Microstructure and Mechanical Properties of Rapidly Quenched L1₂ Alloys in Ni-Al-X Systems

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Ductile L₁₂-type γ' compounds with rather high strengths and large elongations have been found in rapidly quenched Ni-Al-X (X = Cr, Mn, Fe, Co, or Si) ternary systems. The γ' compounds consist of a metastable phase which contains numerous APD with a size as small as about 50 to 75 nm. Further, the ductile γ' wires with circular cross section have been manufactured directly from the liquid state by an in-rotating-water spinning method. The wire diameter is in the range of 85 to 190 μm and the average grain size is about 2 to 5 μm. The Hₚ, σₚ, σₐ, and εₚ of the γ' wires are about 240 to 400 DPN, 390 to 590 MPa, 580 to 910 MPa, and 4 to 10 pct, respectively, for Ni-Al-(Cr, Fe, Co, or Si) systems and about 220 DPN, 260 MPa, 440 MPa, and 27 pct, respectively, for the Ni-Al-Mn system. A cold drawing causes a significant increase in σₚ and σₐ and the attained values are about 2450 MPa and 2480 MPa, respectively, for Ni-20Al-10Cr wire drawn to about 90 pct reduction in area. Around the temperatures where the APB disappear on annealing, the Hₚ, σₚ, σₐ, and εₚ of the γ' wires decrease significantly accompanied with a drastic change in fracture surface morphology from a transgranular type to an intergranular type. It has been therefore inferred that the high strengths and good ductility of the melt-quenched γ' compounds are due to the structural changes to a low degree of ordered state containing a high density of APB and the suppression of grain boundary segregation.

I. INTRODUCTION

In recent years, melt-quenching technique has attracted an increasing interest from scientific and engineering points of view. The main reasons appear to be due to the following two factors: (1) It is possible to produce the materials in the form of wire, sheet, or powder directly from the liquid state, resulting in a remarkable simplification of the fabricating process. (2) From the structural point of view, it is possible to obtain the as-quenched phase having various features such as the refinement of grain size, the extension of solid solubility limit of solute elements, the formation of an amorphous phase or a nonequilibrium crystalline phase, the suppression of segregation, and the introduction of a high density of internal faults.

It is well known that the ordered structure in Ni₃Al (γ') intermetallic compound with an fcc L₁₂ structure remains up to the melting point, as similar to CsCl-type compounds such as Fe₃Al, Ni₃Al, and Co₃Al. Therefore, it is impossible to achieve a disordered state of the γ' compound even by any heat treatments in solid. However, if these compounds are rapidly solidified from the liquid state, there is a high possibility that they may change into a disordered state and/or a low degree of ordered state containing a high density of anti-phase boundaries (APB). As a result, it is expected that the melt-quenched γ' compound exhibits good ductility as well as high mechanical strength by the combination effect of the suppressions of ordering and grain boundary segregation and the grain size refinement, etc., even though the compound prepared by a conventional process is extremely brittle and undergoes an intergranular fracture without plastic elongation. This paper deals with the microstructures and mechanical properties in melt-quenched and annealed states of Ni-Al-X (X = IV ~ VIII A Group transition metals, Cu or Si) ternary alloys which show the L₁₂-type γ' single phase in an equilibrium state.

II. EXPERIMENTAL METHODS

The specimens used in the present work are Ni-Al-X (X = Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Co, Cu, or Si) ternary alloys. All the compositions of these alloys are located in the formation region of only Ni-Al-type compounds. The equilibrium phase diagrams indicate that a chemical formula of the resultant compounds is Ni₃(Al-X) for X = Ti, Zr, V, Nb, Mn, Cu, or Si; (Ni₃)₃(Al-X) for X = Cr, Mo, or Fe; and (Ni-X)₃Al for X = Co. Mixtures of these pure elements (Ni, Al, and X) were melted under argon atmosphere in an induction furnace to prepare the test alloys. The melts were taken up into quartz tubes of about 6 mm inner diameter and solidified in the tubes. Since the difference between weighed and chemically analyzed compositions is less than 0.15 wt pct for aluminum, the compositions are from the weighed values denoted by atomic percentage. From these master alloys, long ribbons with a cross section of about 3 mm × 100 μm were prepared as the test samples for the structural observation by a melt-spinning apparatus. The amount of the alloys melted in a run was about 5 g, and the rotation speed of the copper roller (200 mm in diameter) was controlled at about 1000 rpm. In addition, continuous wires of about 85 to 190 μm diameter were prepared as the samples for measuring mechanical properties by using the in-rotating-water melt spinning technique which is capable of producing wires with a circular cross section directly from the molten metal.

