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Alloy Design of Gamma Titanium Aluminide Intermetallic Compounds

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Abstract:

Gamma titanium aluminide (γ-TiAl) intermetallic compounds are spotlighted as lightweight heat-resistant materials, and their mechanical properties are improved by adding a third alloying element. The phase equilibrium of Ti-Al-X systems (X = Mo, Nb, Cr) at high temperatures was studied by the combination of quenching experiment, high-temperature X-ray diffraction, differential thermal analysis, and diffusion couple experiment. According to the experimental results, ternary equilibrium phase diagrams are proposed to provide a guideline for the Ti-Al-X (X = Mo, Nb, Cr) alloy design. Various γ-TiAl compositions with third alloying element additions were melted on the basis of ternary phase diagrams, and were examined for basic properties (mechanical properties at room temperature and elevated temperatures). The mechanical properties of γ-TiAl were found to drastically change with phase and microstructure. The relations of mechanical properties with phase and microstructure were studied and factors influencing room-temperature ductility and high-temperature strength were identified, and as a result a guideline was set for improving the mechanical properties of γ-TiAl. By alloy design based on newly developed ternary phase diagrams, the microstructure of γ-TiAl was adjusted to develop new γ-TiAl alloys with much better room-temperature ductility and high-temperature strength than those of conventional γ-TiAl alloys.

1. Introduction

There is a demand for materials featuring high strength at temperatures at which conventional heat-resistant materials cannot satisfactorily perform, for future aircraft and energy applications. In recent years, intermetallic compounds with intermediate characteristics between ceramics and metals have attracted attention as structural materials for high-temperature service. Intermetallic compounds have atoms of different elements in an orderly arrangement in the crystal structure. They are generally brittle and difficult to fabricate[1,2]. Gamma titanium aluminide (γ-TiAl) intermetallic compounds feature low density and excellent high-temperature strength, so that they are extensively investigated as lightweight heat-resistant materials for jet

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engines, automotive exhaust valves, and similar applications. In the 1960s, the U.S. Air Force Wright Laboratory carried out elaborate work on γ-TiAl but failed in overcoming its brittleness for practical use. Recent research has succeeded in changing the composition of γ-TiAl and controlling its phase and microstructure by improving its melting and hot working processes, resulting in a significant enhancement of its workability or ductility. Many reports have been published about the relations of phase and microstructure to mechanical properties in γ-TiAl[3-7]. Reports abound on examples in which the properties of γ-TiAl intermetallic compounds are improved by the addition of third alloying elements, but none of them clarifies why any particular third alloying element is effective or what compositional range is optimum. Findings from phase diagrams are especially important for more efficient material design. Research results to date, however, are scanty concerning Ti-Al-X ternary phase diagrams that can represent γ-TiAl systems with the addition of a third alloying element. Phase diagrams necessary for the design of γ-TiAl alloys are yet to be developed.

In this research work, phase diagrams necessary for the material design of γ-TiAl intermetallic compounds were proposed on the basis of experimental data, and the relations of phase and microstructural changes with the mechanical properties of the compounds were investigated using the phase diagrams[8].

2. Ti-Al-X Phase Diagrams

2.1 Study of phase diagram

Study was made into how to construct phase diagrams for gamma titanium aluminide (γ-TiAl) intermetallic compounds at high temperatures, and an optimum method was established. The γ-TiAl intermetallic compounds are very reactive at high temperatures, and their elevated-temperature state is difficult to freeze. Given these properties of γ-TiAl, basic data for phase diagram construction were obtained from a combination of the following methods:

1) Quenching experiment: A specimen was sealed in a quartz tube, heated at a high temperature, then cooled in ice-cold water, and investigated for microstructure, crystal structure, hardness and other properties. The experimental data were analyzed paying particular consideration to the fact that the high-temperature morphology is not frozen but is influenced by the subsequent conditions of cooling.
2) Heat analysis: Differential thermal analysis (DTA) was conducted using a special thermal analysis apparatus. Atmosphere control was thoroughly performed to prevent any reactions at high temperatures, and measurements were made in a helium plus 5% hydrogen atmosphere.
3) Diffusion couple experiment: The equilibrium concentration was determined by use of a diffusion couple to clarify the phase boundary concerning the concentration on the isothermal section of a ternary phase diagram. The electron probe microanalyzer (EPMA) was used for the determination of concentration. Besides the conventional ZAF corrections, correction of concentration was made also for the chemical composition employing the external standard method.
4) In-situ observation: A dedicated X-ray diffraction apparatus that covers the widest possible range of atmosphere control was built and used. To solve the problem of high-temperature reactivity, the optimum heater material and shape were designed, and a measurement system was devised for quick measurement. Emphasis was placed on phase identification by X-ray diffraction analysis at high temperatures.

