Micropillar Compression Deformation of Single Crystals of $\text{Co}_3(\text{Al,W})$ with the L1_2 Structure

Zhenghao M.T. Chen^{1,*}, Norihiko L. Okamoto^{1,2}, Masahiko Demura³, Haruyuki Inui^{1,2}

¹*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*

²*Center for Elements Strategy Initiative for Structure Materials (ESISM), Kyoto University, Kyoto 606-8501, Japan*

³*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

*Corresponding Author Contact Information:

Zhenghao M.T. CHEN

Department of Materials Science and Engineering, Kyoto University

Sakyo-ku, Kyoto 606-8501, Japan

Tel: +81-75-753-5473

Fax: +81-75-753-5461

E-mail: chen.zhenghao.45e@st.kyoto-u.ac.jp

Abstract

The compression deformation behavior of single-crystal micropillars of $\text{L1}_2\text{-Co}_3(\text{Al,W})$ has been investigated at room temperature as a function of pillar size and crystal orientation. The critical resolved shear stress (CRSS) obeys an inverse power-law scaling against pillar size and is independent of orientation. With the bulk CRSS value of $\text{Co}_3(\text{Al,W})$ at room temperature estimated by extrapolating the size dependence of CRSS for micropillars, comparison of high-temperature strength is made on the CRSS values for $\text{Co}_3(\text{Al,W})$ and Ni_3Al -based compounds. $\text{Co}_3(\text{Al,W})$ has turned out not to be strong enough to provide excellent high-temperature strength for Co-based superalloys, at least for ternary composition.

Keywords: intermetallic compounds; size dependence; focused-ion beam (FIB); critical resolved shear stress (CRSS); yield stress anomaly (YSA)

The discovery of the γ' -Co₃(Al,W) phase with the L1₂ structure in the Co-Al-W ternary alloy system by Sato et al. [1] has launched a new era of the development of high-temperature structural materials. The γ' -Co₃(Al,W) phase coherently precipitates in the γ -Co (face-centered cubic (fcc) structure) solid-solution phase, resulting in a $\gamma + \gamma'$ two-phase microstructure with a regular array of cuboidal γ' precipitates, which resembles the typical microstructure of Ni-based superalloys strengthened by the γ' -Ni₃Al phase [1]. Indeed, these $\gamma + \gamma'$ two-phase alloys called Co-based 'superalloys' have demonstrated superior high-temperature strength when compared to conventional Co-based alloys strengthened by solid-solution hardening and carbide precipitation without cuboidal γ' precipitates [1-3]. We have recently investigated the deformation behavior of polycrystals of Co₃(Al,W), the constituent phase of Co-based alloys, revealing that while the yield stress rapidly decreases with the increase in temperature at low temperatures, it increases anomalously with temperature only in a narrow temperature range at high temperatures (950-1100 K) [4, 5]. TEM analysis has indicated that the yield stress anomaly is due to cross slip of superpartial dislocations with $\mathbf{b}$ (Burgers vector) = $1/2[\bar{1}01]$ from (111) to (010) planes [6, 7] as in many other L1₂ intermetallic compounds based on Ni₃Al, although these Ni₃Al-based L1₂ intermetallic compounds are known to exhibit the yield stress anomaly in a much wider temperature range so as to start from a lower temperature such as liquid nitrogen temperature, especially in ternary alloys [8-10]. Since the occurrence of yield stress anomaly in the constituent γ' phase is important for the strength of $\gamma + \gamma'$ two-phase alloys at high temperatures, comparison of the strength of Co₃(Al,W) with those with Ni₃Al-based L1₂ compounds should be made to see how significantly Co₃(Al,W) contributes to the strength of Co-based superalloys especially at high temperatures. However, the critical resolved shear stress (CRSS) has not been available for Co₃(Al,W) due to the difficulties in preparing single crystals of the γ' -Co₃(Al,W) single-phase large enough for the study of plastic deformation [11].

