Q. They are: (1) cleavage in the B2 phase, (2) intergranular fracture of the L12 phase, and (3) interfacial separation along the B2/L12 interfaces. In addition, environmental embrittlement, which was detected in alloy 2Q (see Table 3), should also be taken into account as a cause for low ductility and brittle fracture.

It was shown in Fig. 8 that the fracture path in the B2 phase in alloy 2Q is obviously deflected by more ductile L12 precipitates, indicating that the dispersion provides an improved toughness to the B2 phase in these alloys. This is confirmed by the observation of fracture facets for such B2 phase, Fig. 7(b), being much less cleavage in appearance as compared to as-forged material shown in Fig. 6(b). The second feature is the intergranular fracture of the L12 phase, which could be suppressed by compositional modifications of the phase present in these alloys. As mentioned in the preceding section, special attention should be paid in the present study on the (Al+Ti) concentration of the L12 phases existing in the multi-phase alloys. In Table 2, it is seen that the L12 phase in the alloy 1Q has the Ni-rich composition after annealing for 3d at 1273 K, and the addition of boron to this alloy is thus expected to improve fracture resistance of the L12 phase in the alloy. Accordingly, an attempt is made by adding boron together with other adjustments. The result of this alloy design will be shown in the next section. The origin of the third feature, interfacial separation between the B2 and L12 phases (see Fig. 8(b)), is not clear. The crystallographic orientation relationship between the two phases should be investigated in order to deduce information on coherency between the phases. It is generally known that interfacial strength can be improved by either reducing harmful impurities (such as S and P) or adding beneficial segregates (such as B) to interfaces, or both(28)(29).

4. Environmental effect on room temperature ductility

It is shown in Fig. 5 and Table 3 that there are clear indications of environmental effect on the room temperature ductility of alloy 2Q. For both annealing conditions of 1273 K for 4h and 1273 K/4h+1173 K/3d, plastic elongation is obviously higher for the dry oxygen environment than for air. It means that the alloy is embrittled with the presence of moisture at room temperature.

It is well-known that the brittleness of the L12 poly-crystalline Ni3Al comes from two major factors. One is an intrinsic weakness of grain boundaries and the other is moisture induced hydrogen embrittlement(30-32). As mentioned before, the former has been well-known to be cured by doping with a small amount of boron, although it is effective only at the Ni-rich side of the stoichiometry(33). The latter aspect has become an important issue since it has been shown recently that the room temperature tensile ductility of Ni3Al alloys (23.4 at. %Al)(34-36) can be significantly improved by testing in dry oxygen or in a ultra-high vacuum. It is important to note that the beneficial effect of boron is related to both grain-boundary cohesion and reduction of moisture-induced embrittlement(30-33).

On the other hand, such an environmental effect may or may not be seen in the B2 compounds. It has been shown that the B2 FeAl is susceptible to moisture induced embrittlement(36-37); however, the B2 NiAl seems to be quite inert(38). There has been no work on the environmental effect in the B2 CoAl, possibly because its extreme brittleness has never made tensile tests even feasible.

Finally, a comment should be made on the effect of environment on the 0.2% offset yield strength of alloy 2Q in Table 3. It is seen that a decrease in d0.2 by about 20 to 30 MPa in either heat treatment condition is accompanied by testing in Dry O2 as compared to the value obtained in air. Such difference in yield strength may be larger than what have been reported in the L12 Ni3Al(30-32) and in (Co, Fe)3V(39) single phase intermetallic alloys. It is, however, difficult to clarify how the environment would affect the strength of a multi-phase intermetallic alloy.

5. Design of an alloy for improved room temperature ductility

On the basis of the experimental results and analyses of the ductility and fracture behavior, a new composition has been selected based on alloy 1Q, and its room temperature mechanical properties are investigated. The composition of the alloy, designated as 4Q, is 43 at.%Co-32 at.%Ni-20 at.%Al-5 at.%Ti doped with 200 mass ppm boron. Its composition is located in Fig. 9 near to the L12 corner of the three-phase triangle constructed based on the present results. Thus, alloy 4Q is expected to contain the L12, B2, and (Co, Ni) phases with L12 as the major phase at 1273 K. The compositional modification includes: (1) less volume fraction of the B2 phase as com-
pared to alloy 1Q, and (2) assurance that (Al + Ti) concentration is less than 25 at. % in the L12 phase which can be readily ductilized by the boron addition. The alloy was prepared in the same way as described in the experimental procedures, except that an additional hot rolling at 1473 K was applied after hot forging. The thickness of the plate after the hot fabrication was about 0.9 mm, which was further flattened by cold rolling. The flat tensile test specimens were then punched out and hand polished prior to the tests.

Figure 11 shows the room temperature stress-strain curves of alloy 4Q heat treated at different conditions. The microstructure of the alloy is also included in Fig. 11. Consistent with our prediction, the alloy exhibits excellent room temperature ductility (Table 4) even in the as-rolled condition. The annealed specimen showed an excellent strength, with \( \sigma_{0.2} \) over 600 MPa, and excellent ductility, with elongation over 20%. In comparison with Fig. 3(a) for alloy 1Q annealed for 4h at 1273 K, the B2 phase in alloy 4Q is reduced as designed. A detailed analysis on the microstructure, phase constitution, and fracture path is currently underway; nevertheless, the current work clearly demonstrates the merits of designing ductile multi-phase intermetallic alloys using physical metallurgy principles.

V. Conclusions

Microstructures, phase constitutions and room temperature tensile properties were investigated on multi-phase intermetallic compounds in the Co-Ni-Ti-Al system. The following conclusions are drawn: (1) The alloys consisting of B2/L12 two-phase or B2/L12/(Co, Ni) three-phase microstructures exhibit a few per cent room temperature ductility when properly heat treated and tested in a dry environment. However, the L12/L2 two-phase alloy does not show any ductility under the conditions examined in the present work. (2) Examinations on fracture surfaces and fracture paths revealed that the reasons for brittle fracture in B2/L12 and B2/L12/(Co, Ni) alloys are: (a) cleavage fracture in the B2 phase, although it is suppressed to a certain degree by the L12 precipitates in the phase, (b) the intergranular fracture of the L12 phase, (c) interfacial separation along the B2/L12 interfaces, and(d) moisture-induced hydrogen embrittlement. In the L12/L2 alloy, the presence of the brittle Heusler phase together with an (Al + Ti) concentration > 25 at. % in the L12 phase would be the major reason for the brittleness. (3) By modifying the alloy composition to reduce the volume fraction of the B2 phase and to reduce the tendency for the intergranular fracture of the L12 phase by doping with B, room temperature tensile ductility of over 20% is achieved in a B2/L12/(Co, Ni) three-phase alloy, with a 0.2% flow stress of over 600 MPa and fracture stress of over 1,300 MPa.

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REFERENCES


<table>
<thead>
<tr>
<th>Heat Treatment (Time/K)</th>
<th>Test Environment</th>
<th>( \sigma_{0.2} ) (MPa)</th>
<th>( \sigma_{f} ) (MPa)</th>
<th>Plastic Elongation (%)</th>
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<td>1328</td>
<td>23</td>
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</table>

*\( \sigma_{0.2} \) is the 0.2% offset yield strength and \( \sigma_{f} \) is the fracture stress.
**Plastic elongation is defined here as the elongation to fracture from the offset of stress-strain curve from its linear portion.
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