2.2 Ti-Al-Mo system equilibrium phase diagram

Among the Ti-Al-X ternary systems, the Ti-Al-Mo system is characteristic in that it has molybdenum which is higher in the β phase stabilizing capability than any other transition element. Ti-Al-Mo specimens of various compositions were annealed at 1,573, 1,473 or 1,373K, quenched in ice-cold water, and examined for the phase and microstructure. The experimental results show that the addition of several percent molybdenum precipitates the β phase at grain boundaries of the γ phase, that for the same composition, the volume fraction of the β phase becomes the largest when specimens are quenched from 1,473K, and that these two tendencies accelerate with increasing titanium concentration. Also in the quenching experiment, there is no conclusive evidence that the high-temperature state of the specimens is frozen, which suggests the possibility that the metastable state of the specimens is observed. To directly confirm the equilibrium state, differential thermal analysis and high-temperature X-ray diffraction apparatus were used, and the phase of the specimens at high temperatures was directly identified by in-situ observation. **Fig. 1** shows diffraction patterns obtained from $Ti_{51.4}Al_{45.6}Mo_{3.0}$ at different temperatures. It is confirmed that the phase state of the specimen changes from $\gamma+\beta$ through $\gamma+\alpha+\beta$ to β with heating, and that the volume fraction of the β phase becomes maximum in the vicinity of 1,473K.

The diffusion couple experiment gives direct information on the isothermal sections of phase diagrams. $Ti_{63.5}Mo_{36.5}$ and $Ti_{53.4}Al_{46.6}$ were diffusion bonded and annealed at 1,473K for 72 h. **Fig. 2** shows the cross-sectional microstructure and EPMA results of the diffusion couple interface of the specimen. During the determination of elements by the EPMA, the data obtained by measuring the entire region of $100 \times 100\mu m$ at 1-μm intervals were compared with the chemical analysis values and were also corrected for ZAF to improve the accuracy of quantitative determination. The α phase is formed by diffusion, and the molybdenum diffusion region is present in the β phase.

Fig. 3 shows a Ti-Al-Mo ternary phase diagram at 1,473K constructed in consideration of the results of in-situ X-ray diffraction and differential thermal analysis (DTA). The dotted line indicates the change of composition observed in the diffusion couple experiment. The solid-line triangle denotes the $\alpha+\beta+\gamma$ three-phase region. The Ti-Al-Mo system shown in **Fig. 3** is characterized by the facts that the β phase region projects into the α phase

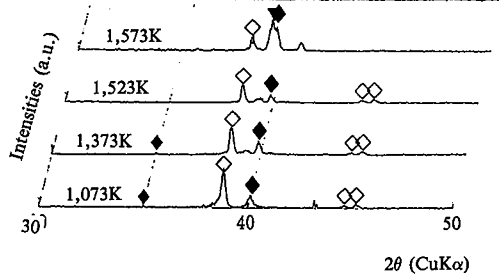

Fig. 1 Change with temperature in diffraction pattern of $Ti_{51.4}Al_{46.5}Mo_{3.0}$ specimen obtained by high-temperature X-ray diffraction

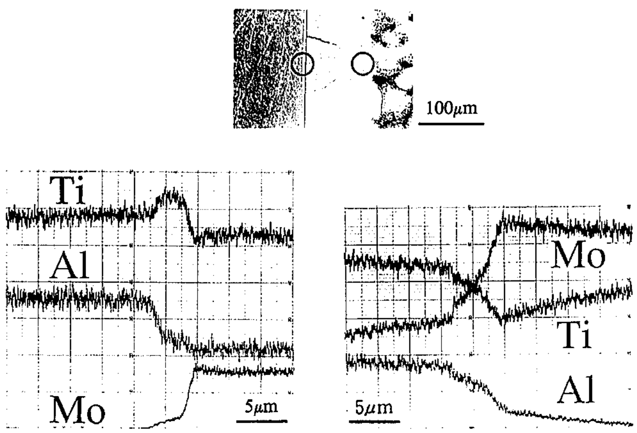

Fig. 2 Cross-sectional microstructure and chemicaly analysis of $Ti_{63.5}Mo_{36.5}$-$Ti_{53.4}Al_{46.6}$ diffusion couple interface