In recent years, however, a method based on compression testing of small pillars of single crystals of the order of micrometer size, which can be prepared from relatively small crystal grains in polycrystals by focused ion beam (FIB) machining, has been developed and opened a way to measure CRSS values of alloys even if large single crystals are unavailable [12-16]. It has been known that the CRSS values of single-crystal micropillars in fcc and body-centered cubic (bcc) metals decrease with the increase in pillar size, obeying an inverse power-law scaling [17-20]. The decrease in CRSS is considered to continue until the pillar size reaches a critical value, where the CRSS value corresponds to that measured in a bulk form [17-20]. Then, the CRSS value in the bulk form can be estimated by extrapolating the inverse power-law scaling of the CRSS values obtained in the micropillar form to the critical micropillar size. For many different metals with the fcc structure, on which the L1₂ structure is based, the critical size has been reported to be in the range of 20-30 μm [12,17,18], while

Uchic et al. reported that the critical size for $L1_2$ - $Ni_3(Al,Ta)$ is 42 μm at room temperature [12]. However, this critical size value obtained for $L1_2$ - $Ni_3(Al,Ta)$ may not be used directly for $L1_2$ - $Co_3(Al,W)$, in view of the fact that the onset temperatures for yield stress anomaly are quite different for these two $L1_2$ compounds (77 K and 950 K respectively for $Ni_3(Al,Ta)$ [21] and $Co_3(Al,W)$ [4]). Cross slip of superpartial dislocations from (111) to (010) planes frequently occurs so as to give rise to yield stress anomaly even at room temperature for $Ni_3(Al,Ta)$, while such cross slip is unlikely to occur at room temperature for $Co_3(Al,W)$. This indicates the necessity to investigate the size dependence of CRSS of micropillars of an $L1_2$ -compound, in which yield stress anomaly is absent at room temperature and the bulk CRSS value of which can be obtained in large-sized single crystals, in order to deduce a critical pillar size suitable for the evaluation of the bulk CRSS value of $Co_3(Al,W)$. Binary stoichiometric Ni_3Al can be used for this purpose, since large single crystals are available and the yield stress anomaly starts just above room temperature [8].

In the present study, we investigate the plastic deformation behavior of single-crystal micropillars of $Co_3(Al,W)$ by compression tests as a function of specimen size and crystal orientation at room temperature, in order to estimate the bulk CRSS value from the size dependence of CRSS for single-crystal micropillars and to compare the deduced bulk CRSS value with those of other Ni_3Al -based $L1_2$ compounds.

Polycrystalline ingots with a nominal composition of Co-12at.% Al-11at.% W and Ni-25at.% Al were prepared by arc-melting under an Ar gas flow. Polycrystals of $Co_3(Al,W)$ were annealed at 1,123 K for 168 h followed by furnace cooling. Single crystals of the stoichiometric Ni_3Al were grown with an optical floating-zone furnace [22]. Single-crystal micropillars of $Co_3(Al,W)$ and Ni_3Al with a square cross-section having an edge length (1-10 μm) and an aspect ratio of 2-3 (Fig. 1a) were fabricated by the FIB technique. Single-crystal micropillars of $Co_3(Al,W)$ were machined from crystal grains whose orientation was determined by electron back-scatter diffraction (EBSD), while those of Ni_3Al were machined from bulk single crystals whose orientation was determined by the X-ray back reflection Laue method. Bulk specimens of Ni_3Al for compression tests with approximate dimensions of $2 \times 2 \times 5 \text{ mm}^3$ were cut from the single crystals by electro-discharge machining. The compression-axis orientations investigated were $[\bar{2}56]$ and $[\bar{1}36]$ for $Co_3(Al,W)$, and $[\bar{1}23]$ for Ni_3Al , as shown in Fig. 1b. Compression tests for single-crystal micropillars of $Co_3(Al,W)$ and Ni_3Al and for bulk single crystals of Ni_3Al were conducted at a strain rate of 10^{-3} s^{-1} at room temperature. Micropillar compression tests were conducted with a flat punch indenter tip on a Shimadzu MCT-211 micro compression tester. Deformation microstructures were observed by scanning electron microscopy (SEM).

