Microstructure Control and Mechanical Properties of Binary Co–Al Alloys Based on B2 Intermetallic Compound CoAl

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Microstructure and mechanical properties are investigated in the binary Co–Al alloys based on B2 intermetallic compound CoAl. The effort is focused on two-phase alloys of the compound with Co primary solid solution in order to impart some ductility to the intrinsically brittle compound. The Co–Al binary phase diagram on the Co-rich side is first examined to confirm the stable phase fields of interest by differential thermal analysis and energy dispersive X-ray spectroscopy. Then the compression tests are carried out on selected two-phase alloys to correlate the 0.2% flow stress as well as compressive ductility with microstructures. Several attempts are also made to refine the microstructure through heat treatments and hot rolling, by which it is found that at least several per cent of compressive plastic strain can be obtained at room temperature in the 72 and 76 at%Co alloys.

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I. Introduction

Some of aluminides with B2 type crystal structure such as CoAl and NiAl have been expected as candidates for new high temperature structural materials because of their high melting points being over 1900 K, relatively low densities, and excellent high temperature oxidation resistances. For these two aluminides, however, it has always been pointed out that there are two major drawbacks as structural materials. One is an extreme brittleness, almost no ability for plastic deformation at room temperature, and the other is insufficient strength at high temperatures over 1200 K^{(1)–(5)}.

Though the B2 type crystal structure is based on bcc with a high crystallographic symmetry, a fairly high ordering energy of the compounds does not permit enough numbers of independent active slip systems to operate to fulfill the compatibility requirement at grain boundaries, which leads to the brittleness⁽⁶⁾⁽⁷⁾. It is conceivable that the insufficient strength at elevated temperatures would be an intrinsic nature of a material based on the unclosed-packed bcc crystal structure in which diffusion of atoms via vacancy migration becomes intense with increasing temperature.

It has been pointed out that CoAl exhibits superior strength at high temperatures, though more brittle at room temperature, than NiAl of the same ordered crystal

structure^{(8)–(12)}. However, there have been only several works on the mechanical properties of CoAl due to its extreme brittleness^{(1)–(4)(8)–(12)} and a recent effort has been limited to an attempt to introduce a fine dispersion of TiB₂ particles and to refine the grain size aiming at an improvement in mechanical properties⁽⁸⁾. On the other hand, investigations on NiAl have been more extensive toward better mechanical properties^{(13)–(36)}. The previous efforts include examination on the deformation mechanism using single crystals⁽²¹⁾⁽²²⁾, the effect of deviation from the stoichiometry^{(23)–(27)}, and the variation in mechanical properties in the pseudo-binary alloys with FeAl^{(28)–(30)}. Also there have been a series of works to introduce a fine dispersion of various carbides and borides to improve both high temperature strength and room temperature ductility^{(31)–(36)}. More recently efforts on microstructural control have gained an increasing attention for the purpose of improving ductility in alloys based on NiAl. In those efforts, introduction of alloy phases neighboring to the B2 NiAl on the equilibrium phase diagram has been carried out with such phases as L1₂ type intermetallic compound Ni₃Al or fcc Ni primary solid solution in the binary Ni–Al and the ternary Ni–Al–Co alloys showing an indication to impart some ductility to the compound by a microstructural control^{(37)–(45)}. It is then noticed that such an effort on microstructural control has not been attempted on the B2 CoAl.

The present authors have designed and undertook a series of works on the development of multi-phase alloys based on the B2 CoAl with good ductility at room temperature and high strength at elevated temperatures in the

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multi-component system in which various ordered or disordered phases are to be chosen as a second phase. The objective of the present work is to furnish the most fundamental information necessary for this purpose, in which, therefore, the work has been initiated with the binary Co–Al system. According to the available Co–Al binary phase diagram found in the literature⁽⁴⁶⁾, two kinds of second phase could be introduced into the B2 phase, one being Co primary solid solution, hereafter denoted as (Co), on the Co-rich side and the other an intermetallic phase δ on the Al-rich side. Comparing the crystallographic symmetry of each phase, (Co) is chosen to be the second phase because the intermetallic δ phase, Al_5Co_2 , is complex and is based on hexagonal crystal structure denoted as $hP28$ by the Pearson symbol. First, an examination on the Co-rich side of the Co–Al binary phase diagram is done by differential thermal analysis and energy dispersive X-ray spectroscopy to confirm the stable phase fields of (Co), CoAl and hence the B2/(Co) two-phase field. Then for the Co–Al binary two-phase alloys being B2/(Co), microstructure-mechanical properties relationship is investigated through optical and transmission electron microscopy and compression tests. Several attempts are finally made to refine the two-phase microstructure to improve the room temperature ductility by heat treatments and hot rolling.