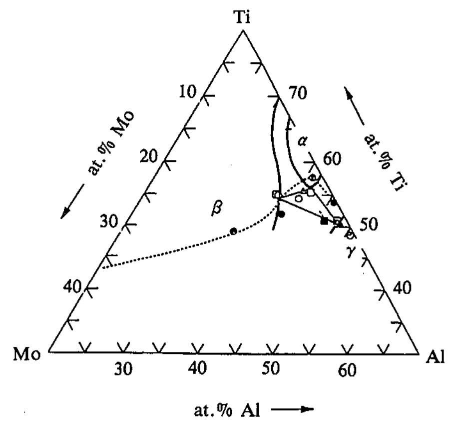

Fig. 3 Ti-Al-Mo ternary phase diagram (1,473K isothermal section)

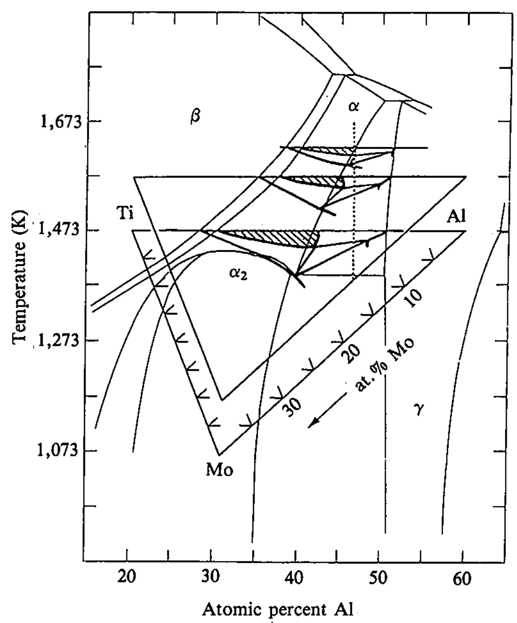

Fig. 4 Projection of Ti-Al-Mo ternary phase diagram on Ti-Al binary phase diagram

region and that the solid solubility of molybdenum in the α phase and the γ phase is not appreciably high. **Fig. 4** shows the 1,473K and 1,573K isothermal sections of a Ti-Al-Mo ternary phase diagram superimposed on a Ti-Al binary phase diagram. It is evident from **Fig. 4** that the γ, β and α phase regions are entangled at the composition near the stoichiometry of γ-TiAl, and that the equilibrium phase drastically changes with the temperature. As predicted from the equilibrium phase diagram, the phase and microstructure produced by heat treatment heavily depend on the temperature. The addition of molybdenum as third alloying element led to the stabilization of the β phase and a change in the β phase region. It is thus known that the $\gamma+\beta+\alpha$ three-phase region is located at the position where several atomic percent molybdenum is added to the Ti-Al binary system, and that the β phase stabilizing tendency is larger than in the Ti-Al binary system.

2.3 Ti-Al-Nb equilibrium phase diagram

Research on phase diagrams is under way for the Ti-Al-Nb system by a procedure similar to that employed for the Ti-Al-Mo system. Niobium is a powerful third alloying element from the point of view of enhancing oxidation resistance and strength. **Fig. 5** shows a Ti-Al-Nb ternary equilibrium phase diagram[9] calculated to be thermodynamically valid from experimental results. The experimental data are plotted, and the phase boundaries predicted from the experimental results are indicated. It is confirmed that a phase diagram calculated by using thermodynamic parameters is qualitatively correct. The reliability of phase boundaries is questionable, however. It is recommended that the phase boundaries be corrected. Also, the results of quenching experiment suggest the presence of the a phase of bcc crystal structure in the $\gamma+\alpha$ phase region. There remains the problem whether the phase is a stable phase or a projection of the nearby β phase region. Work is being carried out on this issue. In the Ti-Al-Nb system, the solid solubility of niobium in both the α phase and the γ phase is large as compared with the Ti-Al-Mo system shown in **Fig. 3**. The $\alpha+\beta+\gamma$ three-phase region is thus situated in the position where 10% or more niobium is added to the Ti-Al binary system.

