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Analysis of Chill-Cast NiAl Intermetallic Compound With Copper Additions

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This study carried out a characterization of chill-cast NiAl alloys with copper additions, which were added to NiAl, such that the resulting alloy composition occurred in the β-field of the ternary NiAlCu phase diagram. The alloys were vacuum induction melted and casted in copper chill molds to produce ingots 0.002 m thick, 0.020 m wide, and 0.050 m long. X-ray diffractometry (XRD) and transmission electron microscopy (TEM) performed in chill-cast ingots identified mainly the presence of the β-(Ni,Cu)Al phase. As-cast ingots showed essentially no ductility at room temperature except for the $Ni_{50}Al_{40}Cu_{10}$ alloy, which showed 1.79% of elongation at room temperature. Ingots with this alloy composition were then heat treated under a high-purity argon atmosphere at 550 °C (24 h) and cooled either in the furnace or in air, until room temperature was reached. β-(Ni,Cu)Al and γ'(Ni,Cu)$_3$Al were present in specimens cooled in the furnace and β-(Ni,Cu)Al, γ'(Ni,Cu)$_3$Al plus martensite-(Ni,Cu)Al were present in specimens cooled in air. Thermogravimetric analysis indicated that martensite transformation was the result of a solid-state reaction with $M_s \sim 470$ and $M_f \sim 430$ °C. Tensile tests performed on bulk heat-treated ingots showed room-temperature ductility between 3 and 6%, depending on the cooling media.

Keywords chill casting, heat treatment, macroalloying, room-temperature ductility

1. Introduction

NiAl intermetallic compound is brittle at room temperature and shows values of tensile ductility from zero to few percentage points.[1] Because this intermetallic compound possesses a variety of properties that could be beneficial for high-temperature (HT) structural applications,[2] attempts have been made to increase its room-temperature ductility, including (among other techniques) solidification processing[3] and the influence of the addition of a third element.[4] During solidification of alloys, the solidification front velocity can lead not only to loss of local interface equilibrium and the reduction in degree of order, but also to solute trapping.[5] Ternary additions to NiAl have been investigated by several researchers;[6-9] for instance, it has been reported[10] that Cu additions substitute equally for both Ni and Al. During solidification of Ni-Al alloys with ternary additions of Fe, Co, Cr, or Cu, ternary elements were distributed into the γ phase; in particular, Cu additions induced formation of the γ′ phase[11], small additions of Cu to NiAl destabilized the β-phase and induced β′ martensite transformation,[12] which deteriorated room-temperature tensile ductility. This work presents results of microstructure in chill-cast ingots and after heat treatment, and the effect on bulk room-temperature ductility of chill-cast NiAl intermetallic compound with copper additions.

2. Experimental Procedure

NiAl alloys with copper additions were prepared using Ni, Al, and Cu elements with 99.9% purity. The elements were placed into a boron nitride crucible and vacuum induction heated until a exothermic reaction was reached; then the melt was cooled to room temperature. Samples weighing 0.1 kg were remelted under an argon atmosphere and casted in copper chill molds to produce ingots 0.002 m thick, 0.020 m wide, and 0.050 m long. Table 1 shows the average chemical composition of the resulting ingots (an average of five analyses). Heat treatments of ingots were performed by heating them in sealed quartz tubes at 550 °C (24 h) and cooling them in the furnace (0.05 K/s) or in air (1 K/s) until room temperature was reached. Characterization of microstructure was carried out using a JEOL 2100 (MA, USA) scanning transmission electron micro-

Table 1 Ingot Identification, Chemical Analysis (a), and Lattice Parameters of Cu Chill-Cast Ingots

Field	Identification	Ni, at.%	Cu, at.%	Al, at.%	Lattice Parameter, Å
β-(Ni,Cu)Al	A1	50 ± 0.5	…	bal.	2.887
β-(Ni,Cu)Al	A2	45 ± 0.5	5 ± 0.4	bal.	2.888
β-(Ni,Cu)Al	A3	40 ± 0.2	10 ± 0.2	bal.	2.893
β-(Ni,Cu)Al	A4	35 ± 0.1	15 ± 0.1	bal.	2.901
β-(Ni,Cu)Al	A5	30 ± 0.1	20 ± 0.1	bal.	2.907
β-(Ni,Cu)Al	A6	bal.	5 ± 0.3	45 ± 0.3	2.889
β-(Ni,Cu)Al	A7	bal.	10 ± 0.2	40 ± 0.26	2.895

(a) Average of five analyses.

