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Microstructures of $L2_1$/$L1_2$ multi-phase intermetallics in Co-Ni-Al-Ti system①

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[Abstract] On the basis of the two ternary systems of Co-Al-Ti and Ni-Al-Ti, a series of high-temperature structural intermetallic alloys comprised of $L2_1$-type $(Co, Ni)_2AlTi$ and $L1_2$-type $(Co, Ni)_3(Al, Ti)$ ordered phases in the Co-Ni-Al-Ti quaternary system were designed and melted to take the advantages of both the high elevated temperature strength of the $L2_1$ phase and the intrinsic room temperature ductility of the $L1_2$ phase. Analysis of the phase equilibrium, phase structure and microstructures of the as-cast and heat-treated alloys were conducted to gain some clues for the further optimization of the compositions, microstructures and processing.

[Key words] Co-Ni-Al-Ti quaternary system; $L2_1$-type $(Co, Ni)_2AlTi$; $L1_2$-type $(Co, Ni)_3(Al, Ti)$; intermetallics
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1 INTRODUCTION

Intermetallic compounds have the promise of high temperature structural application, while the road ahead is hindered by its low high-temperature creep resistance and poor room-temperature ductility. The previous research suggested that multi-component alloying to produce multi-phase system usually produced exceptional strengthening/toughening effect[1]. Developing multi-component multi-phase alloy system consisting of phases with higher high-temperature strength and phases with intrinsic room-temperature ductility may be a feasible approach to solve this problem.

Binary ordered structure $L1_2$ and ternary ordered structure $L2_1$ are two of the most representative structures, and many compounds with these structures exhibit attractive mechanical properties. In 1976, it was notably reported that the ordered Heusler phase Ni_2AlTi with $L2_1$ structure has exceptionally high creep resistance, about three times that of NiAl with B2 structure[2]. Lately, Umakoshi et al[3,4] reported that Co_2AlTi, with the same structure as Ni_2AlTi, exhibited higher brittle-to-ductile transition temperature than Ni_2AlTi, i.e. 1 170 K for the former and 965 K for the latter. However, research on these phases was discouraged for a time by the extremely poor room-temperature ductility. The mechanical properties of $L2_1$-based alloys might be improved by incorporation of another ordered phase with $L1_2$ structure. Single crystals of Ni_3Al with $L1_2$ structure are ductile, but pure polycrystalline Ni_3Al is very brittle at room temperature because of grain boundary fracture[5]. Both single crystal and polycrystalline Co_3Ti with $L1_2$ structure compounds are ductile over a wide temperature range because of the intrinsic high grain boundary strength[6]. The yield strength of Ni_3Al and Co_3Ti presents a positive temperature dependence up to about 1 100 K[7,8]. In the Co-Ni-Al-Ti quaternary systems, it is expected that not only the two $L2_1$ phases, Ni_2AlTi and Co_2AlTi, but also the two $L1_2$ phases, Ni_3Al and Co_3Ti, can form continuous solid solutions, which can be denoted as $(Co, Ni)_2AlTi$ and $(Co, Ni)_3(Al, Ti)$, respectively.

In the present work, quaternary alloys comprised of above two phases are designed to pursue both reasonable room-temperature ductility and excellent high-temperature strength. As one of a series of investigations in several multi-component systems aiming for room-temperature ductility, Matano et al[9,10] made an attempt in this system, and the preliminary results were encouraging, but comprehensive work did not follow up.