2.4 Ti-Al-Cr equilibrium phase diagram

Phase diagram work has been conducted on the Ti-Al-Cr sys-

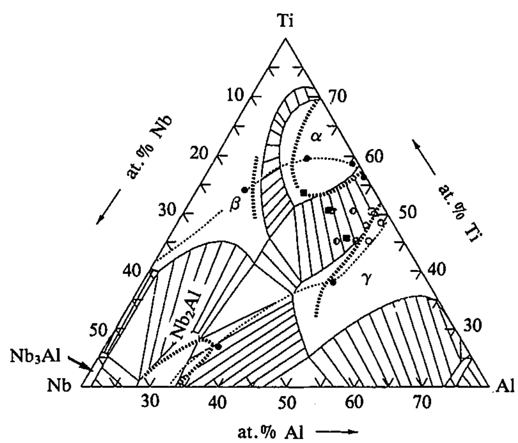

Fig. 5 Ti-Al-Nb ternary equilibrium phase diagram (1,473K isothermal section)

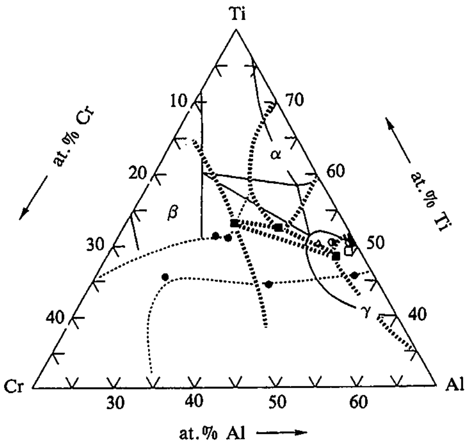

Fig. 6 Ti-Al-Cr ternary equilibrium phase diagram (1,473K isothermal section)

tem as well. Chromium is a powerful alloying element in terms of strength and high-temperature superplastic deformation[10]. Specimens were quenched from 1,373K, 1,473K or 1,573K and observed for microstructure. The microstructural morphology of the specimens and the volume fraction of each phase were analyzed from the results of microstructural observation. Compared with the Ti-Al-Mo system, there is the possibility that the phase equilibrium changed in a complex manner. The results of differential thermal analysis suggest the strong possibility that the 1,564-to-1,640K peak is an overlap of two peaks, and it is likely that the γ, α and β phase regions are entangled. Another important characteristic of the Ti-Al-Cr system is that the melting point is lowered by nearly 20K by the addition of chromium, compared with other Ti-Al-X systems. Although definite conclusions cannot be drawn from these results, the possibility has been confirmed for the first time that the phase diagrams reported to date for the Ti-Al-Cr system significantly deviate from the correct one. **Fig. 6** shows a Ti-Al-Cr ternary phase diagram at 1,473K. The β phase is stabilized by the addition of chromium, and there is the possibility that the projection of the β phase boundary is not as large as observed with other Ti-Al-X systems. It is clear from the proposed Ti-Al-Cr ternary phase diagram that the solid solubility range of chromium is large for the α phase and small for the γ phase.

3. Basic Characteristics of Ti-Al-X

3.1 Experimental methods

Various γ-TiAl compositions determined from Ti-Al-X ternary phase diagrams were melted by the plasma arc remelting process, cast into ingots, hot isostatically pressed, isothermally forged, and microstructurally conditioned. Heat treating conditions were studied to obtain the optimum microstructure from the microstructurally conditioned material. The material was heat treated under the conditions thus established, and round tensile test specimens (with a 4 mm diameter and 20 mm long gage portion) were prepared by electric discharge machining and turning. The specimens were tensile tested in air at an initial strain rate of 1×10^{-3}/s on an Instron tensile testing machine. Room-temperature elongation at break was measured with strain gauges and by fitting broken specimen pieces. The fracture surface and longitudinal section of each of the failed specimens were examined by scanning electron microscopy (SEM) and optical microscopy, respectively, to observe the relationship between the fracture surface and the microstructure in detail. High-temperature mechanical properties were determined using specimens prepared under the same process conditions as for the room-temperature tensile test specimens. The high-temperature tensile test specimens were tested in vacuum at the strain rate of 1×10^{-3}/s and temperature of 1,273K.