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scope (TEM) with microanalysis facilities. X-ray diffractometry (XRD) was performed in a Siemens D-5000 diffractometer (Munich, Germany) with 2° automatic step scanning and Cu-Kα radiation. Tensile tests were carried out using flat specimens (0.05 m long) in both as-cast and as-heat-treated condition in an Instron 1125 testing machine (Canton, MA) at a strain ratio of 6×10^{-3} s^{-1}. Before the tensile test, the specimen was placed between the grips and strengthened 0.1 ± 0.02 kg. After that operation, an extensometer (0.025 m of gauge length) was place on the sample and the load was calibrated to zero. Thermogravimetric analyses were performed in a Perkin-Elmer (Norwalk, CT) instrument by employing 2×10^{-5} kg of the heat-treated alloy, which was heated at 1 K/s under an Ar atmosphere.

3. Results and Discussion

Figure 1(a) shows a portion of the ternary NiAlCu phase diagram.[13] In agreement with Fig. 1a, the resulting alloy composition of chill-cast ingots (see Table 1) lies in the β-(Ni,Cu)Al field. The as-cast microstructure consisted of β-(Ni,Cu)Al dendrites with a dendritic arm spacing, d = 2.5 μm (Fig. 1b). From the dendrite arm spacing ($d = 50\varepsilon^{-1/3}$, where ε is the cooling rate in K/s,[14] a cooling rate of 0.8×10^4 K/s was derived, which was assumed to be reached during the chill-cast experiments. XRD performed on chill-cast ingots showed mainly the presence of the β-phase with a shift in the lattice parameter value from 2.887 Å at stoichiometry composition to values up to 2.907 Å (Table 2), because of the substitution of Ni or Al by Cu, in agreement with the results reported in Ref. 15.

The microstructure of alloys was observed under the TEM and the presence of β-phase was detected in all samples, in agreement with the x-ray results. Commonly observed characteristics in NiAl β-phase with copper contents up to 10 at.% are shown in Fig. 2(a), such as long screw dislocations that become helical by vacancy climb, as reported in quenched Al-Cu alloys[16] and in as-cast NiAl alloys.[17] As the Cu-content increases from 10-15 at.%, the presence of cluster of vacancies in the β-(Ni,Cu)Al matrix (Fig. 2b) was observed. In the NiAl alloy with 20 at.% Cu, the presence of spherical precipitates in

Table 2 Phases Detected by XRD in As-Cast and Heat-Treated Ingots

d-Spacing, Å	As-Cast, 0.8×10^4 K/s	As-Cast and Furnace Cooled, 0.05 K/s	As-Cast and Air Cooled, 1 K/s
3.636	…		M-(Ni,Cu)Al
3.599	…	γ′-$(Ni,Cu)_3Al$	γ′-$(Ni,Cu)_3Al$
2.979	…	…	M-(Ni,Cu)Al
2.887	β-(Ni,Cu)Al	β-(Ni,Cu)Al	β-(Ni,Cu)Al
2.547	…	γ′-$(Ni,Cu)_3Al$	γ′-$(Ni,Cu)_3Al$
2.304	…	…	M-(Ni,Cu)Al
2.100	…	…	M-(Ni,Cu)Al
2.070	…	γ′-$(Ni,Cu)_3Al$	γ′-$(Ni,Cu)_3Al$
2.040	β-(Ni,Cu)Al	β-(Ni,Cu)Al	β-(Ni,Cu)Al
1.799	…	β-(Ni,Cu)Al	β-(Ni,Cu)Al
1.667	β-(Ni,Cu)Al	β-(Ni,Cu)Al	β-(Ni,Cu)Al
1.603	…	γ′-$(Ni,Cu)_3Al$	γ′-$(Ni,Cu)_3Al$
1,475	…	…	M-(Ni,Cu)Al
1.461	…	γ′-$(Ni,Cu)_3Al$	…
1.443	β-(Ni,Cu)Al	β-(Ni,Cu)Al	β-(Ni,Cu)Al
1.292	β-(Ni,Cu)Al	β-(Ni,Cu)Al	β-(Ni,Cu)Al
1.265	…	γ′-$(Ni,Cu)_3Al$	…
1.233	…	…	M-(Ni,Cu)Al
1.178	β-(Ni,Cu)Al	β-(Ni,Cu)Al	β-(Ni,Cu)Al
1.078	…	γ′-$(Ni,Cu)_3Al$	…

