

Mechanical Properties of Co-Based L₁₂ Intermetallic Compound Co₃(Al,W)

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Mechanical properties of L₁₂-Co₃(Al,W) polycrystalline sample are investigated by compression testing at various temperature ranging from room temperature to 1193 K. It was found that at room temperature the 0.2% flow stress is 410 MPa and the compressive ductility is higher than 10%, whereas at 1193 K the 0.2% flow stress is 382 MPa and the compressive ductility is about 10%. Two candidates for the reaction scheme of the Co-rich region of the Co-Al-W ternary phase diagram are proposed by combining the results of microstructure observation, X-ray diffractometry and the previous report. [doi:10.2320/matertrans.MAW200734]

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1. Introduction

Mechanical properties of L₁₂-type intermetallic compound such as Ni₃Al, Ni₃Si and Co₃Ti, have attracted broad attention for more than 50 years since stress anomaly, i.e., the positive temperature dependence of the strength, of Ni₃Si was reported by Lowrie in 1952.¹⁾ Among various L₁₂ compounds, Ni₃Al has been intensively investigated because the compound is the most important strengthening phase for the Ni-based superalloys.^{2,3)} Co-based L₁₂ compounds such as Co₃Ti and (Co,Fe)₃V have also been studied⁴⁻⁶⁾ but these have not been utilized as constituent phases for commercial Co-based heat-resisting alloys because of their low phase stability, i.e., low melting point, significant decrease of the volume fraction with temperature, or low order-disorder transition temperature. However, these Co-based L₁₂ compounds composed of transition metal elements have relatively good ductility even without microalloying of B, which is required to ductilize Ni₃Al and Ni₃(Si,Ti).⁷⁻⁹⁾ Also Rh-based L₁₂ compounds containing transition metal elements, such as Rh₃Ti, Rh₃Nb and Rh₃Ta, were reported to possess good ductility at wide temperature range by the present authors.¹⁰⁾ The low room temperature ductility of intermetallic compound containing active elements such as Al or Si is attributed to the atomic hydrogen formation at the surface by decomposing water vapor.¹¹⁾ However, the brittleness is very difficult to evaluate in general whether it is because of the intrinsic nature or it is affected by extrinsic factors. For example, these "brittle" L₁₂ polycrystal alloys are ductile in the form of single crystal. Moreover, the compressive ductility of these alloys is better than tensile ductility. On the other hand, some of intermetallic alloys show catastrophic crack propagation during compression testing even in the elastic deformation region.

Recently, a new Co-based L₁₂ compound Co₃(Al,W) was found by Sato *et al.*¹²⁾ Co-based two-phase alloys composed of fcc-Co matrix and the compound as precipitates show good high temperature mechanical properties.^{12,13)} According to the result of first principles calculation by Yao *et al.*,¹⁴⁾ the compound is expected to have a shear modulus/bulk modulus ratio of about 0.6. Pugh proposed an empirical rule

that the metallic materials having the shear modulus/bulk modulus ratio larger than 0.5 is brittle,¹⁵⁾ and consequently Yao *et al.* concluded that the new compound may be brittle in nature.¹⁴⁾ However, no experimental study of the mechanical properties of the compound has been conducted. For a further development of Co-based alloys with the new L₁₂ compound, the mechanical properties of Co₃(Al,W) polycrystals are investigated in the present study using compression testing at various temperatures ranging from room temperature to 1193 K. Also the microstructure evolution was investigated and the Co-rich region of the Co-Al-W ternary phase diagram is assessed.

2. Experimental Procedures

The nominal compositions for alloys investigated were Co-10 at%Al-13 at%W (alloy 1) and Co-10 at%Al-12 at%W (alloy 2). The specimens were arc-melted several times in an Ar atmosphere on a water-cooled copper hearth from 99.9% Co, 99.99% Al and 99.9% W in purity. Alloy ingots, being about 20 g, were sealed in quartz tubes and annealed at various temperatures ranging from 1173 K to 1473 K for 24–168 h. Microstructure observation using scanning electron microscopy (SEM) and chemical analysis of constituent phases by wavelength dispersive X-ray spectroscopy (WDS) with pure Co, Al and W as references were carried out on polished samples. The constituent phases are also identified using X-ray diffractometry with Cu-K α (30 kV, 300 mA). The melting point of alloy 1 was determined by differential thermal analysis (DTA) under high purity Ar atmosphere with a heating rate of 10 K/min.