3.2 Room-temperature tensile properties of Ti-Al-X

The mechanical properties of γ-TiAl intermetallic compounds heavily depend on the composition and on the changes in phase and microstructural morphology with the composition. Particularly, the mechanical properties of γ-TiAl are known to depend on the aluminum content to a great extent as can be predicted from the Ti-Al binary phase diagram. The effect of third alloying elements (added 1 to 4 at.%) on the room-temperature tensile strength of γ-TiAl in the tensile test are analyzed in relation to the aluminum content and plotted in **Fig. 7**(a). Gamma TiAl with niobium, an alloying element that exhibits high strength at room temperature, shows a relatively high fracture strength. Gamma TiAl with tantalum suffered cleavage fracture, failed within the elastic limit, and yielded low values of tensile strength. When the tensile test data are arranged by the aluminum content, the tensile strength of γ-TiAl clearly depends on the aluminum content and is high where the aluminum content is 46 to 48 at.%. **Fig. 7**(b) shows the effects of the third alloying element and the aluminum content on the elongation of γ-TiAl. Gamma TiAl with vanadium, chromium, manganese, or niobium added as the third alloying element exhibits elongation of 2.0% or more at room temperature. Gamma TiAl with chromium features high ductility over a wide aluminum content range. Gamma TiAl with niobium, manganese or vanadium exhibits high elongation when the aluminum content is 47 at.% or more. The room-temperature

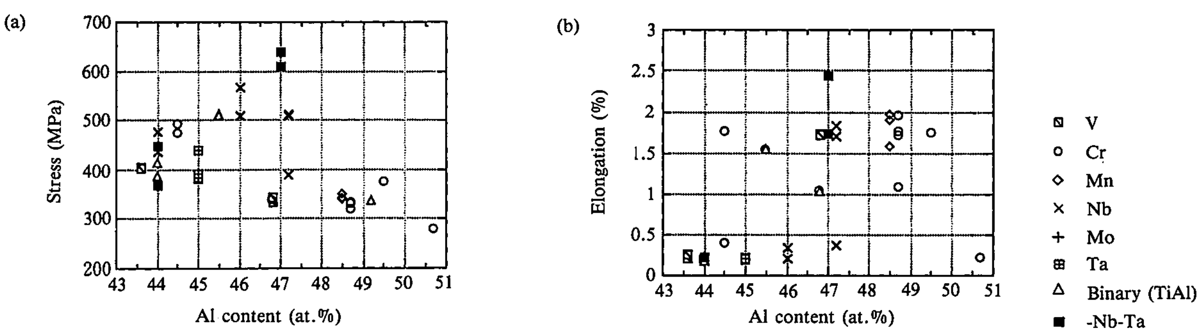

Fig. 7 Effect of third alloying element on room-temperature tensile strength (a) and effects of third alloying element and aluminum content on room-temperature elongation (b)

mechanical properties of γ-TiAl largely depend on the microstructure. The effects of second-phase volume fraction, microstructural morphology, and grain size must be analyzed in greater details. These phases and microstructures can be controlled by changing heat treating conditions. The composition being equal, the mechanical properties widely change with the heat treating conditions.

After the room-temperature tensile test, the fracture surfaces of failed specimens were examined by SEM. The fracture surfaces do not exhibit such a failure mode that the fracture propagates from the crack initiation site as observed in brittle materials, but is predominantly a cleavage fracture. Cleavage fracture is characteristic of fractured specimens, and cleavage facets of approximately the same size are observed. The fracture is considered to have suddenly occurred with the cleavage fracture facets serving as crack propagation path when the strain exceeded a critical value. **Fig. 8** shows the correlation between the cleavage facet size measured from SEM micrographs and the elongation at break determined in the tensile test. The elongation at break increases with decreasing cleavage facet size. The cleavage facet size is about a half of the grain size for specimens of equiaxed grain microstructure. Given this correlation, the grain size must be controlled to 20 μm or less to obtain room-temperature ductility of 2.0% or more.

