

## Mechanical Properties of the Ternary L<sub>12</sub> Compound Co<sub>3</sub>(Al,W) in Single and Polycrystalline Forms

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**Abstract.** The mechanical properties of Co<sub>3</sub>(Al,W) with the L<sub>12</sub> structure have been investigated both in single and polycrystalline forms. The values of all the three independent single-crystal elastic constants and polycrystalline elastic constants of Co<sub>3</sub>(Al,W) experimentally determined by resonance ultrasound spectroscopy at liquid helium temperature are 15~25% larger than those of Ni<sub>3</sub>(Al,Ta) but are considerably smaller than those previously calculated. When judged from the values of Poisson's ratio, Cauchy pressure and ratio of shear modulus to bulk modulus ( $G_h/B_h$ ), the ductility of Co<sub>3</sub>(Al,W) is expected to be sufficiently high. In the yield stress-temperature curve, a rapid decrease and an anomalous increase in yield stress is observed in the low and intermediate (1000-1100 K) temperature ranges, respectively. The former is concluded to be due to the solid-solution hardening effect while the latter is attributed to thermally activated cross-slip of APB-coupled  $a/2\langle 110 \rangle$  superpartial dislocations from octahedral to cube slip planes.

### Introduction

Many intermetallic compounds such as TiAl have been investigated in the last two decades, because of ever-increasing demands for structural materials that can withstand severe oxidizing environments and high operating temperatures [1]. Currently, the most widely used high-temperature structural materials in aircraft engines and power generation systems are Ni-based superalloys containing the L<sub>12</sub>-ordered intermetallic phase. The two-phase microstructure consisting of the solid-solution based on Ni with a face-centered cubic (fcc) structure and the stable L<sub>12</sub>-ordered intermetallic compound based on Ni<sub>3</sub>Al is believed to lead to the excellent high-temperature mechanical properties of these Ni-based superalloys [2-4]. Although Co-based alloys are known to exhibit hot corrosion, oxidation and wear resistance better than Ni-base superalloys, there has been almost no research activity on the development of 'Co-based superalloys' [5,6]. This stems from the fact that there is no stable binary L<sub>12</sub> phase coexisting with the solid-solution based on Co with a fcc structure. However, the recent discovery of the stable L<sub>12</sub>-ordered intermetallic compound, Co<sub>3</sub>(Al,W) coexisting with the solid-solution based on fcc-Co [7] has opened up a pathway to the development of Co-base superalloys, although very recently a significant doubt is thrown on the thermal stability of the ternary L<sub>12</sub> compound [8]. Indeed, two-phase microstructures that resemble those in Ni-base superalloys have been proved to form in Co-Al-W based alloys through higher-order alloying additions [7,9]. However, almost nothing is known about the mechanical properties of the constituent L<sub>12</sub> phase, Co<sub>3</sub>(Al,W) [10-12]. The L<sub>12</sub>-ordered intermetallic compound, Co<sub>3</sub>(Al,W) is expected to exhibit physical properties similar to those exhibited by Ni<sub>3</sub>Al-based compounds that are the constituent phase of Ni-base superalloys. However, the result of the recent first principles calculation of the elastic constants by Yao *et al.* [13] indicates that unlike Ni<sub>3</sub>Al, the L<sub>12</sub>-ordered intermetallic compound, Co<sub>3</sub>(Al,W) is extremely brittle. If this is indeed the case, Co-base superalloys containing the 'brittle' L<sub>12</sub> compound, Co<sub>3</sub>(Al,W) may exhibit low toughness especially at low

temperatures and their practical use will be significantly limited by the brittleness. In the present study, we experimentally investigate the elastic constants of single crystals of  $\text{Co}_3(\text{Al,W})$  with the  $\text{L1}_2$  structure and the compression deformation behavior of polycrystals of the  $\text{L1}_2$  single phase, in order to provide some fundamental mechanical data of the ternary  $\text{L1}_2$  compound, which may be needed for alloy and system design of ‘Co-based superalloys’.