Compression test specimens with 3 × 3 × 6 mm³ in dimension were cut from the alloy 2 (Co-10Al-12W) ingot annealed at 1173 K for 168 h by a wheel cutter and polished with emery papers. An instron testing machine (type 5584) was used for the compression tests at various temperatures ranging from room temperature to 1193 K with an initial strain rate of 1 × 10⁻⁴ s⁻¹. At high temperatures the compression tests were conducted under an Ar-flow atmosphere. The strain rate was alternately changed several times to 1 × 10⁻³ s⁻¹, ten times higher than the initial strain rate, during plastic deformation.

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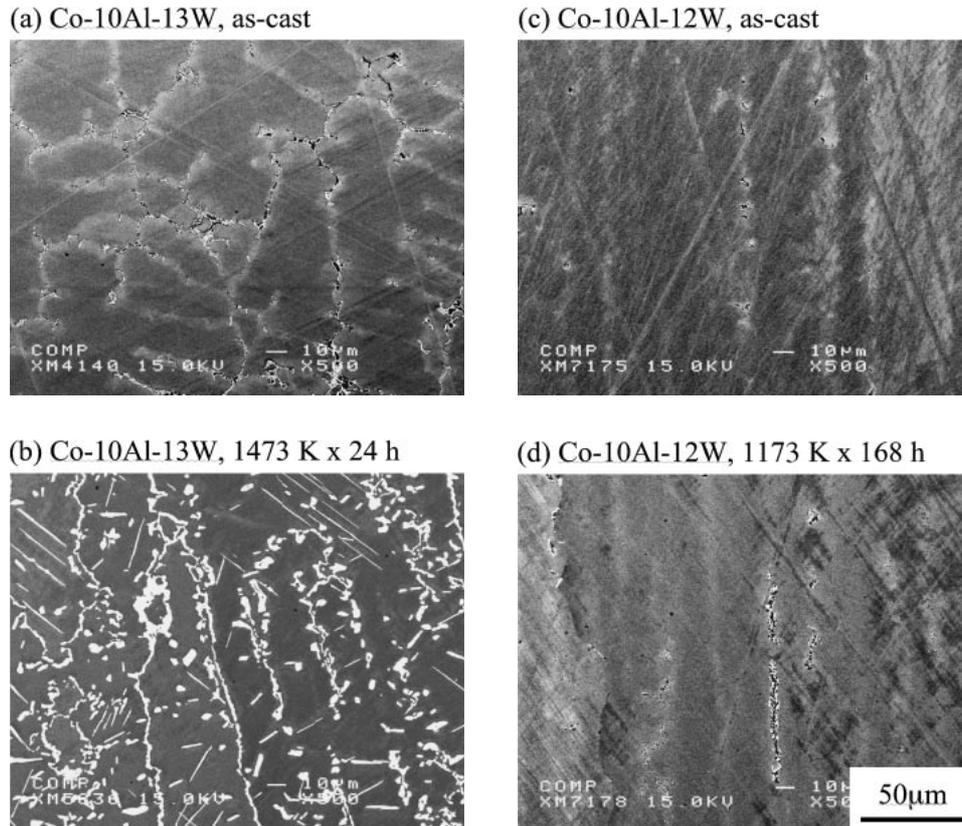


Fig. 1 Microstructures of Alloy 1 and 2: (a) as-cast Alloy 1, (b) as-cast Alloy 2, (c) Alloy 1 annealed at 1473 K for 24 h and (d) Alloy 2 annealed at 1173 K for 168 h.

3. Results and Discussion

3.1 Phase relationship

Figure 1 shows the microstructure of the alloys annealed at various temperatures, together with that of the as-cast alloys, observed using SEM. In as-cast ingots shown in Fig. 1(a) and (b), well-developed dendritic structures are found with small amount of particles at inter-dendritic regions. The inter-dendritic phases (dark and bright) have a lamellar structure, which may indicate these regions were solidified in the manner of a ternary eutectic reaction. Electron probe micro analysis (EPMA) revealed that the bright particles at inter-dendritic regions in alloy 1 contain high W, presumably Co_7W_6 phase, while the dark particles contain high Al, presumably B2-CoAl. The amount and size of minor phases are much smaller in alloy 2 than in alloy 1.