II. Experimental Procedure

Binary Co–Al alloys over a wide compositional range from 40 at%Co to 98 at%Co were prepared by arc-melting under an argon gas atmosphere using raw materials with the highest purity elements readily available, being 99.9% Co and 99.99% Al in purities. All the ingots were then annealed under a flowing argon atmosphere at 1273 K for 600 ks (7 d) and/or at 1423 K for 173 ks (48 h), which are either single or two-phase region in the binary Co–Al phase diagram. Determination of the liquidus and solidus temperatures for (Co) and B2 phases and also of the phase boundaries among, B2, B2/(Co) two-phase, and (Co) were conducted by means of differential thermal analysis (DTA) and energy dispersive X-ray spectroscopy (EDS) equipped on the scanning electron microscope (SEM).

Microstructures of the alloys were examined both optical and transmission electron microscopy (TEM). Optical microscopy was conducted with specimens etched after mechanical polishing in a 3:1 hydrochloric acid-nitric acid solution. Disks for TEM observations were electrolytically thinned in a 10% perchloric acid-ethyl alcohol solution at about 150 K using a twin-jet polisher.

Mechanical properties were measured mainly by compression tests and also by micro-Vickers hardness tests. Compression tests using an Instron type testing machine were carried out at a nominal strain rate of $1.4 \times 10^{-4} \text{ s}^{-1}$ over a wide temperature range between 77 and 1273 K under an argon gas atmosphere except for the tests at 77 K and room temperature. Test specimens were mechanically prepared into a pillar shape with a dimension of 3

mm $\times$ 3 mm $\times$ 6 mm. Electropolishing on the surface in a 10% perchloric acid-acetic acid solution was done before conducting the tests.

III. Results and Discussion

1. The Co–Al phase diagram

Among the Co–Al phase diagrams reported previously^{(46)–(49)}, Fig. 1(a) is one from the most updated issue, the second edition, of the Binary Alloy Phase Diagrams edited by Massalski *et al.*⁽⁴⁶⁾, in which liquidus and solidus lines for the B2 and (Co) phases remain ambiguous. Also it is noted that the phase boundary between the B2 and B2/(Co) two-phase region has been revised since after the previous edition⁽⁴⁷⁾. These observations prove that the binary Co–Al equilibrium phase diagram has not been

Fig. 1 Co-rich side of the Co–Al binary phase diagrams; (a) the most updated version in the Ref. (46), and (b) result of the present work. Open marks are the results of DTA and solid marks by EDS on the compositions of constituent phases.

Fig. 2 An example of DTA heating and cooling curve for a 76 at%Co alloy annealed at 1423 K for 28 ks.

confirmed yet. Figure 1(b) is the present results of DTA, shown by open symbols, and SEM-EDS, by solid symbols, using alloys with 64 to 98 at%Co. Note that the melting temperature for pure Co and the congruent melting point for CoAl are taken from Fig. 1(a). An example of DTA curve is shown in Fig. 2 for a 76 at%Co alloy, where smaller peaks on the heating and cooling curves correspond to the solubility limit of (Co) into the B2 phase, an average of them being taken for Fig. 1(b), and the larger peaks for the liquidus. The solidus temperature can be found on the cooling curve where a small but distinct inflection is detected. Upon comparison of Fig. 1(a) with (b), it is clearly seen that phase relations in Co-rich portion of the Co–Al binary phase diagram and the eutectic temperature and composition are in good agreement. However, the compositional range for the B2/(Co) two-phase region is much narrower in the vicinity of eutectic temperature in the present work as compared to Fig. 1(a). It should be noted that the earlier works on the microstructure and mechanical properties of the Co–Al binary alloys have been motivated toward directional solidification utilizing the eutectic reaction in this system^{(50)–(55)}.

2. Composition dependence of micro-Vickers hardness in binary Co–Al alloys

For the alloys whose Co concentration ranges from 40 to 80 at%, micro-Vickers hardness was measured at room temperature. Figure 3 shows relation between Vickers hardness, H_v , and Co concentration for as-cast alloys and alloys annealed in a few different conditions. For B2 CoAl single phase alloys, together shown are the data from Westbrook⁽¹⁾, H_v increases as the composition deviates from the stoichiometry. This is often found in many Berthollide type intermetallic compounds having a compositional range⁽²³⁾⁽²⁶⁾⁽²⁷⁾⁽⁵⁶⁾. The defect hardening seems to be more intense at Al-rich side than Co-rich side of off-stoichiometry as has been reported previously⁽¹⁾⁽¹²⁾. The B2/ δ two-phase alloys exhibit highest hardness of all, though they are absolutely brittle which can be

Fig. 3 Micro-Vickers hardness, H_v , for the Co–Al binary alloys investigated.

judged by the cracking around an indentation. It is found that the B2/(Co) two-phase alloys shows the values of H_v being comparable with or superior to CoAl single phase alloys. Note that the composition dependence of hardness is affected by the annealing condition, which provides us a possibility to conduct microstructural control toward improvement in mechanical properties.