The longitudinal section of fractured specimens was examined by optical microscopy to observe crack initiation and propagation. In the room-temperature tensile test, the crack propagates in a very short time, and the crack path agrees well with the microstructure where the crack was initiated. When the gage side of a fractured specimen was observed, the crack initiation from the surface of the specimen was evident as shown in **Fig. 9**. The crack entered the lamellar microstructure in the parallel direction and changed to another cleavage plane midway. This suggests that the cleavage resulted from dislocation interaction. Crack propagation along the grain-boundary second phase is observed in some regions, indicating that the presence of a grain-boundary phase does not effectively work in improving the room-temperature ductility.

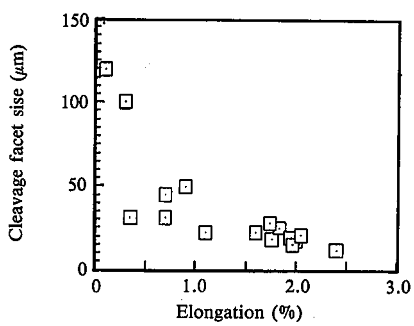

Fig. 8 Relationship between cleavage facet size obtained by fractography and tensile elongation

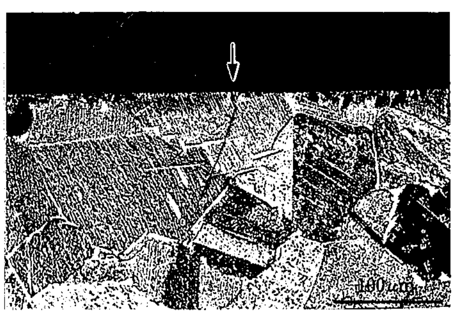

Fig. 9 Cross-sectional microstructure of $Ti_{50.0}Al_{48.4}Mn_{1.6}$ after tensile test (crack initiation indicated by arrow)

3.3 Improvement of high-temperature strength by adding niobium or tantalum

Analyses of findings from ternary phase diagrams and high-temperature tensile test led to the conclusion that the solid solution of a third alloying element is effective in developing high-temperature strength. Gamma TiAl intermetallic compounds with vanadium, chromium, niobium, or tantalum added as the third alloying element were melted, cast into ingots, controlled for microstructure by isothermal forging and heat treatment, and tensile tested at the temperature of 1,273K and strain rate of 1×10^{-3}/s. **Fig. 10** shows the peak stress and elongation for each specimen. Ti-43.6 at.% Al-4.04 at.% V and Ti-44.0 at.% Al-4.7 at.% Nb exhibited a tensile strength of 300 MPa or more at 1,273K. They are Ti-Al-X systems in which both vanadium and niobium are high in solid solubility in the γ phase and the α phase. As can be seen from **Fig. 10**, the high-temperature elongation depends on the aluminum content. Specimens with an aluminum content of 45 at.% or less exhibit a lamellar microstructure and are low in tensile elongation at high temperatures. Specimens with a higher aluminum content exhibit a duplex microstructure composed of lamellar and equiaxed microstructures and are thus high in high-temperature ductility. Superplastic deformation is confirmed in Ti-Al-X systems with the β phase precipitated by the addition of a third alloying element[10]. For the purpose of developing a γ-TiAl alloy with excellent room-temperature ductility and high-temperature strength, Ti-47.0 at.% Al-2.3 at.% Nb-1.0 at.% Ta exhibits room-temperature ductility of 2.4% and 1,273K strength of 271 MPa in a balanced manner.

4. Alloy Design

4.1 Relationship between microstructure and mechanical properties of γ-TiAl

Experimental data about the Ti-Al binary system have been collected and arranged in large amounts in an attempt to relate

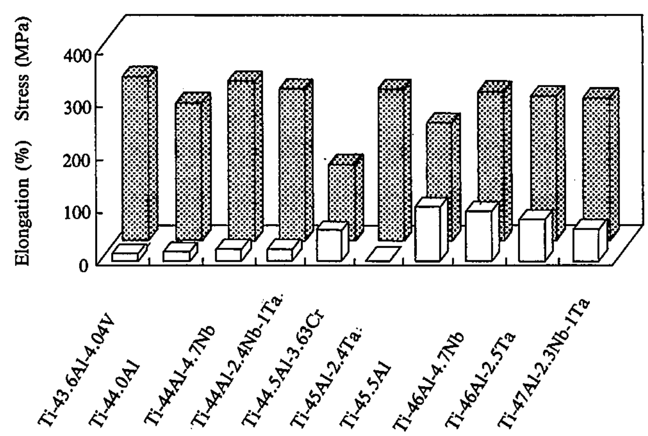

Fig. 10 1,273K tensile strength and elongation of γ-TiAl with third alloying element additions

mechanical properties to phases and microstructures, on the basis of findings from phase diagrams. For Ti-Al-X ternary systems, however, work has not advanced well on the relationship of mechanical properties to the phase and microstructure, partly because their phase diagrams are not yet developed well.