### Experimental procedures

Single crystals of the Co-Al-W ternary system with the  $\text{L1}_2$  single-phase microstructure were grown by the optical floating-zone method from rods with a nominal composition of Co-10 at.%Al-11 at.%W. Specimens with a rectangular parallelepiped shape having three orthogonal faces parallel to  $\{001\}$  were cut from the single crystals by spark-machining for measurements of elastic constants. The measurements were carried out by ultrasound resonance spectroscopy (RUS) at liquid helium temperature [14,15]. Polycrystals of the Co-Al-W ternary system with almost the  $\text{L1}_2$  single-phase microstructure were prepared by Ar arc-melting the constituent elements in a proper ratio of Co-12 at.%Al-11 at.%W. Specimens with a rectangular parallelepiped shape having dimensions of  $1.7 \times 1.7 \times 5 \text{ mm}^3$  were cut from polycrystals by spark-machining for compression tests. Compression tests were made with an Instron-type testing machine at a strain rate of  $1 \times 10^{-4} \text{ s}^{-1}$  in the temperature range from liquid nitrogen temperature to 1273 K.

### Results and discussion

**Single-crystal elastic constants.** Values of single-crystal elastic constants experimentally determined at liquid helium temperature for  $\text{Co}_3(\text{Al,W})$  and  $\text{Ni}_3(\text{Al,Ta})$  are tabulated in Table 1 together with those previously calculated for  $\text{Co}_3(\text{Al,W})$  by Yao *et al.* [13]. The values of all three independent elastic constants of  $\text{Co}_3(\text{Al,W})$  experimentally determined are 15~25% larger than those also experimentally determined for  $\text{Ni}_3(\text{Al,Ta})$  but are considerably smaller than those calculated by Yao *et al.* for the same  $\text{L1}_2$  compound,  $\text{Co}_3(\text{Al,W})$  [13]. Although Yao *et al.* [13] never specified the chemical composition of the  $\text{L1}_2$ -ordered compound  $\text{Co}_3(\text{Al,W})$  they used in their calculation, the melting point for their  $\text{L1}_2$ -ordered compound is considered to be significantly higher than that for the present  $\text{Co}_3(\text{Al,W})$  single crystal with the chemical composition of Co-10 at.%Al-11 at.%W. It should be noted, however, that the solid-solubility range for the ternary  $\text{L1}_2$ -ordered compound  $\text{Co}_3(\text{Al,W})$  is reported to be quite small [7], in accordance with the fact that we could get single crystals only in a very small composition range as reported in [7].

Tabulated in Table 2 are polycrystalline elastic constants evaluated from the single-crystal elastic constants in Table 1 by the Hill’s method. The values of bulk ( $B_h$ ), shear ( $G_h$ ) and Young ( $E_h$ ) moduli experimentally determined for  $\text{Co}_3(\text{Al,W})$  are 15~25% larger than those experimentally determined for  $\text{Ni}_3(\text{Al,Ta})$  but are considerably smaller than those of  $\text{Co}_3(\text{Al,W})$  calculated by Yao *et al.* [13], as in the case of the single-crystal elastic constants. The value of Poisson’s ratio experimentally determined for  $\text{Co}_3(\text{Al,W})$  is smaller than that experimentally determined for  $\text{Ni}_3(\text{Al,Ta})$ , indicative of more significant directionality of atomic bonding in  $\text{Co}_3(\text{Al,W})$  than in  $\text{Ni}_3(\text{Al,Ta})$ . This implies that  $\text{Co}_3(\text{Al,W})$  is more brittle than  $\text{Ni}_3(\text{Al,Ta})$ . The value of Poisson’s ratio calculated for  $\text{Co}_3(\text{Al,W})$  is considerably smaller than that experimentally determined for  $\text{Co}_3(\text{Al,W})$ . When judged from the values of Poisson’s ratio, however, the  $\text{L1}_2$ -ordered compound,  $\text{Co}_3(\text{Al,W})$  is not as brittle as Yao *et al.* [13] expected from their calculation.

Table 1: Single-crystal elastic constants experimentally determined in the present study [12].