3. Microstructures of B2/(Co) two-phase alloys

Typical microstructures observed by optical microscope are shown in Fig. 4(a) through (c) for the alloys with 72, 76 and 80 at%Co after annealing at 1423 K for 173 ks. According to the phase diagram in Fig. 1(a), these alloys are in the B2/(Co) two-phase region at the annealing condition. It is obvious that coarse (Co) precipitates predominantly exist at the grain boundaries of B2 phase in 72 and 76 at%Co alloys, while they appear and increase in volume within the grain with increasing Co content to 76 at%. Microstructure of an 80 at%Co alloy differs from others showing a typical eutectic microstructure being consistent with the binary phase diagrams in Fig. 1(a) and (b). Average grain size of matrix B2 phase is about 70 μm in (68 and) a 70 at%Co alloy and it seems to increase with increasing Co concentration, although the eutectic nature of the 80 at%Co alloy hinders its grain structure. Microstructures for the B2/(Co) two-phase alloys after annealing with a different condition, at 1273 K for 600 ks, are also examined but little difference can be found from those shown in Fig. 4.

For a 76 at%Co alloy, typical transmission electron micrographs are shown in Fig. 5. It is found in Fig. 5(a) that blocky (Co) exists in the B2 matrix, being consistent with optical microscopy shown in Fig. 4(b). In Fig. 5(b), a distinct contrast arising from stacking faults is found in the blocky (Co), which means that it has been transformed from fcc to hcp during cooling from the annealing temperature. By X-ray analysis of the alloy, fcc peaks are also identified, which indicate that there must be some residual fcc phase. In the case for pure Co and

Fig. 4 Optical micrographs of binary Co–Al alloys being B2/(Co) two-phase after annealing at 1423 K for 28 ks, (a) 72, (b) 76, and (c) 80 at%Co alloys.

binary Co–Ni alloys with less than 35 at%Ni, it has been reported^{(57)–(60)} that fcc to hcp martensitic transformation occurs in both thermal and stress induced manners. Hitzenger *et al.*⁽⁵⁷⁾ have pointed out, by *in-situ* TEM observation, that the determination of contrasts originated from whether stacking faults or fcc lamellae formed during the hcp to fcc thermally reversed martensitic transformation is complex and difficult. It is noted that there seems to be a very fine dispersion of (Co), most likely hcp, in the B2 matrix as shown in Fig. 5(c), which would have precipitated during cooling from the annealing temperature as the solubility limit of (Co) decreases with decreasing temperature as shown in Fig. 1. A detailed analysis on the crystallographic orientation relationship

Fig. 5 Transmission electron micrographs for a 76 at%Co alloy being B2/(Co) two-phase after annealing at 1423 K for 172.8 ks, showing (a) blocky (Co) phase in the B2 matrix, (b) contrasts from stacking faults in the blocky (Co) phase, and (c) a fine dispersion of (Co) precipitates in the B2 matrix.

between the precipitate and the matrix by electron diffraction is currently underway.

4. Mechanical properties of B2/(Co) two-phase alloys

(1) Compressive mechanical behavior of B2/(Co) two-phase alloys

Compression tests were carried out for the B2/(Co) two-phase alloys with 68, 72, 76 and 80 at%Co, annealed at 1423 K for 173 ks, which have been expected to show some ductility by judging from the results of microstructural observations and Vickers hardness measurements. For B2 CoAl single phase alloys, preparation of

compression test pieces was unsuccessful even by a careful mechanical cutting because of their extreme brittleness. It is noted that the preparation of test pieces was also tedious even for the B2/(Co) two-phase alloys with 68 and 72 at%Co. In fact, these two alloys fracture before yielding or just after yielding during compression tests at room temperature. The stress-strain curves obtained from the compression test conducted at room temperature for 72, 76 and 80 at%Co alloys are shown in Fig. 6. As the Co content increases from 72 to 80 at%Co, an improved ductility is observed and plastic deformation reaches 4% for a 76 at%Co alloy and exceeds the value for an 80 at%Co alloy, while the 0.2% flow stress decreases instead. Also note that strain dip tests raising the strain rate by an order of magnitude do not lead to an immediate fracture for all the three alloys. It is presumed that the presence of (Co) phase in the B2 matrix could enable the grain boundary compatibility to be restored and satisfied. Pank *et al.*⁽⁴¹⁾⁽⁴²⁾ has recently reported their attempt to improve room temperature ductility of the B2 NiAl by introducing the $L1_2$ Ni_3Al as a second phase. They have shown that the improvement is achieved when the second phase exists continuously along the grain boundary, for which they called as “necklace”, surrounding the matrix B2 phase but not when its morphology is blocky and discrete. An analogy could be drawn for the morphology of (Co), when providing some ductility to CoAl, found in the optical micrographs shown in Fig. 4(b) and (c).