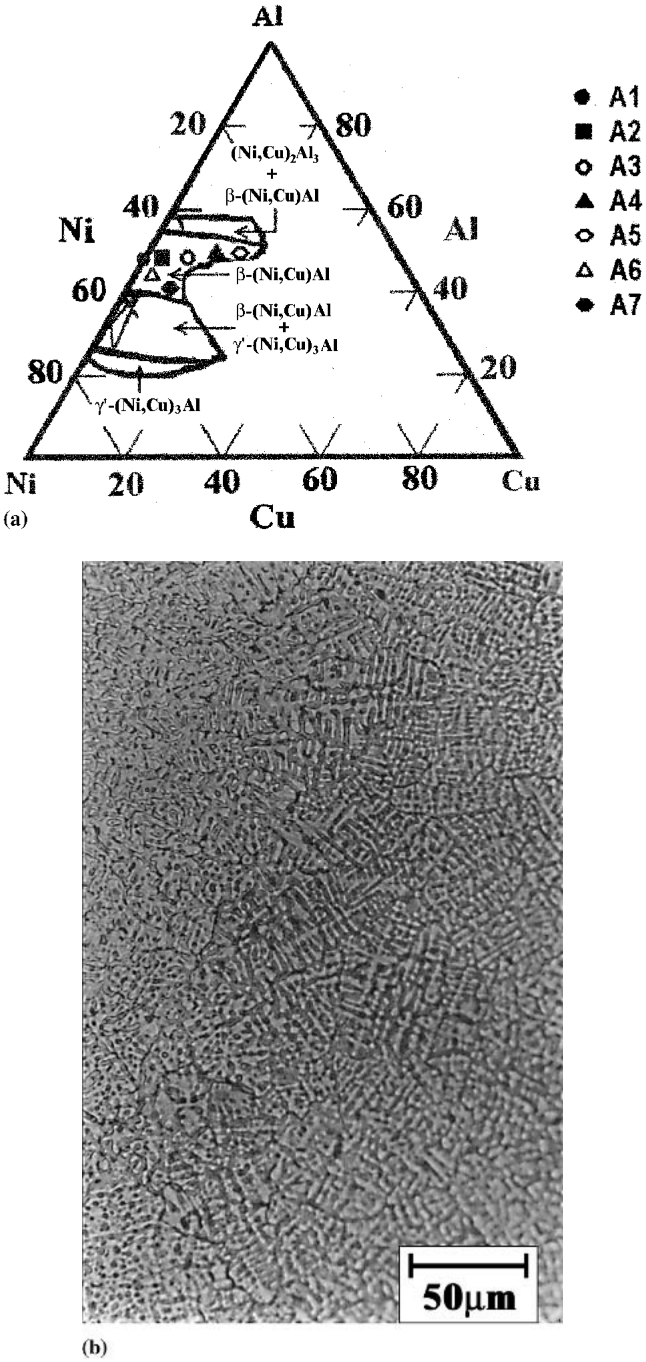

Fig. 1 **(a)** A portion of the ternary NiAlCu phase diagram, where geometric figures show the location of alloys A1 to A7 under study. **(b)** Representative as-cast microstructure with β-(Ni,Cu)Al dendrites