2 EXPERIMENTAL

The experimental alloys were produced using raw materials with high purity elements available, being 99.9% Co, 99.99% Ni, 99.98% Ti and 99.99% Al in purity. Alloy buttons about 40 g each were arc-melted three times on a water-cooled copper hearth under an atmosphere of purified argon. The compositions of the alloys designed in atom percentage are list in Table 1, and the ratio of Co/(Co+ Ni) is kept at 60%. The nominal compositions were adopt-

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Table 1 Nominal compositions of alloys designed and phase compositions in as-cast microstructures determined by EDS mole fraction, %

Alloy No.	Nominal composition				Dendrite composition				Inter-dendrite composition			
	Co	Ni	Al	Ti	Co	Ni	Al	Ti	Co	Ni	Al	Ti
1	40	27	19	14	36.8	26.4	25.3	11.5	47.0	28.4	9.1	15.5
2	40	27	17	16	35.4	23.7	27.1	13.8	45.0	29.2	9.6	16.2
3	40	27	15	18	34.2	23.1	25.9	16.8	44.2	30.3	10.1	15.4
4	40	27	12	21	32.4	22.4	25.1	20.1	41.5	33.1	7.0	18.4
5	36	24	29	11	34.1	21.4	35.0	9.5	49.6	25.4	10.2	14.8
6	36	24	26	14	31.0	21.4	35.2	12.4	46.3	29.6	8.6	15.5
7	36	24	23	17	32.5	20.8	32.1	14.6	45.8	28.9	8.8	16.4
8	36	24	20	20	32.2	22.4	26.2	19.2	42.7	31.2	8.2	17.9
9	36	24	17	23	31.8	20.7	25.5	22.0	43.7	31.3	4.7	20.3

ed because the mass loss is usually less than 0.2%.

The specimens for heat-treatment were sealed in silica tubes evacuated and back-filled with argon. The homogenization heat-treatment were conducted at 1453K for 7.3×10^4 s, followed by isothermal treating at 1273K, for 1.8×10^5 s.

Microstructures of the alloys were examined with a JSM-5800 scanning electron microscope (SEM) and an H-800 transmission electron microscope (TEM). The phase composition measurement was performed by means of the energy dispersive X-ray spectrometer (EDS) equipped on the SEM, and the composition of each phase was measured from three different sites.

3 RESULTS

3.1 Microstructures of as-cast alloys

Typical microstructures of the as-cast alloys are shown in Fig. 1, and the phase compositions at as-cast state determined by EDS are listed in Table 1. It can be seen that some of the as-cast alloys are comprised of two kinds of microstructures, i.e. the dendrite and inter-dendrite matrix (Figs. 1(a), (c) and (d)). Composition analysis shows that the ratio of (Co+Ni):(Al+Ti) of the dendrite phase is close to 1:1~2:1, therefore this phase can be denoted as $(Co, Ni)_2AlTi$ approximately, and the ratio of (Co+Ni):(Al+Ti) of the matrix phase is close to 3:1, denoted as $(Co+Ni)_3(Al+Ti)$ approximately. Phase composition analysis suggests that the element partition takes place between the two phases, Al atoms prefer to distribute over the $L2_1$ phase, while Ti atoms prefer to distribute to the $L1_2$ phase.

It is obvious that a peritectic reaction occurs during solidification. The high melting temperature $L2_1$ dendrite solidifies first from the melt, followed by the $L1_2$ inter-dendrite. Some eutectic microstructures are also observed in Alloys 3 and 4 (Fig. 1(b)) at the Ti-rich side of the two-phase field, but it may be resulted from non-equilibrium solidification under experimental conditions. Because the relation of the large massive $L1_2$ phases rather than the eutectic microstructures surrounding the $L2_1$ phases in Ti-rich alloys keeps unchanged from that in Al-rich alloys, which may rule out the possibility of simple eutectic reaction. It also should be noted that, when the $L2_1$ dendrites solidify in low volume fraction, it can be separated effectively by the matrix (Figs. 1(a) and (b)). On the contrary, when the $L2_1$ dendrites solidify copiously, they will contact each other, separating the $L1_2$ phase into discrete networks (Figs. 1(c) and (d)).

