Influence of Cold-Working and Subsequent Heat-Treatment on Young’s Modulus and Strength of Co-Ni-Cr-Mo Alloy*1

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Changes in Young’s modulus of the Co-31 mass%Ni-19 mass%Cr-10 mass%Mo alloy (Co-Ni based alloy) with cold-swaging, combined with heat-treatment at temperatures from 673 to 1323 K, was investigated to enhance the Young’s modulus of Co-Ni based alloy. After cold-swaging, the Co-Ni based alloy, forming (111) fiber deformation texture, shows the Young’s modulus of 220 GPa. Furthermore, after ageing the cold-swaged alloy at temperatures from 673 to 1323 K, the Young’s modulus increased to 230 GPa, accompanied by a decrease in the internal fiction and an increase in the tensile strength. This suggests that the increment in Young’s modulus is caused by a moving of the vacancies to the dislocation cores and a continuous locking of the dislocations along their entire length with solute atoms (trough model). By annealing at 1323 K after cold swaging, Young’s modulus slightly increased to 236 GPa. On the other hand, the tensile strength decreases to almost the same value as that before cold swaging due to recrystallization. These results suggest that the Young’s modulus and the strength in the present alloy are simultaneously enhanced by the continuous dislocation locking during aging as well as the formation of (111) fiber deformation texture.


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Keywords: cobalt-nickel based alloy, Young’s modulus, internal friction, texture, Suzuki effect, trough model

1. Introduction

Alloys in which Co, Ni, Cr, and Mo are the main components (hereafter referred to as “Co-Ni based alloys”), have excellent cold plastic workabilities in addition to high Young’s moduli, high strengths, high corrosion resistances, and high heat resistances. Due to these characteristics, these alloys are widely used for power generation components and in electronic and medical applications.

In recent years, considerable effort has been expended in enhancing the Young’s modulus of alloys that are used in precision machinery and medical stents. For example, the spring power source of the mainspring in a watch is the torque generated by the restoring force. The higher the elastic modulus of the material is, the larger the torque of the spring will be. Thus, a higher elastic modulus will enhance the performance of the watch. In the case of medical stents, which are used to expand blocked blood vessels, using materials with high Young’s moduli will permit the size of the stent to be reduced while maintaining the same expansive force.

The enhancement of the Young’s modulus of metallic materials has been extensively studied for Fe alloys.1–4) Means for enhancing the Young’s modulus include adding alloy elements, controlling the texture, and forming composites with a second phase that has a high Young’s modulus. For example, texture was controlled in Fe alloys by heat treatment after Y2O3 had been finely dispersed in the alloys. In the case of ferritic steel, the Young’s modulus of the (111) crystal orientation has been increased to 282 GPa.1,2) A Young’s modulus of 300 GPa or higher for TiB2-ferritic steel was achieved by compounding 40 vol% or more of TiB2.3,4)

On the other hand, the Young’s modulus of the Co-Ni based alloy is about 230 GPa after annealing. Among metallic materials, the Co-Ni based alloy has a high Young’s modulus. It is anticipated that the Young’s modulus of Co-Ni based alloys can be further increased through texture control by a cold swaging/heat treatment process, resulting in further improvements in the performance of the above-mentioned applications.

The objective of this study is to further enhance the Young’s modulus of Co-Ni based alloys. Thus, the relationship between the texture of the Co-Ni based alloy after cold swaging and the Young’s modulus was investigated. In addition, the relationship between the texture of the swaged material after aging heat treatment and the Young’s modulus was studied.

2. Experimental Methods

The alloy composition used in this study is listed in Table 1. As is clear from the composition, Co, Ni, Cr, and Mo are the main components of this alloy. The alloy was prepared by melting an ingot of 7 kg in a high-frequency vacuum melting furnace and performing soaking treatment at 1453 K for 36 ks. Subsequently, hot forging was performed at a heating temperature of 1453 K and an end temperature of 1173 K. A 26-mm-diameter round bar was prepared by this method. The obtained hot forged round bar was cold swaged.