In this section, we shall in more detail describe the fabricating condition of the γ' wires by the in-rotating-water spinning technique. In order to get a continuous wire, it is essential that the solidification of the molten stream takes place before droplets tend to form. In general, the time...
before droplet formation is very short because of the inherent instability of a jet due to the low viscosity and high surface tension typical of molten metal jets. Hence, the melt spinning condition must be severely adjusted, based on close examination of the wires spun. As similar to the results for amorphous wires, the melt jet to water velocity ratio was the most important factor for the wire production. Continuous γ' wires with a smooth surface were wound on the inner side of the drum when the water velocity in the drum exceeds the melt jet velocity by about 20 to 30 pct. Further, in this technique it is important to point out that the existence of aluminum appears to accelerate the generation of a very thin oxide film around the liquid jet which prevents its break-up before it is fully solidified.

The other operating parameters were adjusted as follows: (1) the distance between the surface of water and the end of a quartz tube was less than about 3 mm and the angle of the nozzle against the surface of water was about 70 deg, (2) the orifice size of the quartz nozzles varied about 0.05 and 0.3 mm in diameter, (3) the circumferential speed of the drum was approximately 11 m per second, (4) the temperature of cooling water was approximately 278 K, and (5) the melt was ejected by an argon over pressure of about 0.2 MPa at a temperature of about 75 to 100 K above the liquidus.

As-quenched and annealed structures of the specimen were examined by optical microscopy, transmission electron microscopy (TEM), and X-ray diffraction using filtered Cu-Kα radiation. The optical microscope samples were chemically polished in a solution consisting of 96 parts ethyl alcohol and four parts nitric acid at room temperature, and the average grain size was determined from the optical micrographs of longitudinal and cross-sectional area. The TEM specimens were prepared by electrolytically thinning ribbons in a 1:9 volumetric ratio of perchloric acid methanol solution immersed in ice water. The hardness and electrical resistance were measured for the as-quenched and annealed ribbon samples by a Vickers microhardness tester with a 100 g load and by a four-probe method, respectively. All surfaces of the specimen for the electrical resistance measurement were polished to a 0.05 μm finish to minimize error in the calculation of the cross-sectional area, and therefore, the electrical resistivity. The yield strength (σy), tensile fracture strength (σf), and elongation (εb) were measured for the wire samples in as-quenched and one-hour annealed states at room temperature by an Instron-type tensile testing machine at a strain rate of 4.2 × 10⁻⁴ per second. Tensile specimens were cut out from an as-quenched long wire into the short pieces having the gauge dimension of 20 mm length. A specially designed set of grips for the fine wires was used to insure proper specimen alignment within the machine. The fracture surface morphology was examined by scanning electron microscopy. In addition, the bend strain (εb) on the outer surface required for fracture, which is defined as εb = t/(L - t), was measured for the ribbon samples having thicknesses of about 100 μm. Here t is the thickness of the ribbon specimen and L is the distance between parallel plates at fracture.

### III. RESULTS

#### A. Microstructure of Melt-Quenched γ’ Compounds

Figures 1(a) to (c) show the bright-field micrographs of melt-quenched Ni-18 at. pct Al-5 at. pct V (Ni-18Al-5V), Ni-20Al-10Fe, and Ni-22Al-5Cu alloys. The as-quenched structure of these alloys is composed of only γ' phase having a grain size as small as about 2 μm, and no second phase is seen even on the grain boundaries. Also, one can see the numerous contrasts of APB in the individual grains of the γ' phase. The similar structure consisting of γ' single phase was obtained in each alloy of Ni-15Al-8Ti, Ni-18Al-4Zr, Ni-18Al-5Nb, Ni-20Al-12.5Cr, Ni-20Al-2Mo, Ni-18Al-6Mn, Ni-22Al-20Co, and Ni-10Al-12Si. Further, as exemplified for Ni-20Al-10Fe alloy in Figure 2, the γ' single phase of the alloy systems used in the present work is stable against heating and no appearance of second phase is recognized, at least after an annealing for one hour at 973 K. As shown in Figure 1, the as-quenched structures are very similar for three of the alloys. Nevertheless, it was found that the ductility was markedly different among their alloy systems. That is, the γ' ribbons of Ni-Al-X (X = Cr, Mn, Fe, Co, or Si) systems exhibit highly ductile nature and are able to sustain the 180 deg bending. On the other hand, those of Ni-Al-X (X = Ti, Zr, V, Nb, or Cu) systems are extremely brittle and fracture during a bend test. In order to clarify the reason for such a marked difference in bend ductility, the anti-phase domain (APD) structure in melt-quenched γ' compounds was examined in detail by means of a dark-field analysis using a TEM.

Figure 3 shows the dark-field micrographs taken from the 001 superlattice reflection and the selected area diffraction patterns for melt-quenched Ni-20Al-10Cr (a and b), Ni-18Al-6Mn (c and d), Ni-20Al-10Fe (e and f) and Ni-22Al-20Co (g and h) alloys. One can easily notice in Figure 3 that these micrographs were taken in the reflecting...