Fig. 2a shows selected stress-strain curves for bulk single crystals and micropillars of Ni_3Al . The flow stress of the micropillars increases with decreasing pillar size and is considerably higher than that of bulk single crystals. Strain bursts, which are most likely

associated with an avalanche-like collective motion of dislocations [23], occur in the stress-strain curves for all micropillars investigated. The yield stress for micropillars is thus determined as the stress at which the first strain burst occurs. Slip trace analysis has confirmed that slip on $(111)[\bar{1}01]$, the most highly stressed system, is operative for both bulk single crystals and micropillars of Ni_3Al . Values of CRSS for slip on $(111)[\bar{1}01]$ calculated with the yield stress values and the corresponding Schmid factor (0.46) are plotted in Fig. 2b as a function of pillar size in a double logarithmic scale. As reported for single crystals of many fcc and bcc metals, an inverse power-law scaling of CRSS against the pillar size is valid also for slip on $(111)[\bar{1}01]$ in binary stoichiometric Ni_3Al with a power-law exponent of -0.752. The CRSS value of bulk single crystals of Ni_3Al determined as the 0.2% flow stress is 22.5 MPa, when averaged over those obtained from three tests. The determined CRSS value is very close to those previously reported (22~25 MPa [6, 23]). The critical pillar size determined as the cross point of the extrapolation of the inverse power-law scaling of the CRSS values with the CRSS value of bulk single crystals for binary stoichiometric Ni_3Al is in the range of 40-50 μm , which is comparable to that determined by Uchic et al. [13] for $\text{Ni}_3(\text{Al},\text{Ta})$ (42 μm). This may suggest that the critical pillar size for L_{12} compounds does not depend on the operating deformation mechanism and is in the range of 40-50 μm . The critical pillar size for L_{12} compounds is almost twice that for fcc metals (20-30 μm) [18]. This may be related to the fact that the magnitude of Burgers vector for the perfect dislocation in the L_{12} structure is twice that in the fcc structure, since the critical pillar size in fcc metals has often been discussed in terms of the length of double-ended Frank-Read sources at bulk yielding expressed in the unit of the magnitude of Burgers vector for the perfect dislocation.

Figs. 3a and 3c show selected stress-strain curves for single-crystal micropillars of $\text{Co}_3(\text{Al},\text{W})$ with the compression orientations $[\bar{2}56]$ and $[\bar{1}36]$, respectively. As in binary stoichiometric Ni_3Al , strain bursts are observed to occur in micropillars of $\text{Co}_3(\text{Al},\text{W})$ although the extent of strain bursts becomes less significant as the pillar size increases. We thus took the 0.2% flow stress as the yield stress for larger micropillars that do not exhibit strain bursts, while the yield stress for smaller micropillars is determined as the stress at which the first strain burst occurs. The yield stress thus determined increases with decreasing pillar size for both orientations. Figs. 3b and 3d show SEM secondary electron images of deformed micropillars with $[\bar{2}56]$ and $[\bar{1}36]$ orientations, respectively. Slip trace analysis has confirmed that slip on $(111)[\bar{1}01]$, the most highly stressed system, is operative for both orientations, being consistent with our previous observation on bulk polycrystals of $\text{Co}_3(\text{Al},\text{W})$ [4]. Values of CRSS for slip on $(111)[\bar{1}01]$ calculated for $[\bar{2}56]$ and $[\bar{1}36]$ orientations with the yield stress values and the corresponding Schmid factors are plotted in Fig. 3e as a function of pillar size in a double logarithmic scale. The CRSS values of $\text{Co}_3(\text{Al},\text{W})$ measured in the two orientations are virtually identical with each other, exhibiting a similar size dependence of CRSS with the power-law exponent of -0.697. The bulk CRSS