The result of microstructure observation of alloy 1 annealed at 1473 K for 24 h is shown in Fig. 1(c). The small bright particles and acicular particles are identified as Co_7W_6 phase since they have an average composition of 55.4Co-1.8Al-42.8W (at%). The results of XRD are shown in Fig. 2. From these results it was confirmed that the alloy 1 sample annealed at 1473 K are composed of fcc-Co solid solution and Co_7W_6 phases. On the other hand, the phases existing in the alloy 2 sample annealed at 1173 K for 168 h (Fig. 1(d)) are confirmed to be L_{12} phase (matrix) and $\text{D}_{019}\text{-Co}_3\text{W}$ (dark particles) using XRD and EPMA. Very small bright particles at grain boundaries can not be identified though it presumably is a W-rich phase such as Co_7W_6 . These results are consistent

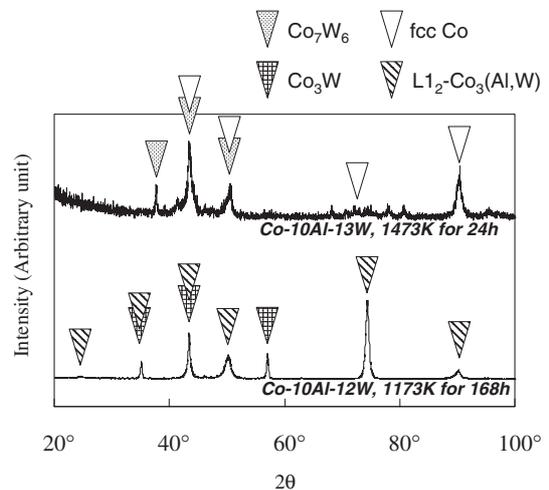


Fig. 2 Results of XRD diffractometry of Alloy 1 annealed at 1473 K for 24 h and Alloy 2 annealed at 1173 K for 168 h.

with the results reported by Sato *et al.*¹²⁾ The average size of L_{12} grains in alloy 2 is about 200 μm .

According to the binary Co-Al and Co-W phase diagrams, the phases appearing in the Co-rich (Co > 50 at%) region at the temperature range around 1000 K are Co, CoAl, Co_3W and Co_7W_6 . Although a metastable Co_3Al binary phase with L_{12} structure was reported,¹⁶⁾ this phase is excluded from the consideration. Therefore, in the Co-rich region, the number of phases is 5 including $\text{Co}_3(\text{Al,W})$. Sato *et al.* reported CoAl

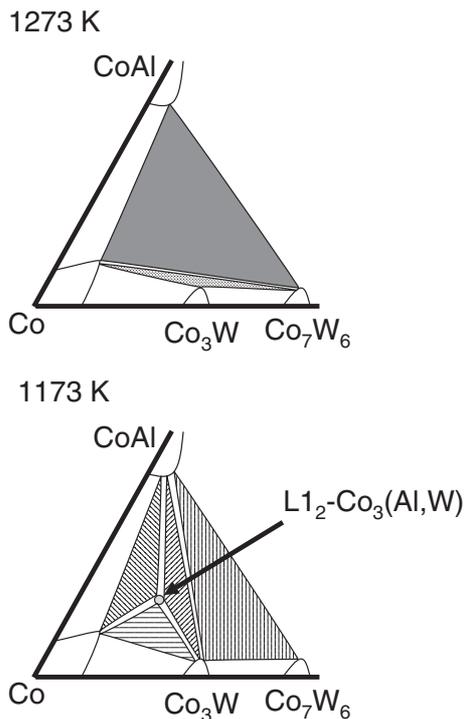


Fig. 3 Schematic presentation of three-phase fields in isothermal sections (a) at 1273 K and (b) at 1173 K.