In the Ti-Al binary system, titanium-rich γ-TiAl intermetallic compounds are found to change drastically in microstructure when heat treated. This is because the $\alpha+\gamma$ two-phase region changes with temperature and because the $\alpha \rightarrow \alpha_2$ ordered transformation occurs at 1,373K. Acicular, lamellar, duplex, and equiaxed microstructures can be produced as representative microstructures by thermomechanical processing or heat treatment. Furthermore, massive transformation has been reported recently[11]. Ti-Al-X ternary specimens were microstructurally controlled, quenched in ice-cold water, air cooled, furnace cooled or otherwise heat treated from 1,373, 1,473, or 1,573K, and examined for the resultant microstructural change. The cooling rate can be changed to control transformation and develop various forms of microstructure. These results suggest the need for not only equilibrium phase diagrams, but also continuous cooling transformation (CCT) diagrams that take the cooling process into account. According to the study results presented here, the following measures are proposed to improve the ductility of γ-TiAl intermetallic compounds:

(1) Form a homogeneous equiaxed microstructure to reduce the facet size.
(2) Since the second phase serves as a crack path, finely disperse the second phase particles, or thermomechanically process them so that the second phase does not precipitate at or within the grain boundaries.
(3) Electrolytically polish or otherwise finish the surface smooth, in order to inhibit crack initiation from the surface.

4.2 Relationship between microstructure and high-temperature strength

Ti-Al-X ternary specimens were high-temperature tensile tested to failure and observed on the longitudinal section. **Fig. 11** shows the microstructure of a Ti-47.2 at.% Al-2.1 at.% Nb specimen that exhibited a large elongation at break. No grain growth is observed, and the grains formed by dynamic recrystallization are of the same size as observed before deformation. A second phase elongated at grain boundaries is evident and is identified as the β phase by X-ray diffraction. As shown in Ti-Al-X ternary phase diagrams, the volume fraction of the β phase can be changed by changing the amount of the third alloying element and the heat treating temperature. It was made clear that controlling the β phase is important in improving workability at high temperatures.

Gamma TiAl intermetallic compounds have been developed for use as structural materials for high-temperature service. The room-temperature ductility and workability of γ-TiAl, critical properties required of structural materials, are improved by adding a third alloying element and through microstructural control. The mechanical properties of γ-TiAl in intended service environments, such as high-temperature strength, creep strength and oxidation resistance, have not yet been fully clarified in study. The present research has analyzed the effects of microstructures and third alloying elements as factors in improving the high-temperature strength of γ-TiAl. The lamellar microstructure was found to be stronger than the equiaxed microstructure. The Ti-Al-X ternary phase diagrams and high-temperature tensile test data suggest that the solid solution of third alloying elements in the γ phase and α phase enhances the high-temperature strength of γ-TiAl.

Fig. 11 Cross-sectional microstructure of Ti-47.2 at.% Al-2.1 at.% Nb specimen after 1,473K tensile test
(β phase etched dark at grain boundaries)

5. Conclusions

The effectiveness of adding a third alloying element to γ-TiAl intermetallic compounds has been studied from the standpoints of microstructure and phase stability. Basic data about phases and microstructures at high temperatures have been accumulated through quenching experiments, high-temperature X-ray diffraction, differential thermal analysis, and diffusion couple experiments. Ti-Al-Mo, Ti-Al-Nb and Ti-Al-Cr ternary phase diagrams have been proposed accordingly.

According to the findings of ternary phase diagrams, γ-TiAl intermetallic compounds with additions of third alloying elements were produced and studied for basic properties (mechanical properties at room and elevated temperatures). It was found as a result that the mechanical properties of γ-TiAl intermetallic compounds heavily depend on phases and microstructures. The relationship of mechanical properties to phases and microstructures has been studied, factors governing the room-temperature ductility of γ-TiAl and those affecting the high-temperature strength of γ-TiAl have been identified, and guidelines have been set for improving the mechanical properties of γ-TiAl.

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