The temperature dependence of compressive 0.2% flow stress for 72, 76 and 80 at%Co alloys is shown in Fig. 7 over a temperature range from 77 to 1273 K. Ductility of three alloys is improved significantly with increasing test temperature. All the alloys exhibit a similar trend in the temperature dependence of strength and a region is found at between about 400 to 800 K where the softening with increasing temperature is suppressed. Since such a behavior has been shown in many B2 type intermetallic compounds including CoAl and NiAl, it must be concluded

Fig. 6 Stress-strain curves obtained from compression tests at room temperature for the Co-Al binary B2/(Co) two-phase alloys with 72, 76, 80 at%Co.

Fig. 7 Temperature dependence of 0.2% compressive flow stress for the Co-Al binary alloys with 72, 76 and 80 at%Co.

ed that the temperature dependence of strength of the B2/(Co) two-phase alloys shown in Fig. 7 would come from the nature of the matrix B2 CoAl phase.

(2) Attempts on microstructural control for an improved ductility

From these results together with the microstructural observation, more homogeneous and finer distribution of the second phase would provide further ductility in the Co-Al binary two-phase alloys based on B2 type CoAl phase, for which two different attempts are made. Firstly, by investigating the Co-Al binary phase diagram revised in the present work, Fig. 1(b), solution treatment in the B2 single phase would be possible for the 72 at% Co alloy at 1573 K. Therefore, quenching after the annealing and subsequent aging at 1373 K to have the (Co) precipitates are performed on the alloy. An optical micrograph after the aging at 1373 K for 3.6 ks is shown in Fig. 8. The micrograph should be compared with Fig. 4(a) which the microstructure of the same alloy air cooled after annealing at 1423 K. Obviously a fine and uniform dispersion of (Co) in the B2 matrix is achieved with thin layers of the (Co) decorating uniformly the grain boundaries.

A second attempt on the microstructural control is made in the B2/(Co) two-phase with 72 and 76 at%Co for which hot rolling at 1373 K followed by a water quench is applied to refine the microstructure. The hot rolling to 30% in reduction of thickness is applied to the 76 at%Co alloy, however, the 72 at%Co alloy exhibits severe surface cracking after 10% in reduction. As is shown in Fig. 9, a finer grain size and a finer second phase distribution are achieved as compared to Fig. 4(b).

In Fig. 10, the compressive stress-strain curves of the alloys above treated for microstructural control are shown together with the corresponding untreated alloys,

Fig. 8 An optical micrograph for a 72 at%Co alloy aged at 1373 K for 3.6 ks after a solution treatment at 1573 K for 3.6 ks.

Fig. 9 An optical micrograph for a 76 at%Co alloy hot-rolled at 1373 K and water quenched.

Fig. 10 Comparisons of stress-strain curves obtained by compression tests at room temperature for the Co–Al binary B2/(Co) two-phase alloys with 72 and 76 at%Co. The effect of aging treatment is shown for the 72 at%Co alloy and that of hot rolling for the 76 at%Co alloy.

taken from Fig. 6, for comparison. In both attempts, the ductility is found to be improved. Although the effect is only slight in the 72 at%Co alloy, it is substantial in the 76 at%Co alloy, for which a plastic strain of about 6% has been accomplished as compared to the value of 4% attained on an as-annealed specimen.

IV. Conclusions

Relationships between microstructure and mechanical properties are investigated in the binary Co–Al alloys. A particular interest is placed on those for two-phase alloys based on B2 intermetallic compound CoAl having as a second phase the Co primary solid solution to look for a possibility to impart some ductility to the intrinsically brittle compound. The following conclusions are drawn.

(1) The Co–Al binary phase diagram is reinvestigated to revise the phase field for the B2/(Co) two-phase region to be much narrower at near eutectic temperature than previously reported.

(2) Room temperature compressive ductility of B2 CoAl is improved from none to several percent by having (Co) as a second phase in the alloys with 76 to 80 at%Co.

(3) A preliminary attempt on microstructural control of the two-phase alloys exhibits an indication to be able to further improve the ductility of the compound.

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Note added on proof:

Regarding the determination of the phase diagram for the Co–Al binary system, a work by Takayama *et al.* should additionally be referred; which is, T. Takayama, M. Y. Wey and T. Nishizawa: J. Japan Inst. Metals, **45** (1981), pp. 341–346.

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