Table 1 Alloy composition of Co-Ni based alloy used in this work.

<table>
<thead>
<tr>
<th>Co</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Nb</th>
<th>Fe</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal</td>
<td>31.8</td>
<td>20.2</td>
<td>9.0</td>
<td>0.0</td>
<td>0.5</td>
<td>1.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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to produce a 7-mm-diameter round bar. During this step, after cold swaging to a diameter of 10 mm, intermediate annealing was momentarily performed. The area reduction after the final cold swaging was 51%. This cold-swaged round bar (diameter: 7 mm) is hereafter called the “cold-swaged material”, and the cold swaging direction will be called “LD”. After cold swaging, an aging heat treatment was carried out at temperatures in the range 673–1073 K for holding times in the range 1.8–7.2 ks. Recrystallization heat treatment was also conducted at 1323 K for 14.4 ks after cold swaging. The Young’s modulus and internal friction were measured by a free resonance method and a damping method (Nihon Techno-Plus Co., Ltd., JE-RT). The structure and texture were evaluated by X-ray diffraction (XRD), orientation imaging microscopy-electron backscatter diffraction (OIM-EBSD), optical microscopy, and transmission electron microscopy (TEM).

3. Results and Discussion

3.1 Texture of swaged/heat-treated samples

The results for XRD measurements of the cross-sectional area perpendicular to the LD of the Co-Ni based alloy are shown in Fig. 1 for (a) the as-cold swaged sample, and for the heat-treated samples at (b) 673 K for 7.2 ks, (c) 1073 K for 3.6 ks, and (d) 1323 K for 14.4 ks. According to the results, a phase change was not observed after the cold swaging/heat treatment and all samples were face-centered cubic (FCC) γ single phase.

The optical microstructures at the center of the cross-sectional area cut perpendicular to the LD are shown in Fig. 2. The microstructures are for (a) the as-cold swaged sample and for the samples heat treated at (b) 673 K for 7.2 ks, (c) 1073 K for 3.6 ks, and (d) 1323 K for 14.4 ks. The optical microstructures of the respective cross-sectional areas cut parallel to the LD are shown in Figs. 2(e)–(h). For the cold-swaged sample (Figs. 2(a) and (e)), numerous striations, which were introduced by cold swaging, were observed in the crystal grains. In the completely recrystallized structure, coarsening of the γ phase particle size relative to the swaged/aged samples occurred (15 to 80 μm) as shown in Figs. 2(d) and (h). Numerous annealing twins with a (111) twin interface were observed. In contrast, thick annealing twins were not observed in the swaged/aged samples as shown in Figs. 2(a)–(c) and Figs. 2(e)–(g), and the numerous fine striations observed after cold swaging were still present.

Bright-field TEM images are presented in Fig. 3. These images are for (a) the as cold-swaged sample and the samples heat treated at (b) 673 K for 7.2 ks, (d) 1073 K for 3.6 ks, and (e) 1323 K for 14.4 ks. Fine plate-like phases were observed in the cold swaged sample and the aged samples. A selected-area diffraction pattern in the vicinity of the plate-like phase is shown in Fig. 3(c). This plate-like phase is (111) twins, and numerous (111) deformation twins are thus shown to be introduced by cold swaging. In addition, numerous dislocations were observed in the microstructure of the cold swaged sample and aged samples. However, crystal grains without dislocations and annealing twins were observed in parts of the 1073 K sample. Thus, recrystallization commences at this temperature. Dislocations were hardly observed in the sample obtained by the recrystallization heat treatment at 1323 K, (Fig. 3(e)), indicating the completion of recrystallization.

Figure 4 shows (111) and (100) pole figures obtained from cross sections cut perpendicularly to the LD for the cold-swaged and the heat-treated samples. The (111) and (100) double fiber texture is formed after both swaging and heat treatment. The maximum intensity shown in Fig. 4 corresponds to the integrated intensity at the center of the pole figure, namely, to the integrated intensities of (111) and (100). The (111) integrated intensity is larger than that of (100) for both samples.