	Temperature (K)	$c_{11}$ (GPa)	$c_{12}$ (GPa)	$c_{44}$ (GPa)
$\text{Co}_3(\text{Al,W})$ experiment	5	271	172	162
$\text{Co}_3(\text{Al,W})$ calculation [13]	0	363	190	212
$\text{Ni}_3(\text{Al,Ta})$ experiment	5	238	154	130

Table 2: Polycrystalline elastic constants calculated by the Hill's method [12].

	Temperature (K)	$B_h$ (GPa)	$G_h$ (GPa)	$E_h$ (GPa)	$\nu$
Co <sub>3</sub> (Al,W) experiment	5	205	101	260	0.289
Co <sub>3</sub> (Al,W) calculation [13]	0	248	148	370	0.251
Ni <sub>3</sub> (Al,Ta) experiment	5	182	82.8	216	0.303

Table 3: Elastic anisotropy parameters [12].

	Temperature (K)	$A$	$E_{111}/E_{100}$	$c_{12}-c_{44}$ (GPa)	$G_h/B_h$
Co <sub>3</sub> (Al,W) experiment	5	3.26	385/137=2.80	10	0.493
Co <sub>3</sub> (Al,W) calculation [13]	0	2.45	495/232=2.13	-22	0.585
Ni <sub>3</sub> (Al,Ta) experiment	5	3.09	315/117=2.69	24	0.455

Anisotropic parameters evaluated from the single-crystal elastic constants in Table 1 are tabulated in Table 3. The value of Cauchy pressure (defined as  $c_{12}-c_{44}$  for crystals with the cubic symmetry) experimentally determined for Co<sub>3</sub>(Al,W) is smaller than that experimentally determined for Ni<sub>3</sub>(Al,Ta). This is again indicative of a stronger directional atomic bonding in Co<sub>3</sub>(Al,W) [16]. Of importance to note, however, is that the directionality of atomic bonding in Co<sub>3</sub>(Al,W) is not as strong as that described with the large 'negative' Cauchy pressure, as calculated by Yao *et al.* [13]. Indeed, Co<sub>3</sub>(Al,W) should be regarded as a ductile material, since the value of  $G_h/B_h$  for Co<sub>3</sub>(Al,W) is far less than 0.57, above which the material of concern is regarded as a 'brittle' material according to the Pugh's criterion [17]. The smaller  $G_h/B_h$  value of Ni<sub>3</sub>(Al,Ta) implies, of course, that Ni<sub>3</sub>(Al,Ta) is more ductile than Co<sub>3</sub>(Al,W). However, when judged from the values of Poisson's ratio, Cauchy pressure and  $G_h/B_h$ , the ductility of Co<sub>3</sub>(Al,W) is expected to be sufficiently high so that Co<sub>3</sub>(Al,W) can be practically used as the constituent phase of 'Co-base superalloys'.

The value of anisotropic factor ( $A = 2c_{44}/(c_{11}-c_{12})$ ) experimentally determined for Co<sub>3</sub>(Al,W) is larger than that experimentally determined for Ni<sub>3</sub>(Al,Ta) but is considerably larger than that calculated for Co<sub>3</sub>(Al,W). The value of  $E_{111}/E_{100}$  experimentally determined for Co<sub>3</sub>(Al,W) is larger than that experimentally determined for Ni<sub>3</sub>(Al,Ta). The large  $E_{111}/E_{100}$  value of Co<sub>3</sub>(Al,W) is beneficial to the formation of cuboidal L1<sub>2</sub> precipitates faceted parallel to {100} in the fcc ( $\gamma$ )/L1<sub>2</sub> ( $\gamma'$ ) two-phase microstructure. In addition, the driving force to form cuboidal precipitates aligned parallel to  $\langle 100 \rangle$  is proportional to the magnitude of  $c_{ij}$ . Since Co<sub>3</sub>(Al,W) has the large values of  $E_{111}/E_{100}$  and  $c_{ij}$ , two-phase microstructures with cuboidal L1<sub>2</sub> precipitates well aligned parallel to  $\langle 100 \rangle$  and well faceted parallel to {100} are expected to form more easily in Co-base superalloys containing Co<sub>3</sub>(Al,W) than in conventional Ni-base superalloys.