value of $\text{Co}_3(\text{Al,W})$ at room temperature estimated by extrapolating the inverse power-law scaling to the critical pillar size of 40-50 μm is 33-38 MPa, which is about one-sixth the yield stress obtained for bulk polycrystals of $\text{Co}_3(\text{Al,W})$ at room temperature (~ 240 MPa) [4]. The absence of the orientation dependence of CRSS is a clear indication that the yield stress anomaly has yet to start at room temperature for $\text{Co}_3(\text{Al,W})$, being consistent with our previous result on the temperature dependence of yield stress for bulk polycrystals of $\text{Co}_3(\text{Al,W})$ [4]. This has indeed been confirmed with bulk single crystals of binary stoichiometric Ni_3Al [8].

The bulk CRSS value (33-38 MPa) of $\text{Co}_3(\text{Al,W})$ is slightly higher than that of binary stoichiometric Ni_3Al at room temperature (22.5-25 MPa) [6], even though $\text{Co}_3(\text{Al,W})$ at the present composition (Co-12at.% Al-11at.% W) contains W in a large amount (11 at.%) to substitute Al atoms so as to contribute to solid-solution hardening. This is in contrast to what is observed for solid-solution hardening in Ni_3Al -based L_{12} compounds, in which the addition of 4 at.% Ta to Ni_3Al , for example, causes the CRSS value at room temperature as high as about 170 MPa [9]. The strengthening in $\text{Ni}_3(\text{Al,Ta})$ at room temperature is also partly due to anomalous strengthening arising from cross slip of superpartial dislocations from (111) to (010) planes because of the low onset temperature for yield stress anomaly, as seen in Fig. 4. Fig. 4 shows strength variations with temperature for $\text{Co}_3(\text{Al,W})$, binary stoichiometric Ni_3Al and $\text{Ni}_3(\text{Al,Ta})$. The strength for Ni_3Al and $\text{Ni}_3(\text{Al,Ta})$ corresponds to the CRSS values obtained for bulk single crystals, while the bulk CRSS values for $\text{Co}_3(\text{Al,W})$ are calculated by multiplying the yield stress values obtained for polycrystals [4] by the yield stress-CRSS conversion ratio (approximately one-sixth) deduced at room temperature, regardless of temperature. The CRSS values of $\text{Co}_3(\text{Al,W})$ and binary stoichiometric Ni_3Al are reversed at ~ 400 K because of the occurrence of yield stress anomaly for Ni_3Al above room temperature. The peak CRSS value of Ni_3Al at $\sim 1,000$ K is as high as 320 MPa [6, 23], which is more than 10 times that at room temperature. The peak CRSS value of $\text{Ni}_3(\text{Al,Ta})$ is also as high as 425 MPa at ~ 700 K [9]. In contrast, the CRSS value of $\text{Co}_3(\text{Al,W})$ is almost unchanged up to ~ 950 K because the onset temperature of yield stress anomaly is high, and the increase in CRSS due to yield stress anomaly is only marginal because of the narrow temperature range for yield stress anomaly (950-1,100 K). As a result, the strength of $\text{Co}_3(\text{Al,W})$ is considerably lower than that of Ni_3Al -based L_{12} compounds at high temperatures. In fact, when Co-based superalloys strengthened by L_{12} - $\text{Co}_3(\text{Al,W})$ precipitates are crept under a high temperature/low stress condition, the strengthening phase $\text{Co}_3(\text{Al,W})$ is observed to be sheared by dislocations [24, 25], while dislocation shearing of Ni_3Al precipitates does not occur in Ni-based superalloys crept under a similar condition [26]. Dislocation shearing of Ni_3Al precipitates in Ni-based superalloys occurs only under a medium temperature/medium (high) stress condition [26]. Hence, it is clear that the γ' - $\text{Co}_3(\text{Al,W})$ is not strong enough to provide excellent high temperature strength for Co-base superalloys, at least for the ternary

compositions. Thus, drastic improvement in the high-temperature strength of $\text{Co}_3(\text{Al,W})$ is immediately needed.