OIM-EBSD images (Fig. 5) of the cold swaged sample and the sample that had been recrystallization heat treated at 1323 K for 14.4 ks ((a) OIM image of the cold swaged sample, (b) OIM image of the sample heat treated at 1323 K for 14.4 ks, (c) orientation distribution in the inverse pole figure for the cold swaged sample, and (d) orientation distribution in the inverse pole figure for the sample heat-treated at 1323 K for 14.4 ks). The orientation distributions in these inverse pole figures (Figs. 5(c) and (d)) show that the (100) orientation becomes weaker after recrystallization while the (111) orientation becomes stronger. This suggests that the (111) fiber texture is more strongly formed in the recrystallization process by heat treatment.

Figure 6 shows the relationship between the aging temperature and the maximum intensity ratio (hereafter referred to as the “max intensity ratio”) for (111) and (100), based on the respective pole figures obtained by XRD measurements. The max intensity ratio R was determined from:

$$ R(\%) = 100 \frac{I}{I_{(111)} + I_{(100)}}. $$

where $I_{(111)}$ and $I_{(100)}$ are the maximum intensities for (111) and (100) pole figures respectively, and $I_{(111)}$ or $I_{(100)}$ is substituted for the value of I. Figure 6 shows that the respective max intensity ratios for (111) and (100) did not change even after heat treatment. In order to evaluate the relationship between the Young’s modulus and the texture, it is necessary to investigate the bulk texture. In that sense, it is considered that the XRD results reflect the bulk properties more than the EBSD results, which are obtained from the surface of the sample. In the EBSD results described above, a
change was observed in the crystal orientations of \( \{111\} \) and \( \{100\} \) before and after recrystallization. However, no obvious change was observed in the XRD data. Accordingly, it can be concluded that the heat treatment did not effect the ratio of \( \{111\} \) to \( \{100\} \) fiber texture in the bulk, which was established by cold swaging.

3.2 Young’s modulus and internal friction of cold swaged/heat-treated samples

The relationship between the heating temperature and the Young’s modulus after the cold swaging/heat treatment of the Co-Ni based alloy for various holding times is shown in Fig. 7. The Young’s modulus for the cold swaged state was
Fig. 3 Bright field images of Co-Ni based alloy for (a) as-cold swaged, and heat-treated sample at (b) 673 K–7.2 ks, (d) 1073 K–3.6 ks and (e) 1323 K–14.4 ks and selected area diffraction pattern in the vicinity of plate-like phase in microstructure (c).

Fig. 4 (111) and (100) pole figures of as-cold swaged and heat treated (673 K–7.2 ks, 1073 K–3.6 ks and 1323 K–14.4 ks) Co-Ni based alloy on vertical plane to longitudinal direction (LD).
220 GPa, which increased to 230 GPa by aging at 673 K, then stayed nearly constant up to an aging temperature of 1073 K before increasing to 236 GPa by the heat treatment at 1323 K. In this case, the Young’s modulus was independent of the holding time at each heating temperature.

The relationship between the heating temperature and the internal friction ($Q^{-1}$) after the cold swaging/heat treatment is shown in Fig. 8. After cold swaging, the samples exhibited a high internal friction. In contrast, the internal friction decreased markedly after the aging heat treatment at 673 K, and remained nearly constant regardless of the heating temperature. The internal friction is mainly attributable to lattice defects such as phase transformations, grain boundaries, and dislocations. Thus, the internal friction is considered to be related to atomic rearrangement in the crystal. It has been reported that the internal friction increases as the number of defects inside a material increases.\textsuperscript{5,6} As shown in Fig. 1, the present alloy is a $\gamma$ single phase after the cold swaging/heat treatment; the formation of a second phase is not visible in Fig. 1. Therefore, the changes in the Young’s modulus and internal friction after the cold swaging/heat treatment observed in Figs. 7 and 8 are unrelated with a phase transformation or the precipitation of the second phase.
Accordingly, the high internal friction of the cold swaged sample is attributed to high-density dislocations introduced by cold swaging and atomic vacancies generated by the interaction of screw dislocations. On the other hand, the internal friction of the 1323 K heat-treated sample, in which the dislocations introduced by cold swaging nearly disappear due to recrystallization, is similar to the internal frictions of other aging heat-treated samples containing high-density dislocations (Fig. 3). Further investigation is necessary to explain this observation.