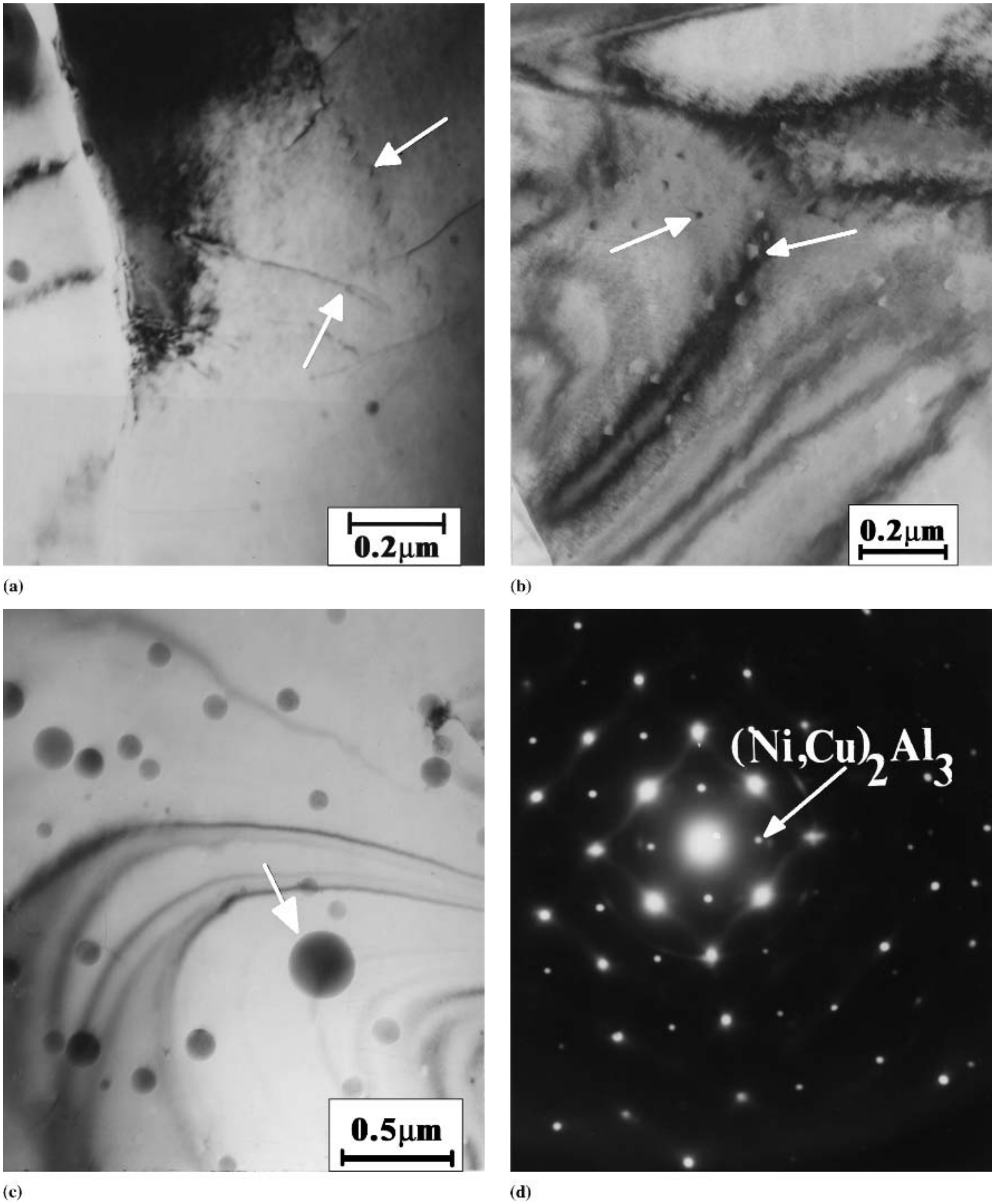

Fig. 2 β-(Ni,Cu)Al phase. **(a)** NiAl with 5-10 at.% Cu shows long screw dislocations that become helical by vacancy climb. **(b)** NiAl with 15 at.% Cu shows the presence of cluster of vacancies. **(c)** NiAl alloy with 20 at.% Cu shows the presence of spherical precipitates in the β-(Ni,Cu)Al matrix. **(d)** Electron diffraction pattern of $(Ni,Cu)_2Al_3$

the β-(Ni,Cu)Al matrix was observed (Fig. 2d), which was identified by means of its electron diffraction patterns and microanalysis as $(Ni,Cu)_2Al_3$ alloys.

Tensile tests performed in as-cast ingots showed nearly zero ductility from ingots identified as A1 to A6, and ingot A7 showed 1.8% elongation (Fig. 3). Despite this low value of tensile ductility at room temperature, ingot A7 was heat treated at 550 °C for 24 h and cooled in the furnace or in air, until room temperature was reached. The cooling rate of the specimen cooled in the furnace was 0.05 K/s, and in air was 1 K/s. XRD performed in the heat-treated ingot and cooled in the furnace detected the presence of β-(Ni,Cu)Al and γ′-$(Ni,Cu)_3Al$ (Fig.