**Compression deformation behavior of polycrystals.** A typical SEM (scanning electron microscope) image of polycrystals used for compression tests is shown in Fig. 1. Although a small volume fraction of CoAl and Co<sub>3</sub>W phases are observed, the microstructure is almost of the L1<sub>2</sub> single-phase, and TEM observations confirm that no thermal APBs are included in the specimens. Values of yield stress obtained for polycrystals in compression are plotted in Fig. 2 as a function of temperature. The yield stress rapidly decreases with the increase in temperature in the low temperature range, followed by a gradual decrease up to 1000 K. Then, it increases anomalously in a narrow temperature range from 1000 to 1100 K, followed by a rapid decrease at high temperatures. Slip trace analyses indicate that the macroscopic slip plane is {111} over the entire temperature range investigated, as shown in Fig. 3.

Our preliminary TEM observations have confirmed that dislocations are dissociated into two collinear partials separated by an APB at least up to the peak temperature. The dislocation structure in the anomalous temperature range consists of screw dislocations locked in the Kear-Wilsdorf

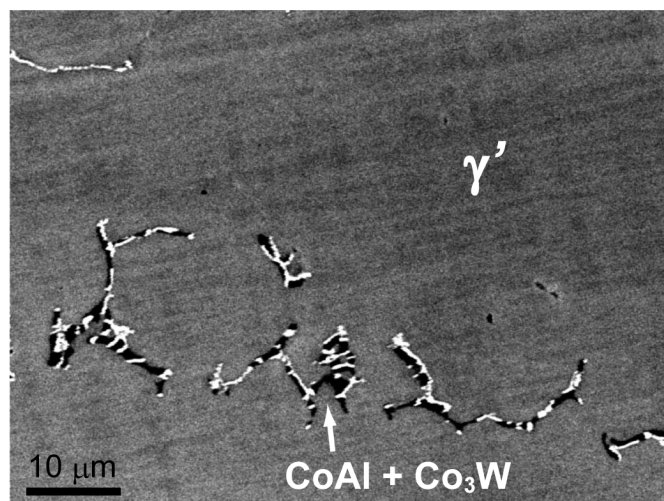


Fig. 1: A typical SEM image of polycrystals used for compression tests.

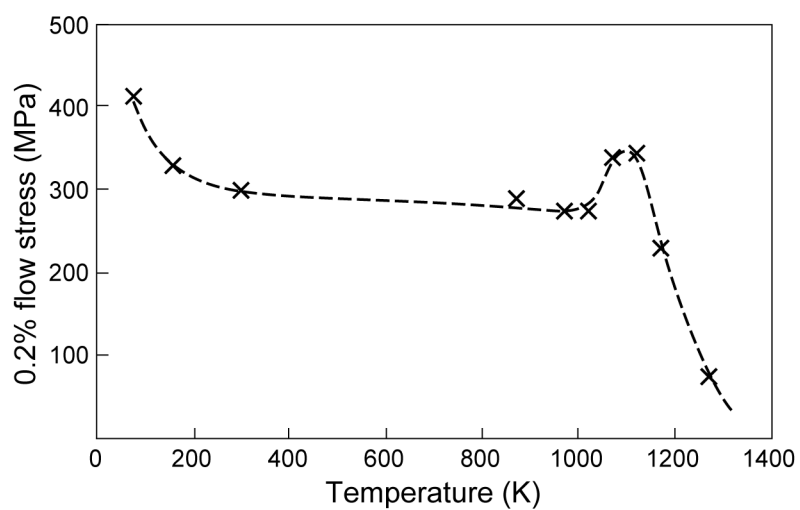


Fig. 2: Temperature dependence of yield stress obtained for polycrystals in compression.