The full-width at half-maximum (FWHM) of the (111) XRD peak of the present alloy after the cold swaging/heat treatment is shown in Fig. 9. The FWHM decreases on aging. As observed in Fig. 3, numerous deformation twins and dislocations were observed in the structure after aging at temperatures in the range 673–1073 K. However, the results shown in Fig. 9 indicate that macroscopic inhomogeneous strain introduced by cold swaging has recovered after aging.

Granato et al. indicated that the internal friction decreases due to the accumulation of atomic vacancies near movable dislocations. In the case of the present alloy, it can also be presumed that randomly distributed vacancies introduced by cold swaging rearranged around the dislocations and twins during aging. This rearrangement of such atomic vacancies around the dislocations and twin boundaries is also considered to be one factor in the reduction in the internal friction shown in Fig. 8, which is caused by aging heat treatment after cold swaging.

3.3 Relationship between internal friction/Young’s modulus and age hardening

Figure 6 shows that the max intensity ratios of (111) and (100) fiber textures, which were formed parallel to the LD by cold swaging, hardly changed even after heat treatment. Tensile test was carried out for the samples which showed high Young’s modulus at each aging temperature. The relationship between the temperatures for aging and the 0.2% proof stress or tensile strength after tensile testing is shown in Fig. 10. The strength increases on aging heat treatment and decreases on heat treatment at 1073 K, where partial recrystallization occurs. The strength recovers to that before cold swaging by heat treatment at 1323 K, where a perfect recrystallization structure is formed. Chiba et al. reported that the strength of this Co-Ni based alloy was significantly increased by aging heat treatment after cold working; in particular, by aging at temperatures in the range 873–973 K. They reported that this was strain age hardening caused by the so-called Suzuki effect. In the Suzuki effect, dislocations, which are introduced by cold working, are extended by heat treatment and form stacking faults; subsequently, solute elements segregate near stacking faults, and the motion of dislocations is locked. Therefore, the increase in the strength after aging heat treatment observed in Fig. 10 can be explained by the locking of dislocations due to the Suzuki effect.
effect. The reduction in the strength after aging heat treatment at 1073 K is considered to be caused by the start and progress of recrystallization as observed in Fig. 3(d).

During heat treatment at 1323 K, lattice defects such as dislocations in the swaged material disappear due to recrystallization. Accordingly, the strength decreases to the value before cold swaging. However, the internal friction remains almost constant at the value of the strain-age-hardened material containing a high density of dislocations (Fig. 8). Thus, the locking of dislocations due to the Suzuki effect, which is the cause of strain age hardening, differs from the localized dislocation locking caused by precipitates. This is presumed to be due to the locking along the entire length of the dislocation line (trough model)\(^{12}\) (referred to as “continuous locking”). The absorption of external vibrational energy by dislocations is also considered to contribute to the internal friction. If the dislocations are continuously locked by the Suzuki effect, as is the case in the present alloy, the dislocation motion that absorbs the external vibrational energy cannot occur. Thus, it does not contribute to the generation of internal friction. The continuous locking mechanism of dislocations due to the Suzuki effect can be considered to be a factor for the reduction in the internal friction of the present alloy after age-hardening heat treatment. However, further study is required to determine the detailed mechanism.