equilibrates with Co_7W_6 at 1273 K and 1173 K.¹²⁾ It can be expected that a monovariant trough, $L(\text{liquid})+CoAl+Co_7W_6$, exists at a higher temperature region. Figure 3 is a schematic drawing of the Co-rich corner of the Co-Al-W ternary system. At 1273 K, there are two three-phase regions composed of $Co-CoAl-Co_7W_6$ and $Co-Co_7W_6-Co_3W$, respectively. According to the microstructure observation, Co solid solution is the primary phase from liquid. In order to introduce the $Co-CoAl-Co_7W_6$ three-phase region during solidification, an invariant reaction composed of $L-Co-CoAl-Co_7W_6$ is needed to exist at a higher temperature, which related to eutectic reactions $L \rightarrow Co+CoAl$ in the Co-Al binary system and $L \rightarrow Co+Co_7W_6$ in the Co-W binary system, and a monovariant trough, $L+CoAl+Co_7W_6$. According to Sato *et al.*, $Co_3(Al,W)$ phase is metastable at 1273 K.¹²⁾ If this means that the $Co_3(Al,W)$ phase appears from the $Co-CoAl-Co_7W_6$ three-phase region in the manner of the ternary peritectoid reaction, two more invariant reactions composed of $Co-Co_7W_6-Co_3W-Co_3(Al,W)$ and $CoAl-Co_7W_6-Co_3W-Co_3(Al,W)$ are required to reach the 1173 K isothermal section with four three-phase regions as depicted in a tentative reaction scheme presented in Fig. 4(a). On the other hand, another set of invariant reactions can be expected. If the $Co_3(Al,W)$ phase appears directly from $Co-CoAl-Co_3W$ three phase region in the manner of peritectoid reaction, an invariant reaction $Co+Co_7W_6 \rightarrow CoAl+Co_3W$, is needed at a temperature between two invariant reactions, $L \rightarrow Co+CoAl+Co_7W_6$ and $Co+CoAl+Co_3W \rightarrow Co_3(Al,W)$. This sequence is also presented in Fig. 4(b). For determining the reaction scheme, additional isothermal sections between 1173 K and 1273 K are needed to be established. These complicated sequences for reaching a

single phase $L1_2-Co_3(Al,W)$ alloy seems to be a large drawback to obtain a single crystal sample of the alloy.

3.2 Mechanical properties

Figure 5 shows the stress-strain curves of Co-10Al-12W alloy (alloy 2) annealed at 1173 K for 168 h. Arrows indicate the strain rate dip tests. At room temperature, the 0.2% flow stress is about 410 MPa and the strain hardening rate at 1% plastic strain is of the order of 6 GPa. The 0.2% flow stress at 865 K is 310 MPa, which is smaller than that at room temperature, and at higher temperatures the 0.2% flow stress increases slightly, while the strain hardening rate decreases. Figure 6 shows the temperature dependence of the 0.2% flow stress. Reported data on various $L1_2$ compounds are also replotted.¹⁰⁾ The 0.2% flow stress of $Co_3(Al,W)$ alloy shows the minimum at 865 K, and it increases more than 20% at 1080 K. Although this stress anomaly is not evident comparing with that of Ni_3Al , a weak positive temperature dependence of strength is recognized. At lower temperature range, relatively large negative temperature dependence of strength appears. Therefore, the temperature dependence of the 0.2% flow stress of this alloy resembles that of Co_3Ti at the overall temperature range, while the room temperature strength of $Co_3(Al,W)$ is much higher than that of Co_3Ti . Although the strengthening at room temperature can be attributed to W and Al atoms occupying the Ti sites in Co_3Ti , the strength at high temperature region is seemingly not affected by W and Al. In the present study it is found that the temperature range at which the 0.2% flow stress shows positive temperature dependence is quite narrow. The apparent activation energy cannot be estimated in the present study, but this should be estimated for the further understanding of the nature of stress anomaly of Co-based $L1_2$ alloys.

Positive temperature dependence of strength has been reported on various intermetallic compounds including B2-CuZn,¹⁷⁾ $L1_0-TiAl$ ¹⁸⁾ and $D0_{19}-Ti_3Al$.¹⁹⁾ Some of them are attributed to the decrease in the degree of order with temperature, while the reason for stress anomaly in most of $L1_2$ alloys are ascribed to the locking of dislocations by the cross-slip motion of $\{111\}$ screw segment onto $\{010\}$ cube plane, i.e., Kear-Wilsdorf mechanism.²⁰⁻²²⁾ The present alloy was subjected to the annealing at 1173 K which is higher than the temperature range at which the positive temperature dependence of the strength appears. Therefore, the lowering of the order parameter never occurs during or prior to the high temperature testing and it can be concluded that the observed stress anomaly is not caused by the decrease of the order parameter. Suzuki *et al.* reported that the regular Shockley-type dissociation of $\{111\}$ dislocations is observed in $L1_2-Co_3(Al,W)$ particle embedded in Co-solid solution matrix deformed at 1073 K.¹³⁾ This strongly suggests that the formation of the Kear-Wilsdorf lock is the reason for the stress anomaly of the present alloy.