3.2 Microstructures of heat-treated alloys

Fig. 2 shows the typical microstructures of the alloys after homogenization at 1453K for 7.3×10^4 s, followed by isothermal treatment at 1273K for 1.8×10^5 s. Almost all the dendrites of the alloys are observed to aggrandize at the expense of the inter-dendrite matrix after homogenization, and rod-like precipitations were decomposed from most of the dendrites during isothermal treatment. Alloys 5 and 6 had transformed into single-phase microstructures after the treatment, and became very brittle and difficult to etch. This means that the composition sites of these alloys in the phase diagram have been covered by the single-phase field at least at temperatures above the isothermal heat-treatment temperature. Though Alloys 1 and 7 also transformed into single phase during homogenization, the secondary precipitates formed during isothermal treatment made the metallographical observation feasible. The phenomena can be understood easily. As the temperature increases, the balanced solubility of the $L2_1$ phase widens toward the $L1_2$ phase, the dendrites aggrandize at the expense of the matrix. And when the temperature is decreased, the $L2_1$ phase becomes supersaturated, the $L1_2$ phase will precipitate secondarily from it, provided the kinetics allows.

Among the alloys with identical (Co+Ni) content, the dendrites of the alloys with higher Al contents are likely to aggrandize upon heating and decompose upon cooling. This may be because the solidus slope at Al-rich side changes with the temper-

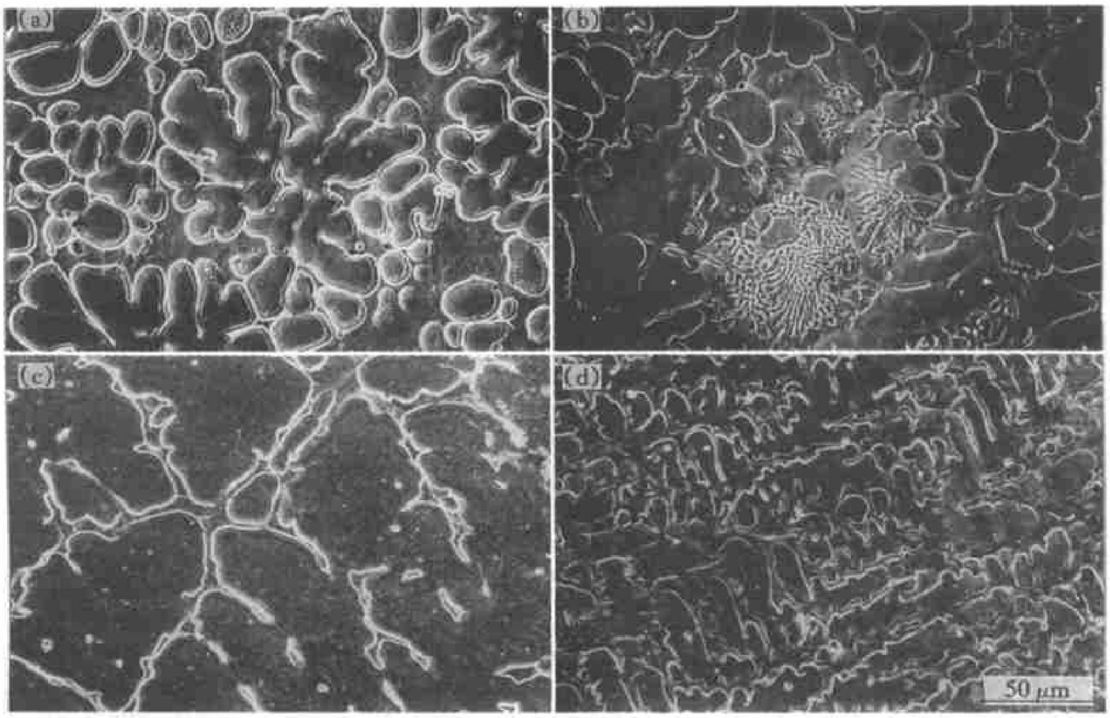

Fig. 1 Typical microstructures of as-cast alloys
(a) —Alloy 1; (b) —Alloy 4; (c) —Alloy 7; (d) —Alloy 9