Considering the above discussion, numerous lattice defects such as dislocations were present even after age-hardening heat treatment (Fig. 3). The internal friction was drastically decreased by the age-hardening heat treatment at a relatively low temperature (673 K). A nearly constant value was obtained by the subsequent aging heat treatment (Fig. 8). This is considered to be due to the recovery of the above-described macroscopic inhomogeneous strain and the microscopic structural change (rearrangement of point defects and a continuous locking of dislocations by the Suzuki effect).

Young’s modulus after aging heat treatment (Fig. 7) can also be explained by a similar discussion as that for the internal friction. That is, Young’s modulus decreases after cold swaging due to the presence of lattice defects such as dislocations and the inhomogeneous strain that they generate. This is because when all or part of the dislocations that are introduced by cold swaging act as movable dislocations, movable dislocation segments bow out due to external vibrations. As a result, the consumed energy appears as a reduction in the Young’s modulus \(E(\Delta E)\) expressed by the following equation.\(^{13,14}\)

\[
\Delta E = -\rho \frac{l^2}{6\alpha} E
\]

Here, \(\rho\) represents the dislocation density, and \(l\) corresponds to the length of the movable dislocation segment of one locking dislocation line. In addition, \(\alpha\) is a function of \(l\). After aging, the movable segments of dislocations that are introduced by cold swaging disappear because of the recovery of inhomogeneous strain, the rearrangement of point defects around the dislocation cores, and the continuous locking of dislocations by the Suzuki effect. This means that \(l\) in eq. (2) becomes zero. Thus, the reduction in the Young’s modulus due to dislocations disappears; as a result, the Young’s modulus is considered to increase. In addition, the increase in Young’s modulus on recrystallization is considered to be caused by the disappearance of dislocations.

Thus, the Young’s modulus of the Co-Ni based alloy decreases by cold swaging (area reduction: 51%). However, the Young’s modulus as well as the strength increases during aging heat treatment. By recrystallization, the Young’s modulus increases slightly; however, the strength decreases. Accordingly, the simultaneous realization of both an increase in strength and an enhancement of the elastic modulus is possible by enhancing the elastic modulus using strain age hardening at a heating temperature at which recrystallization does not occur.

Up until now, the main method for achieving a high Young’s modulus and a high strength for metal alloys has used the precipitation phase with a high elastic modulus. There have been virtually no reports concerning the possibility of achieving high elastic modulus using a continuous dislocation locking mechanism (the Trough model), which was demonstrated in this study. Thus, the present method is promising as a new method for achieving a high Young’s modulus and a high strength.

4. Conclusions

The findings obtained in this study are summarized below:

(1) A cold swaged Co-Ni based alloy (referred to as the “cold-swaged material”) with an area reduction of 51% had a structure containing numerous dislocations. In the alloy, a fiber texture was formed with a strong (111) crystal orientation and a weak (100) crystal orientation to the direction of cold swaging (LD). Numerous deformation structures were still present even after aging heat treatment at temperatures in the range 673–1073 K. By the heat treatment at 1323 K for 14.4 ks, a perfect recrystallization structure was formed. In addition, fiber textures were hardly changed after heat treatment.

(2) The Young’s modulus of the cold swaged material was 220 GPa and it increased to 230 GPa by subsequent aging heat treatment at temperatures in the range 673 K–1073 K. In addition, the maximum tensile strength (1,500 MPa) was achieved by aging heat treatment at 973 K. The increases in the Young’s modulus and the tensile strength by the aging heat treatment at an intermediate temperature are attributable to the following. The dislocations are continuously locked by the segregation of solute elements to extended dislocations in addition to the accumulation of vacancies, which are introduced by cold swaging, around the dislocation cores. When the heat treatment was performed at 1323 K, where a perfect recrystallization structure is generated, the Young’s modulus increased to 236 GPa; however, the tensile strength decreased to 825 MPa.

(3) Even when there is a high density of dislocations, the dislocations are continuously locked by the aging heat treatment at a moderate temperature. Thus, an increase in the internal friction and a decrease in the Young’s modulus do not occur. As a result, a high strength and a high Young’s modulus can be achieved.
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