It is well known that the peak temperature of the strength depends on the onset of high temperature deformation mechanism such as $\{001\}$ cube slip and/or octahedral viscous flow.^{23,24)} As these high temperature deformation mechanisms are thermally activated processes, the onset of these mechanisms are strongly related to the melting point T_m of materials. The 0.2% flow stress of $Co_3(Al,W)$ and

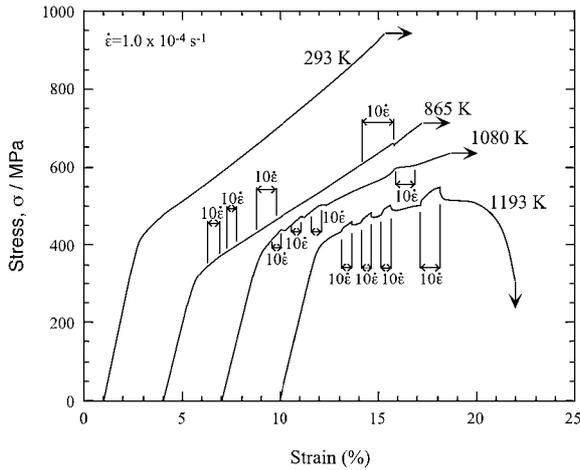


Fig. 5 Stress strain curves of Co₃(Al,W) alloy at various temperatures.

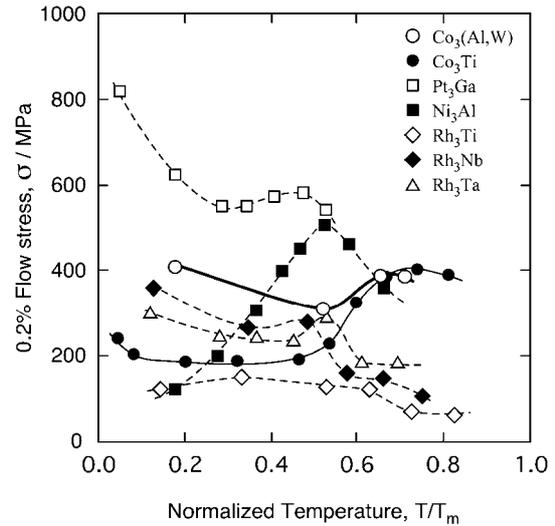


Fig. 7 The dependence of 0.2% flow stress of Co₃(Al,W) and other L1₂ alloys on the normalized temperature T/T_m .¹⁰⁾ T_m is the melting point of alloys and compounds.

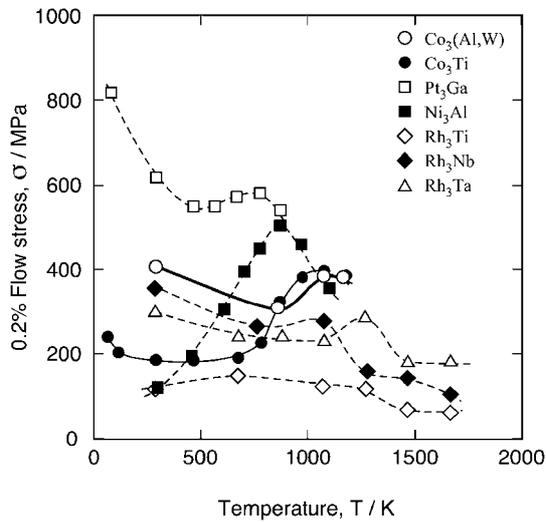


Fig. 6 The temperature dependence of 0.2% flow stress of Co₃(Al,W) and other L1₂ alloys.¹⁰⁾

various L1₂ compounds are plotted as a function of normalized temperature, T/T_m in Fig. 7.¹⁰⁾ As the T_m for the present alloy, the average of the liquidus and solidus temperatures determined by DTA (1730 K and 1550 K, respectively) for the alloy 1, 1640 K, was employed. Although the high temperature phase of the alloy is fcc-Co, the melting point of metastable L1₂-Co₃(Al,W) is expected to be not far below the melting point of Co solid solution. It is clear that the behavior of Co₃(Al,W) is still similar to that of Co₃Ti and the peak strength temperature is relatively higher than those of other L1₂ alloys. It is known that in L1₂ alloys the strain rate dependence is almost negligible at the temperature range below the peak strength temperature, and above peak strength temperature it becomes large because the deformation is governed by thermally activated process(es). In the present study the strain rate dependence of strength is also very small at 865 K, i.e., below the peak strength temperature, while it becomes larger with increasing temperature. However, the degree of stress increment by strain rate dip tests is still smaller than that of Ni₃Al and (Co,Ni)₃(Ti,Al) alloy single crystals in the regime in which