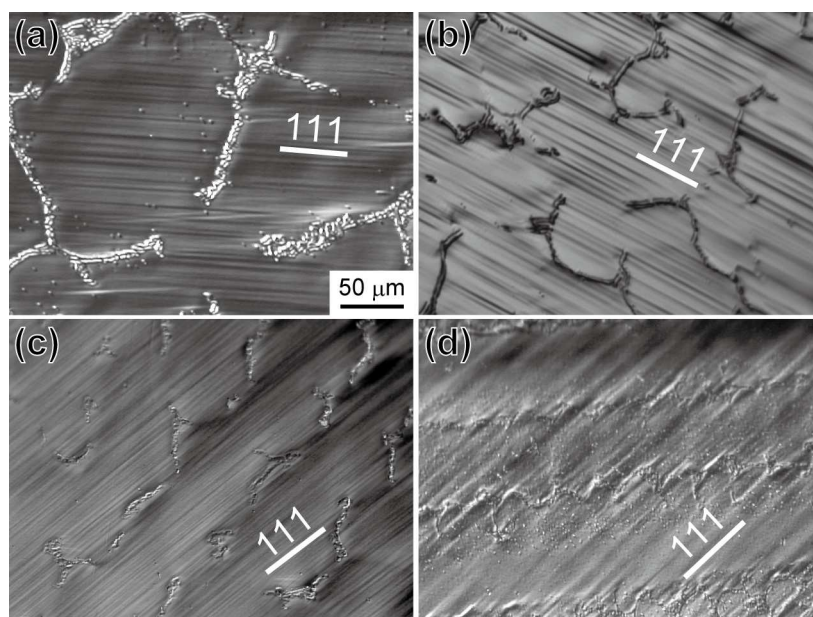


Fig. 3: Slip lines observed for polycrystals deformed at (a) 77 K, (b) 300 K, (c) 1073 K and (d) 1273 K.

configuration, which are connected by superkinks. The anomaly in yield stress is thus attributed to thermally activated cross-slip of APB-coupled  $a/2\langle 110 \rangle$  superpartial dislocations from octahedral to cube slip planes, as observed in many other  $L_{12}$  compounds such as  $Ni_3Al$ . Dislocations introduced by deformation at 77 K are observed to be smoothly curved without any preferred orientation, indicating that the Peierls stress may not be so large. Thus, the rapid decrease in yield stress at low temperatures may not be due to the Peierls-type effect resulting from the sessile core configuration but is concluded to be due to the solid-solution hardening effect. The core of  $a/2\langle 110 \rangle$  superpartial dislocations should thus be glissile at all temperatures.

## Summary

- (1) The values of all three independent single-crystal elastic constants and polycrystalline elastic constants of  $L_{12}\text{-Co}_3(\text{Al,W})$  experimentally determined are considerably smaller than those previously calculated by Yao *et al.* [13]. Unlike the calculation result of Yao *et al.* [13],  $\text{Co}_3(\text{Al,W})$  exhibits a positive value of Cauchy pressure and a  $G_h/B_h$  value less than 0.57. When judged from the values of Poisson's ratio, Cauchy pressure and  $G_h/B_h$ , the ductility of  $\text{Co}_3(\text{Al,W})$  is expected to be sufficiently high so as to be used as the constituent phase of 'Co-base superalloys'.
- (2) Because of the large values of  $E_{111}/E_{100}$  and  $c_{ij}$  of  $\text{Co}_3(\text{Al,W})$ , two-phase microstructures with cuboidal  $L_{12}$  precipitates being well aligned parallel to  $\langle 100 \rangle$  and well faceted parallel to  $\{100\}$  are expected to form very easily in Co-base superalloys. This is indeed confirmed by experiment [7].
- (3) The yield stress rapidly decreases with the increase in temperature in the low temperature range, followed by a gradual decrease up to 1000 K. Then, it increases anomalously in a narrow temperature range from 1000 to 1100 K, followed by a rapid decrease at high temperatures. The rapid decrease in yield stress observed at low temperatures is concluded to be due to the solid-solution hardening effect while the anomalous increase in yield stress observed in the narrow temperature range from 1000 to 1100 K is attributed to thermally activated cross-slip of APB-coupled  $a/2\langle 110 \rangle$  superpartial dislocations from octahedral to cube slip planes, as observed in many other  $L_{12}$  compounds.

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