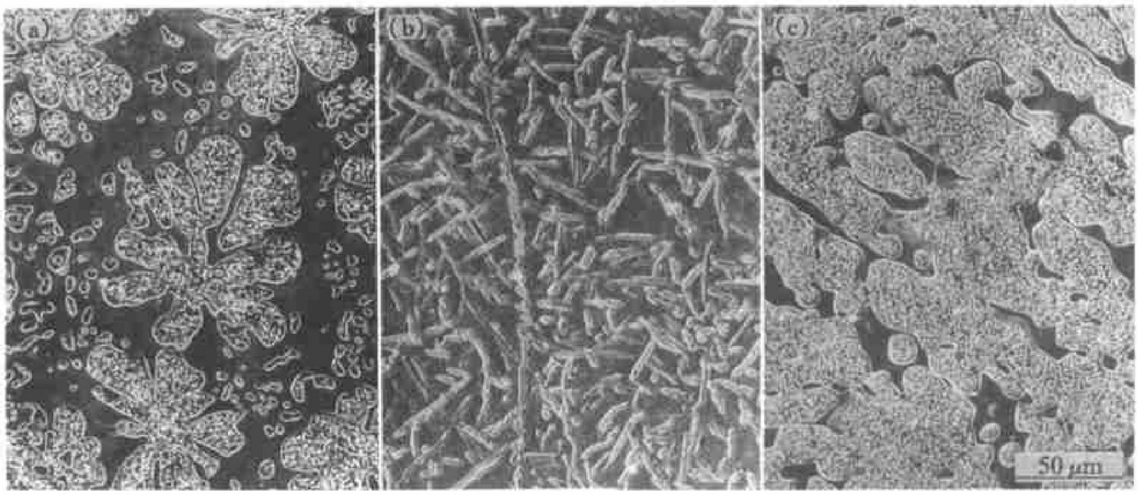

Fig. 2 Microstructures after homogenization and isothermal heat-treatment
(a) —Alloy 4; (b) —Alloy 7; (c) —Alloy 9

ature more dramatically between the two temperatures, or because the lower ordering degree of (Co, Ni)$_2$AlTi makes the diffusions of Al and Ti atoms easier.

3.3 Microstructures under TEM

The TEM photographs of Alloy 4 isothermally treated after homogenization are shown in Fig. 3. From the microstructure of the dendrite with rod-like particles precipitated in it, the dislocation networks can be observed at the interface between the particles and the parent phase, which suggests that the interface is semi-coherent in nature. The diffraction patterns of the two phases (see Figs. 3(b) and (c)) confirm that the structures of the two phases are L2$_1$ and L1$_2$ respectively.

As expected, excellent room-temperature ductility was founded when preparing the specimens for SEM and TEM observations in the alloys that the L2$_1$ dendrites were separated effectively by the L1$_2$ interdendrite matrix. On the contrary, when the L2$_1$ dendrites contact each other, separating the L1$_2$ phase into discrete networks, the materials were brittle. It has been known that it is the alloy composition site in the two-phase field and the homogenization temperature that control the final morphology of primary L1$_2$ phase. In addition, the fraction and morphology of L1$_2$ secondary precipitates affecting the deformability of the dendrite, are controlled by the isothermal aging temperature and duration.

4 CONCLUSIONS

1) A series of high-temperature structural intermetallic alloys comprised of $L2_1$-type $(Co, Ni)_2AlTi$ and $L1_2$-type $(Co, Ni)_3(Al, Ti)$ ordered phases in the Co-Ni-Al-Ti quaternary system are designed and melted. The as-cast microstructures consisting of $L2_1$ dendrite and $L1_2$ inter-dendrite matrix are produced through a peritectic reaction during solidification. In some Ti-rich alloys, eutectic microstructures can be found to distribute among the $L2_1$ dendrites and the $L1_2$ inter-dendrite matrixes, which is resulted from non-equilibrium solidification.

2) Upon high-temperature homogenization, the solubility scope widening leads the dendrite to aggrandize at the expense of the matrix. When the heat treatment temperature is lowered from the homogenization temperature, the secondary $L1_2$ phase precipitates from the supersaturated dendrite.