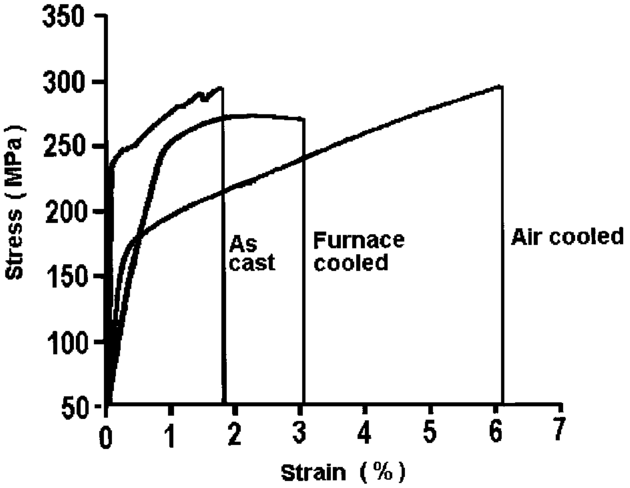

Fig. 3 Tensile test of the $Ni_{50}Cu_{10}Al_{40}$ alloy in the as-cast condition, heat treated at 550 °C (24 h), air cooled and heat treated at 550 °C (24 h), and furnace cooled

4a). Compared to the as-cast ingot, the cooling rate achieved during cooling of the specimen in the furnace was low enough to allow sufficient precipitation of γ′-$(Ni,Cu)_3Al$ from β-(Ni,Cu)Al. The cooling rate achieved during cooling of the specimen in air was high enough to allow the solid-state transformation of martensite-(Ni,Cu)Al from β-(Ni,Cu)Al, which consisted of a plate-like morphology. Inside martensite plates, very fine striations were observed with a separation of 7 nm between them (Fig. 4b).

Thermogravimetric analysis performed in heat-treated ingots showed that during cooling (cooling rate of 1 K/s), a martensite transformation with an M_s temperature of ~470 °C and an M_f temperature of ~430 °C occurred. Regarding the presence of martensite in the $Ni_{50}Cu_{10}Al_{40}$ alloy, Kainuma et al.[11] studied the effect of alloying elements on martensite transformation in the β-NiAl phase, and reported that additions of Ti, V, Cr, Mn, Fe, Zr, Nb, Mo, Ag, Ta, W, and Si stabilize the parent β-phase, lowering the M_s temperature. Conversely, additions of elements such as Co, Cu, and Ag destabilize the β-phase, increasing the M_s temperature. For instance, in the alloy $Ni_{50}Cu_{10}Al_{40}$ with a Cu content of 10 at.%, the M_s temperature was 470 °C.

The room-temperature tensile test performed in the $Ni_{50}Cu_{10}Al_{40}$ heat-treated alloy showed values of ductility of 3.0 and 6.0% when the specimen was cooled in air or in the furnace, respectively. This increase in ductility was attributed to the presence of β-(Ni,Cu)Al grains and γ′-$(Ni,Cu)_3Al$ located mainly at β-grain boundaries. The distribution of γ′-$(Ni,Cu)_3Al$ is almost continuous on the grain boundary of β-(Ni,Cu)Al.

Room-temperature ductility for Ni alloys has shown values, among others, from 0.5% in NiAlCo alloys with necklace microstructures having a film of γ′ ($L1_2$)-Ni_3Al phase on grain boundaries of β-phase.[18] Directionally solidified Ni-30 at.% Al with β-phase and discontinuous rods of γ′ showed 4% tensile ductility, whereas β-phase and continuous rods of γ′ showed 9% tensile ductility.[17] Directionally solidified NiFeCrAl alloys with β and γ lamellae exhibited 17% tensile ductility at room temperature.[19] This variation in ductility of polycrystalline NiAl with or without additions of ternary or quaternary elements is evident, and this difference in ductility in our case can be attributed to a combined effect of solidification processing and resulting microstructure after heat treatment, reaching a bulk tensile ductility of 6%.

4. Conclusions

1) NiAl alloys with copper additions showed the presence of brittle β-(Ni,Cu)Al grains, which gave rise to nearly zero ductility in as-cast ingots. However, alloy $Ni_{50}Cu_{10}Al_{40}$ showed 1.8% of elongation.
2) After heat treatment, the alloy $Ni_{50}Cu_{10}Al_{40}$ cooled in air showed a microstructure consisting of β-(Ni,Cu)Al, γ′-$(Ni,Cu)_3Al$ and M-(Ni,Cu)Al, and when the alloy was cooled in the furnace, showed a microstructure consisting of β-(Ni,Cu)Al and γ′-$(Ni,Cu)_3Al$.
3) This combination of microstructure improved room-temperature ductility of as-cast ingots, showing values of bulk room-temperature tensile ductility up to 6% for the $Ni_{50}Cu_{10}Al_{40}$ heat-treated ingot at 550 °C (24 h) and cooled in the furnace at a cooling rate 0.05 K/s.