The high onset temperature for yield stress anomaly (~ 950 K) should be considerably lowered and the peak temperature for yield stress anomaly ($1,100$ K) should be increased, widening the anomalous temperature range so as to increase the high-temperature strength of $\text{Co}_3(\text{Al,W})$. Our transmission electron microscopy analyses have indicated that the considerably high onset temperature of the yield stress anomaly in $\text{Co}_3(\text{Al,W})$ is attributed to the low energy (137 mJ/m^2) of the complex stacking fault (CSF), which is formed by the sub-dissociation of the superpartial dislocation with $\mathbf{b} = 1/2\langle\bar{1}01\rangle$ into Shockley partials with $\mathbf{b} = 1/6\langle 112\rangle$ [4]. On the other hand, the peak temperature for yield stress anomaly in $\text{Co}_3(\text{Al,W})$ corresponds to the solvus temperature of the γ' phase [4]. Thus, additions of quaternary elements, such as Ni and Ta, which are expected to increase the CSF energy of $\text{Co}_3(\text{Al,W})$ as well as the γ' solvus temperature are believed to be effective to increase the high temperature strength [27]. Effects of the addition of these quaternary elements on the high-temperature strength of $\text{Co}_3(\text{Al,W})$ are currently under investigation and will be reported separately.

In summary, the CRSS value of $\text{L1}_2\text{-Co}_3(\text{Al,W})$ measured in compression at room temperature by the use of single-crystal micropillars obeys an inverse power-law scaling against the micropillar size, and is independent of crystal orientation. The bulk CRSS value of $\text{Co}_3(\text{Al,W})$ at room temperature estimated by extrapolating the inverse power-law scaling to the critical pillar size of $40\text{-}50 \text{ }\mu\text{m}$ is $33\text{-}38 \text{ MPa}$, which is only a little higher than that of binary stoichiometric Ni_3Al . Once the yield stress-temperature curve obtained for polycrystals is converted to the bulk CRSS-temperature curve with the use of the yield stress-CRSS conversion ratio ($\sim$ one-sixth) deduced at room temperature, it is evident that $\text{Co}_3(\text{Al,W})$ is not strong enough at high temperatures to provide excellent high-temperature strength for Co-based superalloys.

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Figure legends

Figure 1. (Color on the Web and grayscale in print) (a) SEM secondary electron image of a single-crystal micropillar of $\text{Co}_3(\text{Al,W})$ before compression. (b) Loading axis orientations of the single crystals of $\text{Co}_3(\text{Al,W})$ and Ni_3Al .

Figure 2. (Color on the Web and grayscale in print) (a) Selected stress-strain curves of Ni_3Al obtained for micropillar specimens as well as for a bulk specimen. The loading axis orientation is $[\bar{1}23]$. (b) Micropillar size dependence of the CRSS values for $\{111\}\langle\bar{1}01\rangle$ slip in Ni_3Al .

Figure 3. (Color on the Web and grayscale in print) Selected stress-strain curves obtained for micropillars specimens of $\text{Co}_3(\text{Al,W})$ with loading axis orientations of (a) $[\bar{2}56]$, and (c) $[\bar{1}36]$, respectively. SEM secondary electron images of deformed micropillars with the orientations of (b) $[\bar{2}56]$, and (d) $[\bar{1}36]$, respectively, showing a $\{111\}$ slip trace. (e) Micropillar size dependence of the CRSS values for $\{111\}\langle\bar{1}01\rangle$ slip in $\text{Co}_3(\text{Al,W})$.

Figure 4. (Color on the Web and grayscale in print) Temperature dependence of the yield stress of $\text{Co}_3(\text{Al,W})$ polycrystals [4], CRSS of the stoichiometric Ni_3Al [6, 23], CRSS of the ternary $\text{Ni}_3(\text{Al,Ta})$ [9], and CRSS of $\text{Co}_3(\text{Al,W})$ deduced with the bulk CRSS value estimated by micropillar compression tests at room temperature.

Figure 1

Figure 2

Figure 3

Figure 4