3) The homogenization temperature, the isothermal heat-treatment temperature and duration for a given alloy are the three important factors affecting mechanical properties through affecting the fraction and morphology of both primary and secondary $L1_2$ phases.

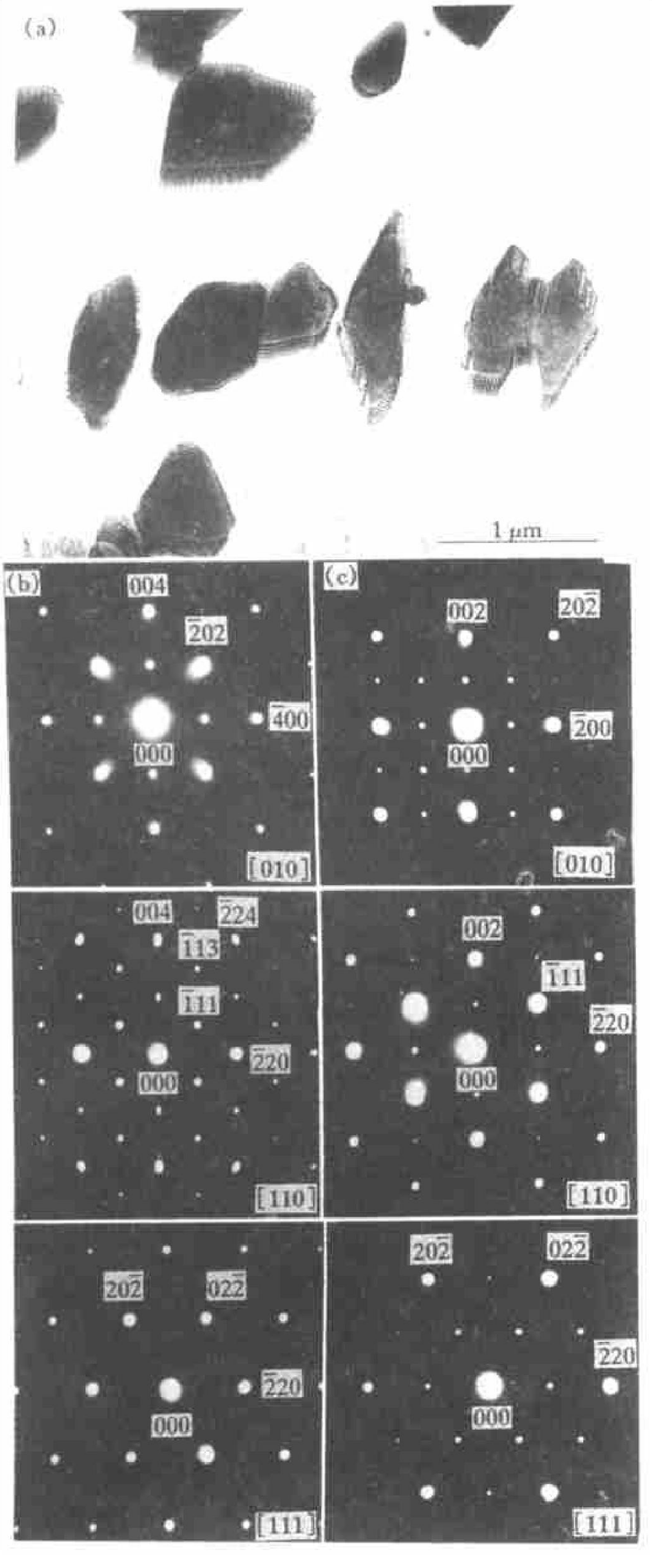

Fig. 3 TEM photographs and diffraction patterns of Alloy 4

(a) —Microstructures of dendrite with particles precipitations;
(b) —Typical diffraction patterns of parent phase in dendrite;
(c) —Typical diffraction patterns of particle in dendrite

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