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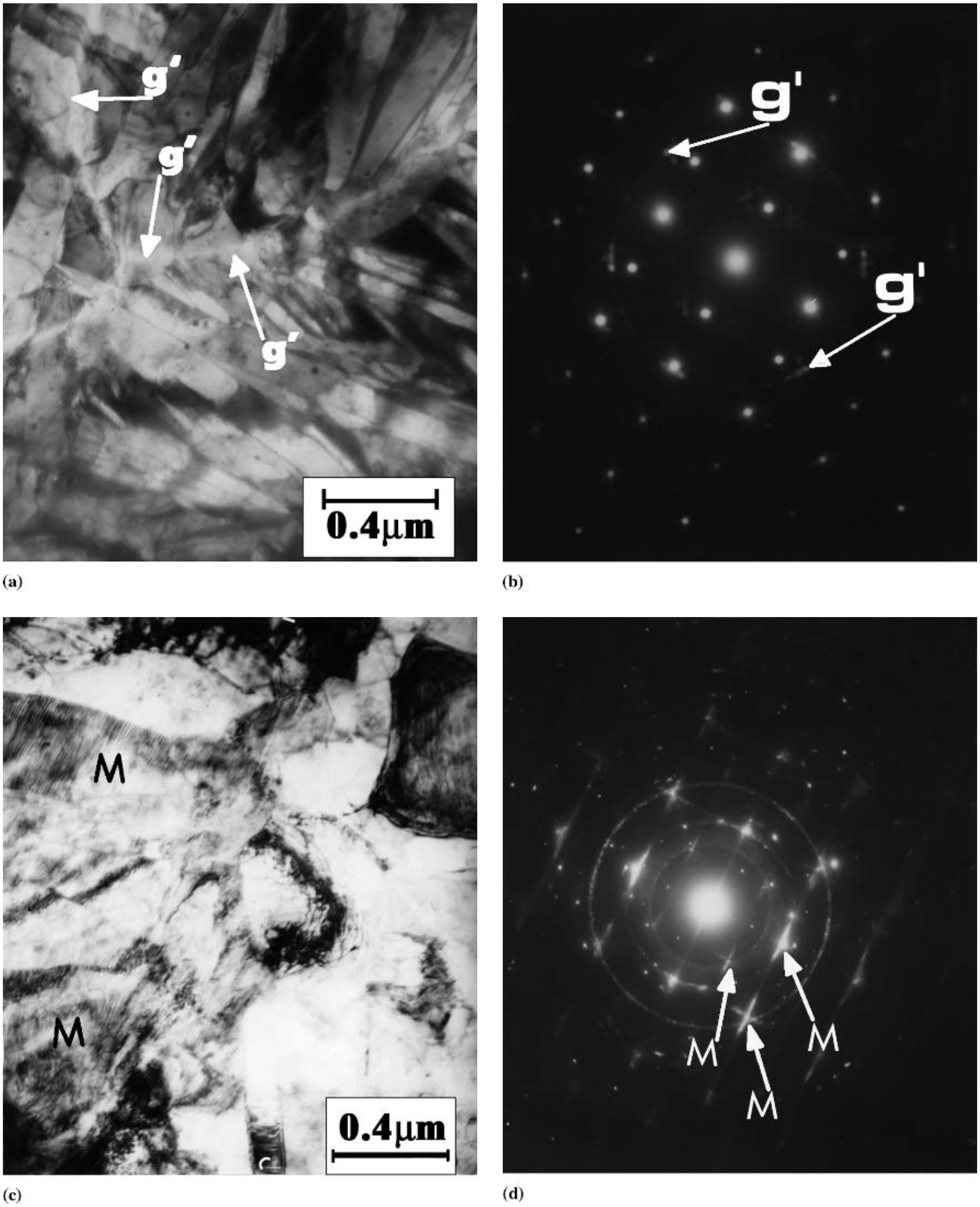

Fig. 4 **(a)** β-(Ni,Cu)Al grains with γ′-$(Ni,Cu)_3Al$ (indicated by g′) at grain boundaries. **(b)** Diffraction pattern of γ′-$(Ni,Cu)_3Al$. **(c)** Martensite-(Ni,Cu)Al, which consisted of a plate-like morphology inside martensite plates; the presence of very fine striations is shown. **(d)** Diffraction pattern of martensite-(Ni,Cu)Al

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