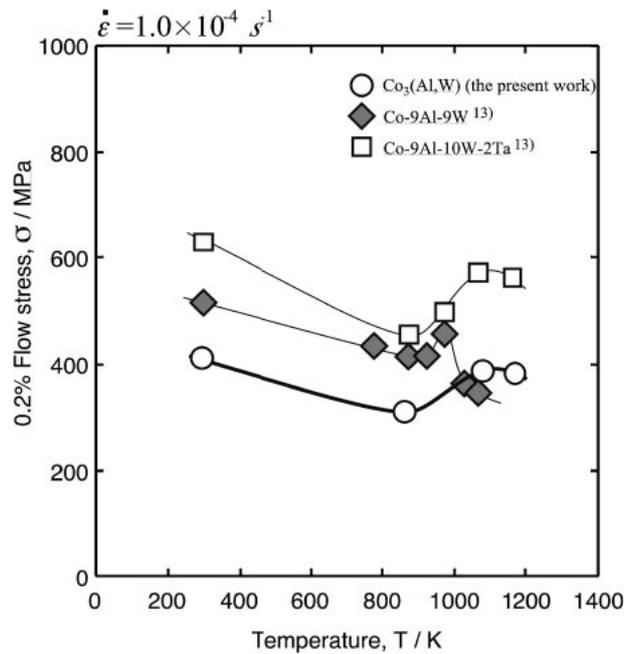


Fig. 8 The temperature dependence of 0.2% flow stress of Co₃(Al,W) compared with those of Co-Co₃(Al,W) two-phase alloys with and without Ta reported by Suzuki *et al.*¹³⁾

cube slip or octahedral viscous flow dominates the deformation.^{23–25)} This implies the relatively good high temperature strength of Co₃(Al,W). In Fig. 8, the present results are compared with the strength of Co-Co₃(Al,W) two-phase alloys with and without Ta.¹³⁾ Two-phase alloys have rather higher strength, but the Ta-free two-phase alloy shows lower strength at higher temperature range. It may be attributed to the dissolution and/or the coarsening of Co₃(Al,W) particles at this temperature range during testing.

As shown in Fig. 5, the compressive ductility is higher than 10% at all test temperatures except for that at 1193 K. In various ductile L1₂ alloys the minimum ductility is observed at a temperature range just above the peak strength temper-

ature. This is attributed to the effect of oxygen,^{26–28)} and a similar behavior is observed in the present $\text{Co}_3(\text{Al,W})$ alloy. On the other hand, the compressive ductility at room temperature is not as small as that of some brittle intermetallic compounds like $\text{DO}_{22}\text{-Al}_3\text{Ti}$ which shatters during compressive deformation. It is, therefore, concluded that the present alloy does not show brittleness as was expected by the previous calculation result.¹⁴⁾

4. Concluding Remarks

Two alloys Co-10Al-13W and Co-10Al-12W were prepared to understand the microstructure evolution and mechanical properties of newly reported $\text{L}_{12}\text{-Co}_3(\text{Al,W})$. As the candidates for the reaction scheme of the Co-rich region of the Co-Al-W ternary system, two diagrams are proposed. The compressive mechanical properties of $\text{Co}_3(\text{Al,W})$ polycrystals having a nominal composition of Co-10Al-12W and small amount of 2nd (and 3rd) precipitates are investigated at various temperatures ranging from room temperature to 1193 K. It is found that $\text{Co}_3(\text{Al,W})$ shows a weak positive temperature dependence of the strength at the temperature range around 1000 K. The small strain rate dependence of strength at high temperature range are also observed. The temperature dependence of the 0.2% flow stress of the present alloy resembles that of Co_3Ti alloy among various L_{12} alloys. Even at room temperature the present $\text{Co}_3(\text{Al,W})$ alloy shows ductile deformation, higher than 10% plastic strain in compression.

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